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OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF PAPERS

ON

ORGANIC CHEMISTRY.

1913. Vol. CIV. Part I.

LONDON:

GURNEY & JACKSON, 33, PATERNOSTER ROW, E.C.

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JOURNALS FROM WHICH ABSTRACTS ARE MADE.

All references to Journals should give the abbreviated title, the year of publication, the series, the volume and the page; thus *Ber.* 1901, **34**, 2455; *Bull. Soc. chim.* 1901, [iii], **25**, 794: *Gazzetta* 1901, **31**, i, 554.

ABBREVIATED TITLE.	JOURNAL.
Amer. Chem. J.	American Chemical Journal.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Physiol	American Journal of Physiology.
Amer. J. Sci.	American Journal of Science.
Anal. Fis. Quim.	Anales de la Sociedad Española Fisica y Quimica.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Ann. Falsif.	Annales des Falsifications.
Ann. Inst. Pasteur	Annales de l'Institut Pasteur.
Ann. Physik	Annalen der Physik.
Ann. sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy.
Arch. expt. Path. Pharm	Archiv für experimentelle Pathologie und Pharmakologie.
Arch. Hygiene	Archiv für Hygiene.
Arch. Néerland.	Archives Néerlandaises des sciences exactes et naturelles.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Sci. phys. nat.	Archives des Sciences physiques et naturelles.
Arkiv Kem. Min. Geol.	Arkiv för Kemi, Mineralogi och Geologi.
Atti R. Accad. Sci. Torino.	Atti della Reale Accademia delle Scienze di Torino.
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deut. bot. Ges.	Berichte der Deutschen botanischen Gesellschaft.
Ber. Deut. pharm. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft.
Ber. Deut. physikal. Ges	Berichte der Deutschen physikalischen Gesellschaft.
* *Bied. Zentr.*	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
Bio-Chem. J.	The Bio-Chemical Journal.
Biochem. Zeitsch.	Biochemische Zeitschrift.
Boll. chim. farm.	Bollettino chimico farmaceutico.
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. Cracow	Bulletin international de l'Académie des Sciences de Cracovie.
Bull. Acad. Sci., St. Pétersbourg.	Bulletin de l'Académie Impériale des Sciences de St. Pétersbourg.
Bull. Assoc. chim. Sucr. Dist.	Bulletin de l'Association des chimistes de Sucrerie et de Distillerie.
Bull. Geol. Soc Amer.	Bulletin of the Geological Society of America.
Bull. Imp. Inst.	Bulletin of the Imperial Institute.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Bull. Soc. ind. Mulhouse	Bulletin de la Société industrielle de Mulhouse.
Centr. Bakt. Par.	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Centr. Min.	Centralblatt für Mineralogie, Geologie und Palaeontologie.
* *Chem. Zentr.*	Chemisches Zentralblatt.
Chem. News	Chemical News.
Chem. Rev. Fett-Harz-Ind.	Chemische Revue über die Fett- und Harz-Industrie.

* Abstracts from the *Zentralblatt* are made only in the case of papers published in journals other than those included in this list.

JOURNALS FROM WHICH ABSTRACTS ARE MADE.

ABBREVIATED TITLE.	JOURNAL.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zeit.	Chemiker Zeitung.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Exper. Stat. Record	Experiment Station Record.
Gazzetta	Gazzetta chimica italiana.
Geol. Mag.	Geological Magazine.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
Jahrb. Min. Beil.-Bd.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie. Beilage-Band.
Jahrb. Radioaktiv. Elektronik.	Jahrbuch der Radioaktivität und Elektronik.
J. Agric. Sci.	Journal of Agricultural Science.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Biol. Chem.	Journal of Biological Chemistry, New York
J. Chim. phys.	Journal de Chimie physique.
J. Geol.	Journal of Geology.
J. Hygiene	Journal of Hygiene.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Brewing	Journal of the Institute of Brewing.
J. Landw.	Journal für Landwirtschaft.
J. Med. Research	Journal of Medical Research.
J. Path. Bact.	Journal of Pathology and Bacteriology.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. pr. Chem.	Journal für praktische Chemie.
J. Roy. Agric. Soc.	Journal of the Royal Agricultural Society.
J. Roy. Soc. New South Wales.	Journal of the Royal Society of New South Wales.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Dyers	Journal of the Society of Dyers and Colourists.
J Washington Acad. Sci.	Journal of the Washington Academy of Sciences.
K. Svenska Vet-Akad. Handl.	Kongl. Svenska Vetenskaps-Akademiens Handlingar.
Kolloid Zeitsch.	Kolloid Zeitschrift.
Koll. Chem. Beihefte	Kolloidchemische Beihefte.
Lancet.	The Lancet.
Landw. Versuchs-Stat.	Die landwirtschaftlichen Versuchs-Stationen.
Le Radium	Le Radium.
Mem. Accad. Sci. Torino	Memorie della Reale Accademia delle Scienze di Torino.
Mem. Coll. Sci. Eng. Kyōtō.	Memoirs of the College of Science and Engineering, Kyōtō Imperial University.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Metallurgie	Metallurgie.
Milch. Zentr.	Milchwirtschaftliches Zentralblatt.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Nuovo Cim.	Il Nuovo Cimento.
Pflüger's Archiv	Archiv für die gesammte Physiologie des Menschen und der Thiere.
Pharm. J.	Pharmaceutical Journal.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Pharm. Zeit.	Pharmazeutische Zeitung.
Pharm. Zentr-h.	Pharmazeutische Zentralhalle.
Philippine J. Sci.	Philippine Journal of Science.

JOURNALS FROM WHICH ABSTRACTS ARE MADE.

ABBREVIATED TITLE.	JOURNAL.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Physikal. Zeitsch.	Physikalische Zeitschrift.
Proc. Amer. Physiol. Soc.	Proceedings of the American Physiological Society.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. K. Akad. Wetensch. Amsterdam.	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Phil. Soc. Glasgow	Proceedings of the Glasgow Philosophical Society.
Proc. Physiol. Soc.	Proceedings of the Physiological Society.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Quart. J. exp. Physiol.	Quarterly Journal of experimental Physiology.
Quart. J. Geol. Soc.	Quarterly Journal of the Geological Society.
Rec. trav. chim.	Receuil des travaux chimiques des Pays-Bas et de la Belgique.
Rend. Accad. Sci. Fis. Mat. Napoli.	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche-Napoli.
Rev. de Métallurgie	Revue de Métallurgie.
Sci. Proc. Roy. Dubl. Soc.	Scientific Proceedings of the Royal Dublin Society.
Sci. Trans. Roy. Dubl. Soc.	Scientific Transactions of the Royal Dublin Society.
Sitzungsber. K. Akad. Wiss. Berlin.	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
Sitzungsber. K. Akad. München.	Sitzungsberichte der königlich bayerischen Akademie der Wissenschaften zu München.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Nova Scotia Inst. Sci.	Transactions of the Nova Scotia Institute of Science.
Trans. Path. Soc.	Transactions of the Pathological Society.
Trans. Roy. Soc. Canada	Transactions of the Royal Society of Canada.
Trans. Roy. Soc. Edin.	Transactions of the Royal Society of Edinburgh.
Trans. Roy. Irish Acad.	Transactions of the Royal Irish Academy.
Tsch. Min. Mitt.	Tschermak's Mineralogische Mitteilungen.
U.S.A. Dept. Agric. Bull.	Bulletins of the Department of Agriculture, U.S.A.
U.S.A. Dept. Agric. Rep.	Reports of the Department of Agriculture, U.S.A.
Verh. Ges. deut. Naturforsch. Aerzte	Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte
Wiss. Abhandl. Phys.-Tech. Reichsanstalt.	Wissenschaftliche Abhandlungen der Physikalisch-Technischen Reichsanstalt.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeitsch. Biol.	Zeitschrift für Biologie.
Zeitsch. Elektrochem.	Zeitschrift für Elektrochemie.
Zeitsch. Kryst. Min.	Zeitschrift für Krystallographie und Mineralogie.
Zeitsch. Nahr. Genussm.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeitsch. öffentl. Chem.	Zeitschrift für öffentliche Chemie.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie
Zeitsch. prakt. Geol.	Zeitschrift für praktische Geologie.
Zeitsch. Ver. deut. Zuckerind.	Zeitschrift des Vereins der deutschen Zucker-Industrie.
Zeitsch. wiss. Photochem.	Zeitschrift für wissenschaftliche Photographie, Photophysik und Photochemie.
Zeitsch. Zuckerind. Böhm.	Zeitschrift für Zuckerindustrie in Böhmen.

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PART I.

Organic Chemistry.

Preparation of $\Delta^{\alpha\gamma}$-Butadiene and its Homologues. BADISCHE ANILIN- & SODA FABRIK (D.R.-P. 252499).—When hydrogenated hydrocarbons of the benzene series containing at least one double bond are heated at high temperatures at the ordinary or (preferably) reduced pressures with an indifferent gas (such as nitrogen), they yield derivatives of butadiene. Isoprene is thus obtained from the lower-boiling fractions furnished by the decomposition of 1-methyl-Δ^1-*cyclo*hexene, or of 1-methyl*cyclo*hexan-2-ol, whilst *cyclo*hexene yields $\Delta^{\alpha\gamma}$ butadiene (erythrene), and 1-methyl-Δ^2-*cyclo*pentene furnishes piperylene, $CH_3\cdot CH{:}CH\cdot CH{:}CH_2$. F. M. G. M.

Preparation of Isoprene. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 251216).—When *as*-dimethylallene (b. p. 39—41°) is dropped on to strongly heated aluminium oxide, preferably under a pressure of about 20—30 mm., it is converted into pure isoprene; the aluminium oxide can be replaced by other catalytic agents, and the formation of higher polymerides must be avoided. F. M. G. M.

Preparation of $\beta\gamma$-Dimethylerythrene. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 253081. Compare A., 1912, i, 741).—The preparation of $\beta\gamma$-dimethylerythrene by heating pinacone (1 part) with dilute sulphuric acid (10 parts) is described in the literature; it is now found that the most favourable proportions are 1 part of sulphuric acid (20%) to 10,000 parts of pinacone heated at 130—140°,

when a yield of over 70% of $\beta\gamma$-dimethylerythrene is obtained. The sulphuric acid can be replaced by methanedisulphonic or naphthalene-1 : 5-disulphonic acid. F. M. G. M.

The History of Distillation and of Alcohol. HERMANN SCHELENZ (*Zeitsch. angew. Chem.*, 1912, **25**, 2526—2527).—Polemical against von Lippmann (A., 1912, i, 824 ; ii, 897). C. H. D.

Preparation of Homologues of Pinacone. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 251330, 251331).—The homologues of pinacone can be readily prepared in satisfactory yield by the action of aluminium amalgam on the homologues of acetone.

$\gamma\delta$-*Diethylhexane*-$\gamma\delta$-*diol*, $OH\cdot CEt_2\cdot CEt_2\cdot OH$, m. p. 27—28°, b. p. 116—119°/17 mm., is thus obtained from diethyl ketone. $\gamma\delta$-*Dimethylhexane*-$\gamma\delta$-*diol*, $OH\cdot CMeEt\cdot CMeEt\cdot OH$, b. p. 78—79°/3 mm., is prepared from methyl ethyl ketone, whilst methyl propyl ketone furnishes $\delta\epsilon$-*dimethyloctane*-$\delta\epsilon$-*diol*, $OH\cdot CMePr^{\alpha}\cdot CMePr^{\alpha}\cdot OH$, m. p. 95°, b. p. 116—170°/15 mm. These reactions can be carried out in either benzene or carbon tetrachloride solutions.

II. States that magnesium and mercuric chloride in the presence of cuprous chloride can replace the aluminium amalgam in these preparations. F. M. G. M.

The Formation of Polyatomic Rings. ADOLF FRANKE and O. KIENBERGER (*Monatsh.*, 1912, **33**, 1189—1203).—In a repetition of the work of Alberti and Smieciuszewski (A., 1906, i, 619) the authors converted $\alpha\kappa$-dihydroxydecane into the chlorohydrin, but found that the product contained also about 15% of the corresponding dichloride, and that the mixture could not be satisfactorily separated ; the constitution of the chlorohydrin was proved by re-conversion into the glycol. Heating the impure chlorohydrin with sodium hydroxide and sand gave rise to a mixture of substances of high molecular weight, but no indication of the heterocyclic isomerides, $C_{10}H_{20}O$, described earlier (*loc. cit.*).

Endeavours to prepare cyclic molecules from $\alpha\kappa$-dibromodecane (Franke and Hankam, A., 1910, i, 460) by the action of ordinary zinc dust in aqueous alcohol produced *n*-decyl alcohol, whilst the action of sodium in ether gave *n*-decane, together with a *substance*, $C_{20}H_{40}$ or $C_{20}H_{42}$, silky needles, m. p. 36°. D. F. T.

Halogen Ethers. A. KARVONEN (*Chem. Zentr.*, 1912, ii, 1266—1271 ; from *Acad. Sci. Fennicae.*, *A*, **3**, 1—103. Compare A., 1909, i, 202). The boiling points and densities have been determined for a number of carefully purified halogen ethers of the series $RO\cdot CH_2X$, $RO\cdot CH_2\cdot CH_2X$, and $RO\cdot CH_2\cdot CH_2\cdot CH_2X$, where $R = H$, Me, Et or Pr, and $X = Cl$, Br or I. They have been compared with some ethylene- and trimethylene-halogen hydrins, and with some simple alkyl haloids.

In the case of metameric halogen ethers, the removal of the halogen atom from the oxygen atom frequently causes a lowering of the boiling point, but as the molecule becomes more symmetrical with regard to the groups R and $(CH_2)_nX$, the boiling point rises. As the distance

of the halogen atom from the oxygen atom increases, the differences between the boiling points of the chloro- and bromo- and bromo- and iodo-compounds diminish. The difference between the boiling points of the methyl and ethyl members of a homologous series is less than that between the ethyl and propyl members. The boiling points of halogen ethers with three, four, and five members in the chain are higher than those of the corresponding alkyl haloids, but with six members in the chain the ethers boil at a lower point. The hydrins boil at higher temperatures than the halogen ethers. As for the densities, the removal of the halogen atom from the oxygen atom causes an increase in density, and the halogen ethers take a mean place between the hydrins and the alkyl haloids. In general, the simultaneous separation of two negative substituents in the molecule causes an increase in density.

General methods for the preparation and purification of these compounds are discussed. The α-halogen ethers were usually prepared by the action of the hydrogen haloid on a mixture of the alcohol with trioxymethylene (compare Litterscheid, A., 1904, i, 364); the β-chloro- and bromo-ethers by the action of the phosphorus haloid on alkyloxylated alcohols, and the γ-ethers by the action of alcohols or alcoholates on alkylene haloids, the halogenating of ethers, or by the transformation of ethers into one another. The halogen ethers are all colourless, mobile liquids. The α-ethers have pungent, aldehydic odours and fume in the air, but the β- and γ-ethers are agreeable.

The following compounds are described:

A. *α-Halogen Ethers.*—Chloromethyl ether, b. p. 59·1°/766 mm., gives a *pyridine* compound, $Py,CH_2Cl{\cdot}OMe$, colourless, hygroscopic tablets; *platinichloride*, $(Py,CH_2Cl{\cdot}OMe)_2PtCl_4$, reddish-yellow needles, m. p. 189°. Bromomethyl ether, b. p. 87·2°/740·6 mm.; *pyridine* compound, $Py,CH_2Br{\cdot}OMe$, very hygroscopic powder. Iodomethyl ether, b. p. 25°/13 mm. Chloromethyl ethyl ether, b. p. 83°/763·1 mm.; *pyridine* compound, $Py,CH_2Cl{\cdot}OEt$, colourless, hygroscopic tablets; *platinichloride*, $(Py,CH_2Cl{\cdot}OEt)_2PtCl_4$, reddish-yellow prisms, m. p. 182°. *Bromomethyl ethyl ether*,

$$OEt{\cdot}CH_2Br,$$

from ethyl alcohol, trioxymethylene, and hydrogen bromide, b. p. 109·2°/745·7 mm.; *pyridine* compound, $Py,CH_2Br{\cdot}OEt$, white, hygroscopic. *Iodomethyl ethyl ether*, $OEt{\cdot}CH_2I$, with hydrogen iodide, b. p. 31°/11 mm.; *pyridine* compound, $Py,CH_2I{\cdot}OEt$, colourless, hygroscopic. Chloromethyl propyl ether, b. p. 109°/759·7 mm.; *pyridine* compound, $Py,CH_2Cl{\cdot}OPr$, colourless, very hygroscopic; *platinichloride*, $(Py,CH_2Cl{\cdot}OPr)_2PtCl_4$, m. p. 185°. *Bromomethyl propyl ether*, $OPr{\cdot}CH_2Br$, from normal propyl alcohol, trioxymethylene, and hydrogen bromide, b. p. 133·9°/744·4 mm.; *pyridine* compound,

$$Py,CH_2Br{\cdot}OPr,$$

colourless, hygroscopic lamellæ. *Iodomethyl propyl ether*, $OPr{\cdot}CH_2I$, with hydrogen iodide, b. p. 39°/5 mm.; *pyridine* compound,

$$Py,CH_2I{\cdot}OPr,$$

colourless.

B *β-Halogen Ethers* — Methyl Bromomethyl ether

by the action of phosphorus pentachloride on ethylene glycol monomethyl ether, $OMe\cdot CH_2\cdot CH_2\cdot OH$, and not by Fileti and Gaspari's method, b. p. 89·4°/763·3 mm. *Methyl β-bromoethyl ether*, $OMe\cdot CH_2\cdot CH_2Br$, from methyl β-iodoethyl ether and bromine, b. p. 110·3°/759·4 mm. Methyl β-iodoethyl ether (A., 1909, i, 202), $D_4^{20} = 1{\cdot}8241$. Ethyl β-chloroethyl ether, from ethylene glycol monoethyl ether and phosphorus trichloride, b. p. 107°/751·8 mm. Ethyl β-bromoethyl ether, b. p. 40°/24 mm., from ethyl β-iodoethyl ether (*ibid.*). Propyl β-chloroethyl ether, from ethylene glycol monopropyl ether and phosphorus pentachloride, b. p. 130°/756·3 mm. *Propyl β-bromoethyl ether*, $OPr\cdot CH_2\cdot CH_2Br$, from ethylene glycol monopropyl ether and phosphorus tribromide or hydrogen bromide, b. p. 149°/757·8 mm., 42°/11 mm. Propyl β-iodoethyl ether, $D_4^{20} = 1{\cdot}5464$ (*ibid.*).

C. *γ-Halogen Ethers.*—Methyl γ-chloropropyl ether, b. p. 110·4°/756·6 mm. *Methyl γ-bromopropyl ether*, $OMe\cdot[CH_2]_3\cdot Br$, from trimethylene bromide, methyl alcohol, and zinc oxide, b. p. 132°/764·4 mm. *Methyl γ-iodopropyl ether*, $OMe\cdot[CH_2]_3\cdot I$, from the chloro-ether and calcium iodide, b. p. 158—158·5°/761·8 mm. Ethyl γ-chloropropyl ether, b. p. 129°/754·7 mm. Ethyl γ-bromopropyl ether, by Noyes's method (A., 1898, i, 59), b. p. 147·8°/750 mm. *Ethyl γ-iodopropyl ether*, $OEt\cdot[CH_2]_3\cdot I$, from the chloro-ether and calcium iodide, b. p. 172·5°/778·7 mm.

D. *Halogen Hydrins and Alkyl Haloids.*—Ethylene chlorohydrin, $OH\cdot CH_2\cdot CH_2Cl$, from ethylene glycol and hydrogen chloride, b. p. 129·5°/761·1 mm. Ethylene bromohydrin, $OH\cdot CH_2\cdot CH_2Br$, with hydrogen bromide, b. p. 45·6°/11 mm. Ethylene iodohydrin,

$$OH\cdot CH_2\cdot CH_2I,$$

from the chlorohydrin and sodium iodide, b. p. 61°/7 mm. Trimethylene chlorohydrin, $HO\cdot CH_2\cdot CH_2\cdot CH_2Cl$, from trimethylene glycol and hydrogen chloride, b. p. 160°/734·1 mm. Trimethylene bromohydrin, $HO\cdot CH_2\cdot CH_2\cdot CH_2Br$, b. p. 62°/5 mm. Trimethylene iodohydrin, $HO\cdot CH_2\cdot CH_2\cdot CH_2I$, b. p. 88°/4 mm.

n-Propyl chloride, b. p. 46·6°/770·5 mm.; *n*-propyl bromide, b. p. 70·8°/769·2 mm.; *n*-propyl iodide, b. p. 101·9°/765·5 mm. *n*-Butyl chloride, b. p. 77·8°/762·7 mm.; *n*-butyl bromide, b. p. 100·2°/745·6 mm.; *n*-butyl iodide, b. p. 129·4°/746·4 mm. *n*-Amyl chloride, b. p. 105·7°/759·3 mm.; *n*-amyl bromide, b. p. 127·9°/762·4 mm.; *n*-amyl iodide, b. p. 35°/7 mm. *n*-Hexyl chloride, b. p. 132·9°/764·7 mm.; *n*-hexyl bromide, b. p. 153·4°/766·3 mm.; *n*-hexyl iodide, b. p. 51°/6 mm.

J. C. W.

Preparation of Carbonic Esters. RUDOLF SCHEUBLE and A. HOCHSTETTER (D.R.-P. 252758).—*Glyceryl carbonate*, m. p. 148°, crystallises from pyridine, and is obtained in theoretical yield when anhydrous glycerol (2 parts) is heated at 140° with phenyl carbonate (7 parts) and the phenol subsequently removed in a vacuum; in this case the glycerol is fully esterified. When twice this proportion of glycerol is employed and the product extracted with a small quantity of acetone, any of the foregoing ester is left insoluble, and the acetone furnishes a complicated mixture of esters in which the glycerol is not fully esterified. These compounds can also be prepared by the action

of ethyl carbonate or carbonyl chloride on glycerol dissolved in an indifferent acid absorbing medium, and find employment in pharmacy.

F. M. G. M.

Preparation of Halogen Formyl Esters. EMANUEL MERCK (D.R.-P. 251805. Compare A., 1912, i, 877).—Chloroformyl esters can be obtained by the interaction of hydroxy-compounds with carbonyl chloride in the presence of an indifferent base or acid absorbent: $R\cdot OH + COCl_2 = RO\cdot COCl + HCl$.

Methylhexylcarbinyl chloroformate, a colourless oil, b. p. 75°/6 mm., is obtained when a cooled benzene solution of methylhexylcarbinol (130 parts) is treated with carbonyl chloride with the subsequent slow addition of pyridine (79 parts) dissolved in 500 parts of benzene; when treated with ammonium hydroxide, it furnishes the corresponding known carbamyl ester (m. p. over 55°).

Thymyl chloroformate has b. p. 106°/10 mm., and menthyl chloroformate, b. p. 96°/5 mm.

Ethyl bromoformate, an oil with a characteristic odour, b. p. 132°/760 mm. with partial decomposition, is obtained from carbonyl bromide and ethyl alcohol in absolute ethereal solution in the presence of quinoline, whilst ethyl chloroformate is analogously prepared in the presence of methylaniline. F. M. G. M.

Preparation of Esters of Butenol. CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHERING (D.R.-P. 252160).—When $\Delta^{\alpha\gamma}$-butadienes of the general formula $CH_2{:}CR\cdot CH{:}CH_2$ (where R is hydrogen or alkyl) are treated with a fatty acid in the presence of a condensing agent (such as sulphuric acid, zinc chloride, or potassium hydrogen sulphate), they furnish esters which are readily purified, have a characteristic odour, and on hydrolysis yield the corresponding alcohol.

Methylbutyl acetate, an oil, b. p. 100° (about), D 0·870, and saponification number 418 (about), is obtained when isoprene (100 parts), acetic acid (300 parts), and concentrated sulphuric acid (1 part) are heated together during five hours at 50°. F. M. G. M.

The Mercury Compounds of Ethyl Nitroacetate. W. PRAGER (*Monatsh.*, 1912, **33**, 1285—1289).—The formation of ethyl mercuri-*aci*-nitroacetate anhydride, $O{<}{\genfrac{}{}{0pt}{}{NO}{Hg}}{>}C\cdot CO_2Et$, from the interaction of ammonium *aci*-nitroacetate and mercuric chloride (Scholl and Nyberg, A., 1906, i, 563), is probably preceded by the formation of a compound, $CO_2Et\cdot CH{:}NO_2\cdot HgCl$, ethyl mercuri-*aci*-nitroacetate chloride, which, however, could not be isolated. In agreement with this idea, the yield of ethyl mercuri-*aci*-nitroacetate is increased by the addition of an equivalent quantity of sodium acetate.

The solution of ethyl mercuri-*aci*-nitroacetate in sodium hydroxide solution contains *ethyl sodium mercuri-*aci*-nitroacetate hydroxide*,

$$CO_2Et\cdot C({:}NO_2Na)\cdot Hg\cdot OH,$$

which can be obtained as a greenish-yellow substance by evaporation with exclusion of atmospheric carbon dioxide. Ethyl mercuri-*aci*-

nitroacetate anhydride dissolves also in potassium cyanide solution, forming presumably the analogous *cyanide* compound,

$$CO_2Et \cdot C(:NO_2K) \cdot Hg \cdot CN.$$

Attempts to obtain substances of analogous structure to the above from nitroacetamide, dinitromethane, and ω-nitrotoluene produced only substances of the type $CHR:NO_2 \cdot HgCl$; nitroacetamide gave a *substance*, $Hg(NH \cdot CO \cdot CH:NO_2 \cdot HgCl)_2$; the potassium derivative of dinitromethane with mercuric chloride gave yellow needles of an explosive *substance*, $NO_2 \cdot CH:NO_2 \cdot HgCl$, together with an amorphous, yellow *substance* also containing chlorine. D. F. T.

Action of Aluminium Chloride on Acetic Anhydride. JACOB BÖESEKEN and MEYER CLUWEN (*Rec. trav. chim.*, 1912, **31**, 367—369).—When acetic anhydride is added to warmed aluminium chloride, acetyl chloride distils off, leaving a heavy, white precipitate of aluminium monochlorodiacetate, which forms an *additive* compound with ether, $OEt_2,2AlCl(OAc)_2$, in large, limpid crystals. J. C. W.

Soaps. ALBERT REYCHLER (*Bull. Soc. chim. Belg.*, 1912, **26**, 485—495. Compare Krafft and Stern, A., 1894, i, 439, 440; Krafft and Wiglow, A., 1896, i, 80; Krafft and Strutz, A., 1896, ii, 467; Krafft, A., 1899, ii, 471, 472, 473).—When sodium palmitate is crystallised from its aqueous solution, an acid soap separates, and the mother liquor becomes alkaline. Recalculation of the data given by Krafft shows that as the sodium palmitate solution decreases in concentration, so also does the concentration of sodium hydroxide in the mother liquor, the latter value, however, finally becoming constant. This is confirmed by experiments performed by the author, who, however, contrary to Krafft, finds that fatty acids are also retained in the mother liquors.

Krafft has shown that palmitic acid may be almost completely extracted from solutions of sodium palmitate by treatment with successive quantities of toluene. The author has performed a number of experiments on the quantitative extraction of the acid by a single treatment of aqueous solutions of sodium palmitate and oleate with measured amounts of toluene, and finds that the extractability depends both on the m. p. of the acid and on its solubility in toluene. The percentage of acid extracted is inversely proportional to the concentration of sodium hydroxide in the soap solution.

The bearing of the above results on the divergent action of soap is discussed, and the conclusion drawn that this action lies rather in the power of the soap solution to emulsify the grease than in the saponification of the latter by alkali. A partly rancid fat should thus be readily emulsified by a solution of soap of suitable concentration, whilst, on the other hand, a neutral fat would first acquire the necessary acidity by extraction of a portion of the acid from the soap solution. H. W.

Dissociation Constants of Aliphatic Hydroxy- and Alkyloxy-acids. MATTI H. PALOMAA (*Chem. Zentr.*, 1912, ii, 595—597; from *Ann. Acad. Sci. Fennicae.*, 1911, *A*, **3**, 1—34).—The dissociation constants of a number of aliphatic hydroxy- and alkyloxy-acids have been

determined with a view to ascertaining how this constant is affected by the positions of the oxygen atoms in the ·OH or ·OR group with respect to the carboxyl group. In general, the dissociation constant diminishes with increasing distance between the two groups, until in the δ-compounds it is nearly as low as in the normal fatty acids. Attempts to calculate the effect of distance on the specific influence of the ethereal oxygen atom by means of the equations $(y/y+2\cdot66)^{-x}=K_0^{\alpha}/K_0^{\beta}$ and $(y/y+2\times2\cdot66)^{-x}=K_0^{\alpha}/K_0^{\gamma}$ showed that $x=2\cdot6$ in methoxy-compounds and 2·9 in ethoxy-compounds, the values of y being 1·45 and 1·78 respectively for the same compounds.

The following substances are described: n-*Butoxyacetic acid*, D_4^{15} 1·0256, D_4^{20} 1·0213, b. p. 113—116°/9—10 mm., K 0·0219, is a colourless liquid with a not unpleasant odour. iso*Butoxyacetic acid*, D_4^{15} 1·0117, D_4^{20} 1·0074, b. p. 114°/9 mm., K 0·0214, is a colourless liquid. *α-Ethoxypropionic acid*, b. p. 97°/11 mm., K 0·0246. *β-Methoxypropionic acid*, D_4^{15} 1·1064, D_4^{20} 1·1020, b. p. 107°/10 mm., K 0·00346. *β-Ethoxypropionic acid*, D_4^{15} 1·0508, D_4^{20} 1·0641, b. p. 119—120°/19 mm., K 0·00319. δ-*Methoxyvaleric acid*, D_4^{15} 1·0387, D_4^{20} 1·0344, b. p. 133—134°/13·5 mm., K 0·00191. T. A. H.

Action of Magnesium Methyl Iodide and Bromide on Di-α-bromo*iso*propyl Ketone and on α-Bromo*iso*propyl *tert.*-Butyl Ketone (Pentamethylbromoacetone): Synthesis of β-Hydroxy-pentamethyl-*n*-valeric Acid and Pentamethylvalerolactone. (Mlle.) A. UMNOVA (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1395—1406).—Instead of the expected methyldi*tert.*-butylcarbinol, the products of the interaction of di-α-bromo*iso*propyl ketone, magnesium methyl iodide, and water are: (1) *iso*propyl *tert.*-butyl ketone (compare Nef, A., 1900, i, 349), formed from the intermediate compound,

$$CMe_3\cdot CO\cdot CMe_2\cdot MgBr,$$

and (2) methyl*iso*propyl*tert.*-butylcarbinol (?), b. p. 65—75°/12 mm.

The action of magnesium methyl bromide on di-α-bromo*iso*propyl ketone yields the compound $CMe_3\cdot CMe(OMgBr)\cdot CMe_2\cdot MgBr$, the latter being converted by carbon dioxide into *β-hydroxy-ααβγγ-pentamethylvaleric acid*, $CMe_3\cdot CMe(OH)\cdot CMe_2\cdot CO_2H$, m. p. 128—129°, which has the normal molecular weight in boiling ether; the *silver* and *calcium* salts were analysed. Attempted oxidation of the sodium salt of the acid with potassium permanganate and subsequent distillation of the solution with sulphuric acid yields *ααββγ-pentamethylvalerolactone*, $CMe_2{<}\begin{matrix}CMe_2\cdot O\\ CMe_2\cdot CO\end{matrix}$, m. p. 59—60°, b. p. 215—220°, which has the normal molecular weight in freezing benzene; the formation of the lactone is shown to be due to the following isomeric change effected by the sulphuric acid: $CMe_3\cdot CMe(OH)\cdot CMe_2\cdot CO_2H \longrightarrow OH\cdot CMe_2\cdot CMe_2\cdot CMe_2\cdot CO_2H$. β-Hydroxy-ααββγ-pentamethylvaleric acid may also be obtained by the action of carbon dioxide and water on the product of the interaction of magnesium methyl iodide and α-bromo*iso*propyl *tert.*-butyl ketone. T. H. P.

Optically Active Dichlorosuccinic Acids. BROR HOLMBERG (*Svensk. Kem. Tid.*, 1912; Reprint, 6 pp.).—The dichlorosuccinic

anhydride obtained by the action of chlorine on a solution of maleic anhydride in carbon tetrachloride (compare Holmberg, A., 1911, i, 767; McKenzie, T., 1912, **101**, 1196) is a mixture of a less soluble racemic dichlorosuccinic anhydride with a more soluble *meso*-anhydride in the approximate proportions 5 : 1. This behaviour is in marked contrast with the oxidation of maleic acid by potassium permanganate, when the sole product is *meso*-tartaric acid. The anhydrides on treatment with cold water gave the respective acids: r-*dichlorosuccinic acid*, tablets, m. p. 173—174° (decomp.); meso-*dichlorosuccinic acid*, prisms, m. p. 215° (decomp.).

By fractional recrystallisation of the salt of the racemic acid with *d*-α-phenylethylamine from warm water, there was obtained d-α-*phenylethylamine* d-*dichlorosuccinate*, m. p. 142—142·5°, from which the pure d-*dichlorosuccinic acid*, prisms, m. p. 164—165° (decomp.), $[\alpha]_D^{23}$ +80·41° (in ethyl acetate), could be separated by acidifying with sulphuric acid and extracting with ether. The mother liquor from the first crystallisation of the racemic salt contained a lævorotatory acid, which, when combined with *l*-phenylethylamine and crystallised from warm water, gave a salt of the same m. p. as that containing the *d*-acid and *d*-base; the acid isolated from this salt was pure l-*dichlorosuccinic acid*, m. p. 164—165°, $[\alpha]_D$ (in ethyl acetate) −80·38°.

The racemic acid, m. p. 173—174°, could be re-obtained by mixing equal amounts of these aenantiomorphs. D. F. T.

New Method of Preparation of Muconic Acid.

Robert Behrend and Gerhard ten Doornkaat Koolman (*Annalen*, 1912, **394**, 228—247).—Malonic acid (2 mols.) and the sodium hydrogen sulphite compound of glyoxal are boiled with water for about an hour. The solution is evaporated to a syrup, which is boiled with glacial acetic acid for about six hours, and is then treated with 36% hydrochloric acid. The sodium chloride is removed, and the filtrate is evaporated with water to a syrup, which deposits crystals after one to two days. These are treated with 95% alcohol, collected, and crystallised from hot 80% alcohol. The product is the *lactone* of *sodium hydrogen* β-*hydroxy*-γ-*sulphoadipate*, $\begin{matrix} CO_2H\cdot CH_2\cdot CH\text{——}O \\ SO_3Na\cdot CH\cdot CH_2 \end{matrix}\!\!>\!CO,3\tfrac{1}{2}H_2O$, prismatic crystals, m. p. 270—272° (decomp.), occasionally melting at 80—85° in its water of crystallisation, re-solidifying, and melting again at 270—272°. The *lactone* of the corresponding potassium hydrogen salt, m. p 262—264° (decomp.), is obtained in a similar manner. The *lactone* of the *sodium ethyl* salt, obtained from that of the sodium hydrogen salt, boiling 95% alcohol, and 1 drop of concentrated hydrochloric acid, forms long, felted needles containing H_2O, and has m. p. 145—147° (decomp.).

By heating on the water-bath for four hours with an alkali hydroxide and a little water, the lactone of sodium hydrogen hydroxysulphoadipate is decomposed, yielding, after solution in water and acidification, about 30% of muconic acid and 60% of succinic acid.

Muconic acid has m. p. 301—305° (decomp.), and is soluble in about 5000 parts of cold water and in about 100 parts of cold absolute alcohol.

A by-product in the preparation of the lactone is a *substance*, which is isolated as the amorphous *barium* salt, $C_{10}H_{14}O_{13}SBa_2$, from which muconic acid in a yield of 38%, but not succinic acid, can be obtained by heating with an alkali hydroxide and a little water on the water-bath.

For the preparation of muconic acid there is no need to isolate the lactone. Malonic acid and the sodium hydrogen sulphite compound of glyoxal are boiled with water for an hour, the solution is evaporated to a syrup, which is heated at 140—160° until gas almost ceases to be evolved, and is then treated with an alkali hydroxide and a little water on the water-bath, as above. C. S.

Elucidation of the Constitution of Cholic Acid by Bromination. BAREND C. P. JANSEN (*Zeitsch. physiol. Chem.*, 1912, **82**, 326—341).—On bromination of cholic acid, a brown, amorphous mass is obtained, which is decomposed by sodium hydroxide, losing part of the bromine. The bromine is not completely removed on reduction either with zinc dust and alcoholic hydrogen chloride or with aluminium amalgam. Bromination in acetic acid solution is accelerated by sunlight; it is a process of substitution. The product, bromodehydrocholic acid, crystallises from acetic acid or from acetone in needles, decomp. 180°; when crystallised from alcohol, it forms octahedra, decomp. ±140°.

Ethyl bromodehydrocholate is obtained either by brominating ethyl dehydrocholate or by esterification of bromodehydrocholic acid. The bromine is removed quantitatively by means of sodium hydroxide from either bromodehydrocholic acid or its ester. The bromo-acid is immediately oxidised by boiling Fehling's solution or ammoniacal silver solution. Zinc dust or magnesium reduce it to dehydrocholic acid.

E. F. A.

Preparation of the *p*-Bromophenylhydrazine Compound of Glycuronic Acid. ADOLF JOLLES (*Ber.*, 1912, **45**, 3280—3281).—In presence of traces of impurity the crystallisation of the *p*-bromophenylhydrazine compound of glycuronic acid is prevented (Neuberg, A., 1899, i, 933). After recrystallisation of the hydrazine, the lustrous, golden-yellow needles described by Neuberg are obtained without difficulty. E. F. A.

The Action of *p*-Bromophenylhydrazine on Glycuronolactone. GUIDO GOLDSCHMIEDT and ERNST ZERNER (*Monatsh*, 1912, **33**, 1217—1231).—Attempts to prepare Neuberg's compound of *p*-bromophenylhydrazine with glycuronic acid (A., 1899, i, 933), which has also been prepared and analysed by Jolles (A., 1911, i, 709), have entirely failed either when Neuberg's original directions or modifications are followed. The products actually obtained were salts of *glycuronic acid* p-*bromophenylosazone*,
$CO_2H\cdot CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot C(N_2H\cdot C_6H_4Br)\cdot CH{:}N_2H\cdot C_6H_4Br$; *sodium* salt, hygroscopic, yellow needles, m. p. 185—190°, $[\alpha]_D$ (in alcohol and pyridine mixture) $-259°$; *barium* salt, hygroscopic, yellow

needles, m. p. 215—217° (decomp.); the *calcium*, *potassium*, *zinc*, and *lead* salts were also prepared.

It is suggested that the formation of the barium salt, which occurs easily and in good yield, constitutes a much more satisfactory test for glycuronic acid than does the evidently uncertain reaction of Neuberg.

D. F. T.

The Mechanism of Oxidation Processes. OSCAR LOEW (*Ber.*, 1912, **45**, 3319).—When cuprous oxide is added to an alkaline solution of formaldehyde a vigorous evolution of hydrogen takes place, formic acid being formed. This experiment supports Wieland's idea (A., 1912, i, 944) that the oxidation of an aldehyde to an acid is a process of dehydrogenation.

T. S. P.

αα-Bromomethylpropaldehyde. II. The Friedel-Crafts Reaction. ADOLF FRANKE and ARTUR KLEIN (*Monatsh.*, 1912, **33**, 1233—1241).—Polymeric αα-bromomethylpropaldehyde (monoclinic crystals, $a:b:c = 2{\cdot}6:1:4{\cdot}9$; $\beta = 90°7'$) only enters into synthetic reactions when the conditions are such as to cause depolymerisation (Franke, A., 1900, i, 206, 427). When treated with benzene, carbon disulphide, and aluminium chloride, hydrogen bromide is vigorously evolved and phenyl *iso*propyl ketone formed; the oxime, tablets, m. p. 75°, with acetic anhydride yielded an *acetate*, b. p. 147—149°/10 mm. Reduction of the ketone in aqueous alcohol by sodium amalgam gave phenyl*iso*propylcarbinol; *acetate*, b. p. 106—108°/9·5 mm.; the b. p. (222—224°) of the free carbinol was considerably lower than that given earlier (Claus and Sauer, A., 1892, i, 985). Finely divided silver or copper acts on the polymeric bromomethylpropaldehyde at 150° with the formation of *iso*butaldehyde, together with products of higher b. p.

D. F. T.

Catalytic Reactions at High Temperatures and Pressures. XXV. VLADIMIR N. IPATIEV (*Ber.*, 1912, **45**, 3218—3226).—In addition to reduction with hydrogen under pressure in the presence of reduced nickel as catalyst, the author investigates the action of reduced palladium as catalyst. In some cases the apparatus in which the reduction was being carried out was shaken at intervals only, whilst in other cases the contents were stirred continuously by means of a stirrer actuated by a solenoid.

Reduction of β-methyl-β-ethylacraldehyde takes place at 130° in the presence of reduced nickel, but the yield of alcohol is very small, a considerable quantity of condensation products being formed. With palladium as catalyst and a hydrogen pressure of 110 atmos., reduction takes place at 110° with the formation of γ-methyl-*n*-amyl alcohol, b. p. 145—146°/758 mm., D^{18} 0·8227. The reduction takes place slowly unless continuous stirring is resorted to. Attempts to reduce the above acraldehyde in the author's apparatus, using Skita's method (A., 1909, i, 479), were unsuccessful, either at the ordinary temperatures or at 100°.

With palladium as catalyst, mesityl oxide is slowly reduced at 100° to methyl *iso*butyl ketone, whereas with nickel as catalyst a

mixture of methyl *iso*butyl ketone and methyl*iso*butylcarbinol is obtained at 145°.

The reduction of citral in the presence of palladium at 110°, or of a mixture of reduced nickel and nickel oxide at 140°, takes place slowly when the apparatus is continuously shaken. A mixture of products is obtained, from which $\beta\zeta$-dimethyloctane and $\gamma\eta$-dimethyloctanol were separated. When the reduction is carried out with continuous stirring, it proceeds rapidly to completion, the only product being decanol, b. p. 107—108°/12 mm., D^{18} 0·8296.

Under the same conditions as with citral, geraniol gives a mixture of decanol with small quantities of decane and condensation products when continuous shaking is resorted to, whereas with continuous stirring decanol and small quantities of decane are obtained.

At 109°, under a hydrogen pressure of 116 atmos., and in the presence of palladium as catalyst, acetylacetone is reduced to amylene $\beta\delta$-glycol, b. p. 197—198°, D^{18} 0·9602. With reduced nickel as catalyst, the reduction proceeds very slowly, the final product being a mixture of the original acetonylacetone with methyl *n*-propyl ketone.

By means of the apparatus with continuous stirring, the carbohydrates can readily be reduced; 20—30% aqueous-alcoholic solutions are used, the temperature being 110° with palladium as catalyst, and 130—135° with a mixture of reduced nickel and nickel oxide as catalyst; the hydrogen pressure is 100 atmos. With both catalysts, lævulose gives *d*-mannitol ($[\alpha]_D$ +0·71°), but the reduction is incomplete; dextrose is reduced to *d*-sorbitol ($[\alpha]_D$ +0·25°). Lactose is reduced to dulcitol. T. S. P.

The System Acetonephenylhydrazone-Water. JAN J. BLANKSMA (*Chem. Weekblad*, 1912, **9**, 924—927. Compare Reisenegger, A., 1883, 798; Schmidt, A., 1889, 1159; Arnold, A., 1897, i, 409).—The physical data for acetonephenylhydrazone given by the investigators named are incorrect. On heating acetone with a solution of phenylhydrazine in water or dilute acetic acid, an oil is formed. When it is washed with water, dried with potassium carbonate, and distilled under reduced pressure, the product is a pale yellow liquid, b. p. 140°/16 mm., 153°/31 mm., 160°/44 mm., 163°/50 mm. Repeated solidification by cooling with a freezing mixture yielded colourless crystals, m. p. 26·6°, which on exposure to air became yellow and then brown. It forms a colourless hydrate, turned brown, and ultimately resinified by the action of air.

The author gives the fusion curves of acetonephenylhydrazone, its hydrate, and water. The solubility of the hydrate per 100 c.c. of water is 0·09 gram (0°), 0·187 gram (15°), and 0·412 gram (32·8°). A. J. W.

Syntheses by means of Mixed Organo-zinc Derivatives, α-Polychloroketones. Constitution of the Ordinary Trichloroacetone. EDMOND E. BLAISE (*Compt. rend.*, 1912, **155**, 1252—1253. Compare A., 1912, i, 606).—Dichloroacetyl chloride readily condenses with α-hydroxy*iso*butyric acid to form *dichloroacetoxy*iso*butyric acid*, $CHCl_2\cdot CO_2\cdot CMe_2\cdot CO_2H$, m. p. 95°. The corresponding *acid chloride*,

b. p. 103°/12 mm., yields an *anilide*, m. p. 99—100°, and condenses with zinc ethyl iodide, giving the cyclo*acetal*, $C_8H_{12}O_3Cl_2$, m. p. 51°, b. p. 124·5—125°/16 mm., which on hydrolysis with a mixture of acetic and hydrochloric acids yields *dichloromethyl ethyl ketone*,

$$CHCl_2 \cdot COEt,$$

b. p. 138·5—139°. This ketone with hydroxylamine gives ethyl glyoxaldioxime, m. p. 128°. Attempts to convert the ketone into the corresponding keto-aldehyde were not successful.

*Trichloroacetoxy*iso*butyryl chloride*, b. p. 113°/18 mm., can be similarly prepared, and gives an *anilide*, m. p. 100°. The *acid* has m. p. 117°, and with zinc methyl iodide gives the cyclo*acetal*,

$$C_7H_9O_3Cl_3,$$

m. p. 98—99°, which on hydrolysis yields *as*-trichloroacetone, $CCl_3 \cdot COMe$, b. p. 134°. Its *semicarbazone* crystallises in needles, m. p. 140°. Ordinary trichloroacetone, b. p. 172°, obtained by the chlorination of acetone, must therefore be the unsymmetrical compound (compare Schotterbeck, A., 1909, i, 553). W. G.

Action of Halogen Compounds of Phosphorus on Ketones: Bromo-ketones, and Keto-alcohols. Alexei E. Favorski (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1339—1395).—According to Henry (*Ber.*, 1875, **8**, 400) the action of phosphorus pentachloride on di*iso*propyl ketone results in replacement of the carbonylic oxygen by two atoms of chlorine, the compound thus formed giving $\beta\delta$-dimethyl-$\Delta^{\beta\gamma}$-pentadiene when treated with alcoholic potassium hydroxide. The author finds, however, that the principal product of this action is not a dichloro-compound, but *iso*propyl α-chloro*iso*propyl ketone,

$$CMe_2Cl \cdot CO \cdot CHMe_2.$$

Further, in the case of *iso*propyl *tert.*-butyl ketone, the reaction proceeds similarly, α-chloro*iso*propyl *tert.*-butyl ketone being mainly obtained. With phosphorus pentabromide, the reaction takes place in the above direction with all ketones, and of a number of these compounds examined, only pinacolin underwent to some extent replacement of its carbonylic oxygen by two bromine atoms.

The ability of the carbonyl group of a ketone to react with phosphorus pentahaloid depends on the structure of the ketone and on its greater or less capacity to undergo enolisation. Ketones of normal structure (mono- and di-substituted acetones) readily react in the cold with phosphorus pentachloride by means of their carbonyl group, the oxygen of which is replaced by chlorine. On the other hand, such ketones as di*iso*propyl ketone, and, more especially *iso*propyl *tert.*-butyl ketone, react with phosphorus pentachloride only in the hot, when they undergo enolisation, the action of the chlorine liberated by dissociation of the pentachloride resulting in the formation of a monochloroketone:

$$(1)\ CMe_2{:}O + PCl_5 = CMe_2Cl \cdot OPCl_4 = POCl_3 + CH_3 \cdot CCl_2 \cdot CH_3;$$

$$(2)\ CHMe_2 \cdot CO \cdot CHMe_2 \longrightarrow CMe_2{:}C(OH) \cdot CHMe_2 + Cl_2 = CMe_2Cl \cdot CO \cdot CHMe_2 + HCl.$$

Phosphorus pentabromide dissociates more readily, both on heating and in solution, than the pentachloride, and exerts, therefore, increased enolising action on the ketones, which yield mainly bromoketones.

$CMe_2{:}O \longrightarrow CH_3{\cdot}C(OH){:}CH_2 + Br_2 = CH_3{\cdot}CO{\cdot}CH_2Br + HBr$. Experiment shows, indeed, that the action of bromine on ketones yields the same products as that of phosphorus pentabromide, the latter, however, acting more vigorously owing to the enolising action of the bromine formed on dissociation of the pentabromide being more energetic than the action of free bromine; for instance, *iso*propyl α-bromo*iso*propyl ketone is not acted on by bromine, but is converted into the dibromo-derivative when heated with phosphorus pentabromide on a water-bath.

The first bromine atom enters the ketone molecule in the α-position with respect to the carbonyl group and mostly replaces a hydrogen atom of the less highly hydrogenated hydrocarbon group. The second bromine atom proceeds mostly to the same carbon atom as the first, so that unsymmetrical αα-dibromoketones are obtained in preponderating amount. If, however, the first bromine atom replaces the only hydrogen atom combined with the first of the α-carbon atoms, the second bromine atom becomes united with the other carbon atom adjacent to the carbonyl group, symmetrical dibromoketones being obtained. Tribromoketones may also be formed by the replacement of all three hydrogen atoms united to the carbon atoms in the α-positions.

[With I. Idelson and (Mlle.) A. Umnova.]—iso*Propyl α-chloro*iso*propyl ketone*, $CMe_2Cl{\cdot}CO{\cdot}CHMe_2$, is a colourless liquid, b. p. 142°/760 mm., 92°/150 mm., D_0^0 0 9800, D_0^{20} 0·9592, giving no compound with semicarbazide. By alcoholic potassium hydroxide it is converted into iso*butyryldimethylcarbinol*, $OH{\cdot}CMe_2{\cdot}CO{\cdot}CHMe_2$, which is a colourless liquid with an odour like that of camphor, b. p. 164·5—165°/761 mm., D_0^0 0·9408, D_0^{20} 0·9239, and forms a *semicarbazone*, $C_8H_{17}O_2N_3$, m. p. 196°, in either aqueous or alcoholic solution (compare Kling, A., 1905, i, 503). Reduction of the keto-alcohol yields: (1) βγ-dihydroxy-βδ-dimethylpentane, $OH{\cdot}CMe_2{\cdot}CHPr^{\beta}{\cdot}OH$, m. p. 59°, and (2) di*iso*propylcarbinol. Conversion of di*iso*propylcarbinol into the corresponding γ-iodo-βδ-dimethylpentane, $CHMe_2{\cdot}CHI{\cdot}CHMe_2$, and treatment of the latter with alcoholic potassium hydroxide yields *βδ-dimethyl-Δ^{β}-amylene*, $CMe_2{:}CHPr^{\beta}$, b. p. 82—84°, oxidation of which gives *iso*butyryldimethylcarbinol (see above) (compare Blaise and Herman, A., 1910, i, 534).

[With E. Fricman.]—iso*Propyl* tert.*-butylcarbinol*,

$$OH{\cdot}CHPr^{\beta}{\cdot}CHMe_3,$$

obtained by the action of magnesium *tert.*-butyl chloride on *iso*butaldehyde, is a liquid, b. p. 150—151°/760 mm., D_0^0 0·8479, D_0^{20} 0·8298, m. p. −13°, with a camphor-like odour. On oxidation it yields iso*propyl* tert.*-butyl ketone*, $COPr^{\beta}{\cdot}CHMe_3$, which is a mobile liquid, b. p. 134—135°/760 mm., D_0^0 0·8240, D_0^0 0·8065, with an intense camphor-like odour; neither the hydrazone nor the semicarbazone could be obtained. Treatment of the ketone with phosphorus pentachloride in a sealed tube at 140° gives: (1) *α-chloro*iso*propyl* tert.*-butyl ketone*, $CMe_2Cl{\cdot}CO{\cdot}CMe_3$, b. p. 79—110°/18 mm., which yields Butlerov's oxoctenol, $\begin{matrix}CMe_2\\ | \\ O\end{matrix}\!\!>\!C(OH){\cdot}CMe_3$ (A., 1882, 936), on treatment with

potassium hydroxide solution; (2) *γγ-dichloro-ββδ-trimethylpentane*, $CMe_3\cdot CCl_2\cdot CHMe_2$, b. p. 122—125°/19 mm.

[With B. ISATSCHENKO.]—The action of phosphorus pentabromide on acetone yields bromoacetone, and that of the pentabromide or bromine (1 mol.) on methyl ethyl ketone gives *methyl α-bromoethyl ketone*, which is a liquid, b. p. 35—38°/12 mm., D_{20}^{20} 1·4380. With 2 mols. of bromine, methyl ethyl ketone yields (1) *bromomethyl α-bromoethyl ketone*, $CH_2Br\cdot CO\cdot CHMeBr$, b. p. 194—195°, 80—83°/10 mm., D_{20}^{20} 1·9729; (2) a tribromo-derivative of the ketone.

[With A. VANSCHEJDT.]—The action of phosphorus pentabromide on methyl *iso*propyl ketone yields: (1) *Methyl α-bromo*iso*propyl ketone*, $CH_3\cdot CO\cdot CMe_2Br$, b. p. 49°/22 mm., 139°/760 mm., D_4^{20} 1·3377, which is converted into acetyldimethylcarbinol (compare Diels and Johlin, A., 1911, i, 254) when heated in a sealed tube with potassium formate at 130° (compare Kling, A., 1905, i, 503); the *acetyl* derivative of the carbinol, $C_7H_{12}O_3$, b. p. 65°/15 mm., 170—171°/760 mm., forms the *oxime*, $C_7H_{13}O_3N$, m. p. 102—103°. (2) *Bromomethyl α-bromo*iso*propyl ketone*, $CH_2Br\cdot CO\cdot CMe_2Br$, which is best obtained by the action of bromine on the preceding compound, and is a colourless liquid, b. p. 99°/18 mm., m. p. 10°, D_{20}^{20} 1·830, yielding no crystalline products with hydroxylamine, phenylhydrazine, or semicarbazide. With alcoholic potassium hydroxide (compare Favorski, A., 1895, i, 496; Semenov, *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 693) it yields ββ-dimethylacrylic acid (compare Weinig, A., 1895, i, 17). (3) *Dibromomethyl α-bromo*iso*propyl ketone*, $CHBr_2\cdot CO\cdot CMe_2Br$, which forms colourless, silky needles, m. p. 52°, b. p. 110—115°/6 mm., D_{21}^{52} 2·051, D_{21}^{21} 2·268. By aqueous potassium hydroxide, this ketone is converted into ββ-dimethylglyceric acid, $OH\cdot CMe_2\cdot CH(OH)\cdot CO_2H$, the iso*butyl* ester of which, $C_9H_{18}O_4$, is a viscous liquid, b. p. 230° (decomp.), 121°/11 mm., D_{21}^{21} 1·0774, D_4^{21} 1·0752. When distilled in presence of sulphuric acid, ββ-dimethylglyceric acid yields α-hydroxy*iso*butaldehyde. These three bromo-ketones are also obtainable from methyl *iso*propyl ketone by the action of bromine, which gives, in addition, a *tetrabromo*-derivative, $C_5H_6OBr_4$, b. p. 157°/27 mm., D_{21}^{21} 2·446.

[With T. VELITSCHKOVSKI.]—The action of phosphorus pentabromide on pinacolin yields: (1) *Bromomethyl* tert.-*butyl ketone*, $CH_2Br\cdot CO\cdot CMe_3$, which is a liquid with a pungent odour, b. p. 70—73°/9 mm., D_0^{20} 1·3274, D_0^0 1·3508, and reduces Fehling's solution in the cold. When heated with water and freshly-precipitated barium carbonate, it yields *hydroxymethyl* tert.-*butyl ketone*, $OH\cdot CH_2\cdot CO\cdot CMe_3$, which is a liquid, b. p. 158—160°, 52·5°/12 mm., m. p. + 9·5°, D_{20}^{20} 0·95295, D_0^{20} 0·95164, $D_0^{13\cdot 5}$ 0·9576, and yields an *oxime*, $C_6H_{13}O_2N$, m. p. 89—90°, and a *phenylosazone*, $C_{18}H_{22}N_4$, m. p. 119—120°. Oxidation of this keto-alcohol yields first the corresponding keto-aldehyde and then α-hydroxy-ββ-dimethylbutyric acid, $CO_2H\cdot CH(OH)\cdot CMe_3$. (2) Dibromomethyl *tert.*-butyl ketone, $CHBr_2\cdot CO\cdot CMe_3$ (compare Kondakov, A., 1899, i, 859; Wittorv, A., 1900, i, 421). (3) *ββ-Dibromo-γγ-dimethylbutane*, $CH_3\cdot CBr_2\cdot CMe_3$, m. p. 191—191·5°.

[With D. Sciborski.]—The action of phosphorus pentabromide on ethyl *iso*propyl ketone yields: (1) *Ethyl α-bromo*iso*propyl ketone*, $CBrMe_2 \cdot COEt$, b. p. 50—53°/13 mm., D_4^{20} 1·2847, D_4^0 1·3098, which gives *ethyl α-hydroxy*iso*propyl ketone*, $OH \cdot CMe_2 \cdot COEt$, b. p. 95—97°/100 mm., D_4^0 0·9548, D_4^{20} 0·9446, D_{20}^{20} 0·9405, when heated with water and freshly-precipitated barium carbonate, and (2) *α-bromoethyl α-bromo*iso*propyl ketone*, $CHMeBr \cdot CO \cdot CMe_2Br$, b. p. 80—81°/13 mm.

[With P. Aschmarin.]—*Ethyl*tert.-*butylcarbinol*, $OH \cdot CHEt \cdot CMe_3$, obtained by the interaction of magnesium *tert.*-butyl chloride and propaldehyde, is a liquid, b. p. 132—135°, 42—44°/15 mm., D_4^0 0·84078, D_4^{20} 0·82462. It forms an *acetyl* derivative, $C_9H_{18}O_2$, b. p. 157—159°/770 mm., and on oxidation yields *ethyl* tert.-*butyl ketone*, $CMe_3 \cdot COEt$, b. p. 125—126°/769 mm., D_4^0 0·8303, D_4^{20} 0·8125, which gives a *semicarbazone*, $C_8H_{17}ON_3$, m. p. 144°. The action of phosphorus pentabromide on this ketone yields: (1) *α-Bromoethyl* tert.-*butyl ketone*, $CHMeBr \cdot CO \cdot CMe_3$, b. p. 67·5—68·5°/11 mm., D_4^0 1·2687, D_4^{20} 1·2456, and (2) *αα-dibromoethyl* tert.-*butyl ketone*, $CMeBr_2 \cdot CO \cdot CMe_3$, m. p. 77·5—79°/10 mm., D_4^0 1·5955, D_4^{20} 1·5674. *Trimethylacetylmethylcarbinol*, $OH \cdot CHMe \cdot CO \cdot CMe_3$, obtained by way of its *acetyl* derivative, $OAc \cdot CHMe \cdot CO \cdot CMe_3$, b. p. 189—191°, from α-bromoethyl *tert.*-butyl ketone, is a liquid, b. p. 100—101·5°/100 mm., D_4^0 0·9483, D_4^{20} 0·9301, with a faint camphor-like odour and yields a *semicarbazone* in two modifications, m. p. 98—100° and 135° respectively.

[With (Mlle.) A. Umnova.]—The action of bromine on di*iso*propyl ketone yields iso*propyl α-bromo*iso*propyl ketone*, $CMe_2Br \cdot CO \cdot CHMe_2$, b. p. 166—168°, 50—51°/10 mm., D_0^0 1·2763, D_0^{20} 1·2636, which is converted by phosphorus pentabromide into *di-α-bromo*iso*propyl ketone*, $CO(CMe_2Br)_2$, a yellow liquid with an odour of camphor, b. p. 84—85°/9 mm., D_0^0 1·6441, D_0^{20} 1·6174. *Di-α-hydroxy*iso*propyl ketone*, $CO(CMe_2 \cdot OH)_2$, obtained by the action of aqueous potassium hydroxide on the dibromo-ketone, forms rhombic plates, m. p. 42—43°, b. p. 101·5—102°/11 mm., gives a *diacetyl* derivative, $C_{11}H_{18}O_5$, m. p. 51—52°, and is converted by magnesium methyl iodide and water into *pentamethylglycerol*,

$$OH \cdot CMe_2 \cdot CMe(OH) \cdot CMe_2 \cdot OH,$$

which crystallises in slender, shining needles or prisms, m. p. 118—119°. When heated with 2% sulphuric acid solution, the trihydric alcohol decomposes into acetone and methyl *iso*propyl ketone.

[With G. Briliant.]—The action of phosphorus pentabromide on *iso*propyl *tert.*-butyl ketone yields *α-bromo*iso*propyl* tert.-*butyl ketone*, $CMe_3 \cdot CO \cdot CMe_2Br$, b. p. 91—93°/40 mm., 62—64°/12 mm., D_0^0 1·2441, D_0^{20} 1·2233, which gives a good yield of Butlerov's oxoctenol (see above) when heated with 10% aqueous potassium hydroxide.

[With (Mlle.) A. Zacharova.]—iso*Propyl*iso*butylcarbinol*,

$$CHMe_2 \cdot CH(OH) \cdot CH_2 \cdot CHMe_2,$$

obtained by the action of magnesium *iso*butyl bromide on *iso*butaldehyde, has b. p. 156°, D_0^0 0·8325, D_0^{20} 0·8222, and on oxidation yields iso*propyl* iso*butyl ketone*, $CHMe_2 \cdot CO \cdot CH_2 \cdot CHMe_2$, b. p. 147—148°, D_0^0 0·82705, D_0^{20} 0·81223. *α-Bromo*iso*propyl* iso*butyl ketone*, $CMe_2Br \cdot CO \cdot CH_2 \cdot CHMe_2$, obtained by the action of either bromine or

phosphorus pentabromide, has b. p. 75—78°/12 mm., 81—85°/21 mm., D_0^0 1·2187, D_0^{20} 1·1979, and, when heated with potassium formate and methyl alcohol in a sealed tube at 120°, yields iso*butyryldimethylcarbinol*, $OH\cdot CMe_2\cdot CO\cdot CH_2\cdot CHMe_2$, b. p. 67—70°/13 mm., D_0^0 0·9159, D_0^{20} 0·8962, the *semicarbazone* of which, $C_9H_{19}O_2N_3$, m. p. 126°, was prepared; oxidation of the keto-alcohol gives valeric acid. *α-Bromo*iso*propyl α-bromo*iso*butyl ketone*, $CMe_2Br\cdot CO\cdot CHBr\cdot CHMe_2$, b. p. 103—105°/21 mm., is also formed by the action of phosphorus pentabromide on *iso*propyl *iso*butyl ketone.

[With N. Mandryk.]—*Phenyl*iso*propylcarbinol*, $OH\cdot CHPh\cdot CHMe_2$, prepared by the action of magnesium *iso*propyl iodide on benzaldehyde, has b. p. 110—111°/13 mm., D_0^0 0·9933, D_{20}^{20} 0·9790, forms the *acetyl* derivative, $C_{12}H_{16}O_2$, b. p. 118—120°/16 mm., and on oxidation yields *phenyl* iso*propyl ketone*, $CHMe_2\cdot COPh$, which is a colourless liquid, b. p. 95—98°/10 mm., D_0^0 0·9996, D_{20}^{20} 0·9848, and forms the *semicarbazone*, $C_{11}H_{15}ON_3$, m. p. 166—167°. The action of phosphorus pentabromide on the ketone yields phenyl α-bromo*iso*propyl ketone, b. p. 129—130°/12 mm., D_0^0 1·3845, D_{20}^{20} 1·3652 (compare Collet, A., 1898, i, 477). *Benzoyldimethylcarbinol*, $CMe_2Bz\cdot OH$, b. p. 116—118°/9 mm., D_0^0 1·0928, D_{20}^{20} 1·0775, when kept in a sealed tube for some months, forms the *compound*, $CMe_2Bz\cdot O\cdot CMe_2Bz$ or

$$\begin{matrix} O \\ | \\ CMe_2 \end{matrix} \!\!>\! CPh\cdot O\cdot CPh \!<\!\! \begin{matrix} O \\ | \\ CMe_2 \end{matrix},$$

m. p. 185—186°.

[With (Mlle.) L. Kolotova.]—The action of phosphorus pentabromide on *cyclo*hexyl methyl ketone yields *bromo*cyclo*hexyl methyl ketone*, $CBrAc{<}\begin{matrix} CH_2\cdot CH_2 \\ CH_2\cdot CH_2 \end{matrix}{>}CH_2$, b. p. 97—101°/13 mm., and this, with heated with aqueous potassium hydroxide, gives 1-*acetyl*cyclo*hexan*-1-*ol*, $C_6H_{10}Ac\cdot OH$, b. p. 92—94°/18 mm., D_0^0 1·04259, D_0^{20} 1·02569, which forms the *semicarbazone*, $C_9H_{17}O_2N_3$, m. p. 102° (decomp.), but does not yield a phenylosazone or react with Fehling's solution. On oxidation, 1-acetyl*cyclo*hexan-1-ol yields *cyclo*hexanone and acetic acid.

[With M. Charitonova.]—The action of phosphorus pentabromide on cyclo*hexyl* iso*propyl ketone*, $C_6H_{11}\cdot CO\cdot CHMe_2$, b. p. 83°/11 mm., which was prepared from magnesium *cyclo*hexyl bromide and *iso*butaldehyde, yields cyclo*hexyl α-bromo*iso*propyl ketone*, $C_6H_{11}\cdot CO\cdot CMe_2Br$, b. p. 111—112°/10 mm., m. p. 29°. On oxidation, the latter gives cyclo*hexyl α-hydroxy*iso*propyl ketone*, $C_6H_{11}\cdot CO\cdot CMe_2\cdot OH$, b. p. 97—98°/11 mm., D_0^0 0·9764, D_0^{20} 0·9655, the *semicarbazide* of which, $C_{11}H_{21}O_2N_3$, m. p. 183°, was prepared. Oxidation of the keto-alcohol yields hexahydrobenzoic and acetic acids. T. H. P.

Sugar Solutions and Calcium Hydroxide. P. J. H. van Ginneken (*Zeitsch ver. deut. Zuckerind*, 1912, 1293—1295).—Polemical. A reply to the criticisms of Weisberg (A., 1912, i, 608). E. F. A.

Photolysis of Sucrose by Ultra-violet Rays. Daniel Berthelot and Henri Gaudechon (*Compt. rend.*, 1912, **155**, 1016—1018. Compare A., 1910, ii, 813, 814; 1912, i, 750).—Working with rays ($\lambda = 0{\cdot}25\mu$)

the photolysis of sucrose can be shown to take place in two stages, the first, lasting six hours and consisting of hydrolysis of the sucrose to dextrose and lævulose, the solution remaining neutral, and no gas being evolved; and the second, of the decomposition of these two hexoses with the evolution of carbon monoxide and hydrogen, the relative volumes of these gases liberated pointing to the more rapid decomposition of the lævulose than the dextrose. With the extreme ultra-violet rays the first stage is very rapid, and the separation of the two phases is somewhat difficult. W. G.

Composition of Press Cakes from Sugar Refineries. LÉON LINDET and CHARPENTIER (*Bull. Soc. chim.*, 1912, [vi], 11, 956—958). —It is shown that these cakes, after having been properly washed by the slightly ammoniacal water produced by condensing steam from the evaporating pans, contain no free lime. The sugar, which can be extracted by washing them with water, is present in the free state. The cakes always contain insoluble tribasic calcium saccharate, owing to the fact that this compound is not decomposed in the customary rapid treatment with carbon dioxide. T. A. H.

Plant Colloids. II. The Stability of Starch Solutions. MAX SAMEC (*Koll. Chem. Beihefte*, 1912, 4, 132—174. Compare A., 1912, ii, 144).—The ageing of starch solutions is accompanied by a very considerable reduction of the viscosity, and the influence of foreign substances on the changes which occur during the process of ageing has been investigated by means of viscosity measurements. The same starch was used for all the experiments, and the solutions prepared by mixing a weighed quantity of the starch to a paste with 25 c.c. of cold water and then adding the paste to 75 c.c. of boiling water. After boiling for one minute, the starch paste was heated for two hours at 120° and then filtered under pressure, the age of the starch solution being reckoned from the time of the completed filtration.

The rate of diminution of the viscosity of such starch solutions is greater for dilute than for more concentrated solutions. It is also greater for solutions which have been shaken than for corresponding solutions which have been kept undisturbed. The addition of hydrochloric acid diminishes the initial viscosity, but retards the further progress of the change, and thus increases the stability of the solutions. With increasing concentration of the acid, the influence on the stability increases at first and passes through a maximum. Potassium hydroxide raises the viscosity when added in very small quantity; if larger amounts are present the viscosity is diminished, however, and this effect is very pronounced in the case of solutions which contain alkali hydroxide in more than $0 \cdot 001 N$-concentration. Ammonium sulphate and ammonium thiocyanate both diminish the initial viscosity, but in concentrated solution the influence of the two salts on the stability of the starch solution is quite different, in that the sulphate increases the stability, whilst the thiocyanate is comparatively inactive.

The viscosity change is irreversible in character, and the sensitiveness of the starch solutions towards electrolytes diminishes with the time which has elapsed since their preparation. The ageing of the

solutions is also found to be accompanied by an increase in the electrical conductivity.

An explanation of some of the observed facts is suggested, in which the author assumes that the active constituent is a complex compound of starch and phosphoric acid. H. M. D.

Photochemical Synthesis of Carbohydrates. JULIUS STOKLASA JOHANN ŠEBOR, and WENZEL ZDOBNICKÝ (*Biochem. Zeitsch.*, 1912, **47**,, 186—188. Compare A., 1912, i, 606).—A reply to the criticisms of Walther Löb (A., 1912, i, 750). S. B. S.

Existence of a Hydrate of Nitrocellulose. TH. CHANDELON (*Bull. Soc. chim. Belg.*, 1912, **26**, 495—502).—The viscosities of solutions of dry and moist nitrocelluloses in mixtures of alcohol and ether have been examined, together with the viscosities of solutions of dry nitrocellulose in the same mixture to which small quantities of water have been added.

The author is led to the conclusions: (1) that the greater solubility of moist nitrocellulose in a mixture of alcohol and ether does not depend on the existence of a hydrate, but simply on the dilution of the solvent by the water contained in the moist substance; (2) that it is immaterial whether this water is contained in the moist nitrocellulose or previously added to the solvent, and (3) that a mixture of alcohol and ether which contains small quantities of water has a solvent action towards nitrocellulose superior to that of an anhydrous mixture of the two solvents. H. W.

A New Nitrocellulose. TASSART (*Bull. Soc. chim.*, 1912, [iv], **11**, 1009—1011).—By the successive action of sulphuric acid and nitric acid on cotton with avoidance of rise in temperature, the author has obtained a white, powdery unstable compound which is provisionally termed α-nitrocellulose and which contains about 13·5% nitrogen. When heated on the water-bath it becomes pasty, evolves nitrous fumes with increasing intensity, and ultimately ignites. In thin layers, however, heating can be conducted without inflammation, when the residue, after cessation of evolution of nitrous fumes, is found to contain 6% nitrogen and to reduce Fehling's solution. The latter property is not possessed by α-nitrocellulose to any marked extent.

Certain substances, such as diphenylamine, dextrose, diaminophenol hydrochloride, α-naphthylamine, tetramethyldiaminobenzophenone, etc., when warmed with α-nitrocellulose on the water-bath cause darkening and subsequent charring without evolution of nitrous fumes or inflammation. On the other hand, the tendency of α-nitrocellulose towards spontaneous inflammability is accentuated by the presence of *p*-phenylenediamine.

α-Nitrocellulose is insoluble in water, soluble in methyl and ethyl alcohols, aldehyde, and acetone. Treatment with water or aqueous sodium hydroxide leaves it unaffected, but alcoholic sodium hydroxide causes marked alteration in properties, and renders it completely soluble in water.

Dextrose and amidon, when similarly treated with sulphuric and nitric acids, yield similar products. H. W.

Formylated Cellulose. EDWARD C. WORDEN (*J. Soc. Chem. Ind.*, 1912, **31**, 1064—1068).—The author discusses at some length the several methods of preparing cellulose acetates and formates which have been published, also the means which have been devised for converting these esters into plastic substances resembling celluloid.

Results of work carried out with the object of converting cellulose formate, obtained by the action of formic acid (99%) and zinc chloride on a cellulose prepared by denitrating nitro-cellulose with ammonium sulphide solution, into a modification having more valuable properties, such as greater solubility in common organic solvents, are recorded.

The crude solutions of cellulose formate as obtained directly from the cellulose were treated with small quantities of water for varying periods. Generally speaking, the effect of this treatment is to increase the solubility of the product in solvents such as acetone, chloroform, and tetrachloroethane, the solubility becoming greater as the proportion of water employed or the period of treatment is increased. W. H. G.

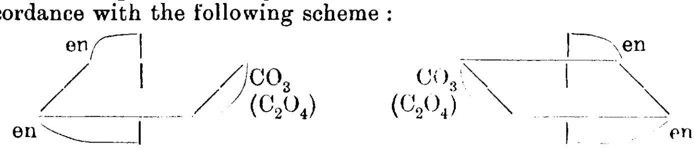
Neurine Bromide. ERNST SCHMIDT and A. SEEBERG (*Apoth. Zeit.*, 1912, 71; Reprint, 2 pp.).—The conversion of large quantities of trimethylbromoethylammonium bromide into neurine by moist silver oxide is often accompanied by serious loss, due to the formation of trimethylamine. A cheaper and more satisfactory method is described, in which barium hydroxide is used in place of silver oxide.

Neurine bromide on heating with hydrobromic acid at 165—170° gives, as already observed, trimethyl-β-bromoethylammonium bromide, but the mother liquors contain another substance, apparently the isomeric *trimethyl-α-bromoethylammonium bromide*, crystallising in tablets. D. F. T.

The Asymmetric Cobalt Atom. VI. ALFRED WERNER and MCCUTCHEON (*Ber.*, 1912, **45**, 3281—3287).—The active compounds of cobalt which have hitherto been prepared belonging to the series $[en_2CoX_2]X$ contain two monobasic acid residues in direct combination with the cobalt atom, for example, $[Cl_2Co\,en_2]X$ and $[(NO_2)_2Co\,en_2]X$. The authors have now investigated the compounds in which the two X-groups have been replaced by one dibasic acid residue, for example, the oxalic and carbonic acid residues, in order to see if they show mirror-image isomerism. These compounds have the following structural formulæ: $\left[\begin{array}{l}\mathrm{O{:}C{\cdot}O}\\ \quad\;| \\ \mathrm{O{:}C{\cdot}O}\end{array}\!\!>\mathrm{Co\,en_2}\right]X$ and

$$\left[\mathrm{O{:}C}\!<\!{}^{\mathrm{O}}_{\mathrm{O}}\!>\!\mathrm{Co\,en_2}\right]X.$$

It has been shown previously (A., 1912, i, 78) that geometrical isomerides do not exist, and that the acid residues occupy neighbouring co-ordination positions. Optical isomerides should, however, exist in accordance with the following scheme:



It was not found possible to resolve the inactive compounds into their active components, bnt the individual isomerides have been obtained directly from the active 1:2-dichlorodiethylenediaminecobaltic salts by the action of potassium carbonate and oxalate respectively, for example: $[Cl_2Co\ en_2]Cl + K_2CO_3 = [CO_3Co\ en_2]Cl + 2KCl$. The fact that such active isomerides have been prepared forms further support for the *cis*-structure of these compounds.

The active carbonato-salts possess an intense red colour, so that their rotatory power could only be determined for red light (*C*-line). The observed specific rotations are fairly large, for example, the chloride has $[\alpha]_C \pm 350°$, and it is noteworthy that the various salts show very different rotatory powers, the iodide having $[\alpha]_C \pm 250°$ and the dithionate $[\alpha]_C \pm 216°$. In cold aqueous solution the salts are fairly stable, undergoing racemisation very slowly, the rotation diminishing by one-half in about eight days. At 90° racemisation is complete in a short time. The products of racemisation consist of the inactive carbonato-salts, and are formed probably by one of the valencies of the carbonato-residue becoming loosened for a time, the radicle $[Co\ en_2]$ then undergoing a structural change.

The oxalo-salts possess a smaller specific rotation than the carbonato-salts, the chloride and nitrate having $[\alpha]_C \pm 200°$ and the iodide $[\alpha]_C \pm 160°$. They are quite stable, the aqueous solutions showing no tendency to racemise even on warming.

The sign of rotation of the various carbonato- and oxalo-salts is the opposite to that of the dichloro-salts from which they are obtained.

Carbonato-salts, YX, where $Y = [CO_3Co\ en_2]$.—The d- and l-*chlorides*, YCl, are obtained by heating a mixture of 1 gram of the active dichloro-chloride with the calculated quantity of potassium carbonate and 0·5 c.c. of water on the water-bath until the colour changes to red (2 mins.). The reaction product is then rapidly cooled in a freezing mixture and rubbed with a platinum spatula, when the chloride separates as a red, crystalline powder, forming a mixture of the active and racemic compounds. The racemate is less soluble than the active salt, and is left undissolved when sufficient water is added to dissolve about three-quarters of the solid. The pure active chloride is then obtained from the aqueous solution by precipitation with a mixture of alcohol and ether. $[\alpha]_C \pm 350°$, $[M]_C \pm 960°$; 100 c.c. of water dissolve 5 grams of the active chloride at 18°.

The active *iodides*, YI, and *dithionates*, $Y_2S_2O_6$, were obtained from the active chlorides by double decomposition with ammonium iodide and sodium dithionate respectively. The former have $[\alpha]_C \pm 250°$, $[M]_C \pm 915°$, and dissolve to the extent of 1 gram in 100 c.c. of water at 18°; the latter has $[\alpha]_C + 216°$ and $-220°$, $[M]_C + 689°$ and $-702°$, the solubility being 3·5 grams of the salt in 100 c.c. of water at 18°.

Oxalo-salts, YX, where $Y = [C_2O_4Co\ en_2]$.—The active *chlorides*, YCl,H_2O, are prepared similarly to the carbonato-salts, using potassium oxalate, the chief difference being that the racemate is more soluble than the active salt, the latter separating out fairly pure. $[\alpha]_C + 200°$ and $-204°$, $[M]_C + 641°$ and $-653°$; 100 c.c. of water

dissolve 2 grams of the salt at 18°. The active *iodides*, YI, and *nitrates*, YNO_3,H_2O, were obtained from the chloride by double decomposition with ammonium iodide and silver nitrate respectively. Their solubilities are respectively 1 gram and 4 grams in 100 c.c. of water at 18°. The former have $[\alpha]_C +160°$ and $-155°$, $[M]_C +630°$ and $-610°$, the latter having $[\alpha]_C +204°$ and $-200°$, $[M]_C +689°$ and $-676°$.

T. S. P.

The Asymmetric Cobalt Atom. VII. ALFRED WERNER and YUJI SHIBATA (*Ber.*, 1912, **45**, 3287—3293).—Optically active 1 : 2-diamminediethylenediaminecobaltic salts have now been obtained. They could not be prepared by resolution of the racemates, but were obtained from the active 1 : 2-bromoammine salts by the action of liquid ammonia, in accordance with the equation : $\left[\begin{matrix}Br\\NH_3\end{matrix}Co\,en_2\right]X_2 + NH_3 = \left[\begin{matrix}NH_3\\NH_3\end{matrix}Co\,en_2\right]\begin{matrix}X_2\\Br\end{matrix}$. This reaction denotes a change from an asymmetric cobalt compound to one showing molecular asymmetry I (compare A., 1911, i, 839).

1 : 2-Bromoamminediethylenediaminecobaltic bromide was used in the first experiments, but it was found that the active 1 : 2-diammine bromide obtained was always contaminated with the inactive 1 : 6-salt. The formation of the 1 : 6-isomeride was completely prevented, however, when the bromocamphorsulphonate was used instead of the bromide Recrystallisation of the product of the action of liquid ammonia on 1 :2-bromoamminediethylenediaminecobaltic *d*-bromocamphorsulphonate gives immediately pure d-*diamminediethylenediaminecobaltic* d-*bromocamphorsulphonate.*

The active salts show very marked dispersion of the rotation, for example, the chloride has $[\alpha]_C \pm 15°$, $[\alpha]_D \pm 50°$; in the three-field polarimeter the *d*-salts give a yellow middle field and orange outer fields, the colours being reversed for the *l*-salts. Their rotatory powers for the *D*-line agree approximately with those of the dinitro-salts, and are about one-third of the values obtained for the triethylenediamine salts for both the *C*- and *D*-lines.

The solubilities of the active salts are, as a rule, greater than that of the racemate. Of the bromocamphorsulphonates, the *dd*- and *ll*-salts are sparingly soluble, whilst the *dl*- and *ld*-salts are easily soluble.

The cold aqueous solutions of the active salts can be preserved indefinitely without undergoing racemisation; on boiling for some time, racemisation occurs, being accompanied by a complete decomposition of the compounds.

d-*Diamminediethylenediaminecobaltic* d-*bromocamphorsulphonate* and the corresponding ll-*salt* were obtained by dissolving *d*-bromoamminediethylenediaminecobaltic *d*-bromocamphorsulphonate or the corresponding *ll*-salt in liquid ammonia. After a short time the solution turns yellow, and one recrystallisation of the residue after allowing the ammonia to evaporate gives the pure salt, $[\alpha]_D^{24} +81°$ and $-80°$.

The following active diamminediethylenediaminecobaltic salts, YX_3,

where $Y = [(NH_3)_2Co\ en_2]$, were obtained from the active bromocamphorsulphonates by treatment with concentrated solutions of the appropriate acids. The *chlorides*, YCl_3, form golden-yellow prisms; the *bromides*, YBr_3, crystallise in deep-yellow needles; the *perchlorates*, $Y(ClO_4)_3$, form yellow, prismatic crystals, and the *nitrates*, $Y(NO_3)_3$, give slender, golden-yellow, flat crystals. The *iodides*, YI_3, dark yellow crystals, and the *dithionates*, $Y(S_2O_6)_3,3{\cdot}5H_2O$, small, cubical crystals, are obtained from the bromides by double decomposition with ammonium iodide and sodium dithionate respectively; the nitrate can similarly be obtained, using silver nitrate.

The specific and molecular rotations of the various salts are shown in the following table:

	$[\alpha]_D$.	$[M]_D$.	$[\alpha]_C$.	$[M]_C$.	Temp.
d-Chloride	+50°	+159·8°	+15°	+47·94°	21·0°
l-Chloride	−51	−162·99	−16	−51·14	22·0
d-Bromide	+37	+164·0	+11	+48·75	23·0
l-Bromide	−37	−164·0	−9	−39·89	22·0
d-Iodide	+29	+172·3	—	—	24·0
l-Iodide	−28	−166·32	—	—	24·0
d-Nitrate	+46	+183·7	+14	+55·89	21·5
l-Nitrate	−44	−175·65	−12	−47·90	23·5
d-Perchlorate	+32	+163·7	—	—	22·0
l-Perchlorate	−33	−168·83	−7	−35·81	22·0
d-Dithionate	+24	+116·86	—	—	23·0

T. S. P.

The Asymmetric Cobalt Atom. VIII. ALFRED WERNER and G. TSCHERNOV (*Ber.*, 1912, **45**, 3294—3301).—Optically active 1:2-chlorobromodiethylenediaminecobaltic salts, $\left[\begin{matrix}Cl\\Br\end{matrix}Co\ en_2\right]X$, are described. The inactive 1:2-chlorobromo-bromide, which was used as the starting point, was obtained as follows: 1:6-dichlorodiethylenediaminecobaltic chloride (compare A., 1912, i, 82) was prepared, and transformed into 1:2-chloroaquodiethylenediaminecobaltic sulphate. From the latter, chloroaquodiethylenediaminecobaltic bromide was obtained and transformed, by heating at 105°, into a mixture of the 1:2- and 1:6-chlorobromodiethylenediaminecobaltic bromide, from which the 1:2-isomeride is obtained by means of its lesser solubility (compare A., 1912, i, 83).

The active chlorobromo-salts were obtained by treating an aqueous solution of the racemic bromide with active ammonium bromocamphorsulphonate (compare the preparation of the active dichloro-salts, A., 1912, i, 11). After a short time, when ammonium *d*-bromocamphorsulphonate is used, a microcrystalline precipitate of *l*-chlorobromodiethylenediaminecobaltic *d*-bromocamphorsulphonate separates, whereas ammonium *l*-bromocamphorsulphonate gives the *dl*-salt. The salts are very unstable in aqueous solution, readily giving the bromoaquo-salts, so that all operations must be carried out as quickly as possible.

The various active salts were obtained from the bromocamphorsulphonates by trituration with the requisite concentrated mineral acid until complete solution was attained; the strongly-cooled solutions were then precipitated with alcohol.

The following table (rows 1 and 2) gives a summary of the rotatory powers of the various salts; for the sake of comparison, the rotations of the dichloro-salts are also given (rows 3 and 4):

	Chloride.		Bromide.		Nitrate.		Sulphate.		Dithionate.	
	[α].	[M].	[α].	[M].	[α].	[M].	[α].	[M]/2.	[α].	[M]/2.
d-Salt...	+164°	+571°	+148°	+581°	+144°	+513°	+144°	+506°	+116°	+445°
l-Salt...	−176	−612	−155	−608	−152	−542	−148°	−520	−120	−460
d-Salt...	+184	+558	+168	+554	+164	+511	+180	+536	+160	+542
l-Salt...	−200	−607	−176	−581	−164	−511	−182	−540·5	−164	−556

The above are the maximum values observed, since racemisation takes place very rapidly.

l-*Chlorobromodiethylenediaminecobaltic* d-*bromocamphorsulphonate*, $Y(SO_3{\cdot}C_{10}H_{14}OBr)$, where $Y=\left[\begin{matrix}Cl\\Br\end{matrix}Co\,en_2\right]$, forms a grey, crystalline powder with a violet shade; $[\alpha]^{20}-40°$, $[M]^{20}-242°$. The corresponding dl-*salt* is similar; $[\alpha]^{20}+32°$, $[M]^{20}+193°$. The active *chlorobromodiethylenediaminecobaltic chlorides*, YCl,H_2O, are dark, greyish-violet, crystalline powders, as also are the *bromides*, YBr,H_2O, and the *nitrates*, YNO_3. The *sulphates*, Y_2SO_4,H_2O, and *dithionates*, $Y_2S_2O_6,H_2O$, are respectively light violet, crystalline powders and light grey leaflets.
T. S. P.

α-Aminobutyric Acid and its Derivatives. Emil Abderhalden and Erich Wurm (*Zeitsch. physiol. Chem.*, 1912, **82**, 167—171. Compare Abderhalden and Chang, A., 1912, i, 338).—When pure α-aminobutyric acid is treated with concentrated hydrochloric acid under the conditions prevailing during protein hydrolysis, only about 5% of the acid undergoes decomposition. Alanine and leucine remain unchanged under these conditions.

The conditions for the preparation of pure formyl-*d*- and -*l*-aminobutyric acid are described. Formyl-*d*-aminobutyric acid has $[\alpha]_D^{20}$ −27·74°, the value for the isomeride being +27·98°.

The formyl group is readily hydrolysed by water.

On feeding *dl*-aminobutyric acid or glycyl-*dl*-aminobutyric acid to rabbits, neither the acids nor their components could be detected in the urine.
E. F. A.

Preparation of Creatine from Urine. Alois Viquerat (D.R.-P. 251937).—A modification of Neubauer's method (compare Abderhalden, *Lehrbuch Biochem. Arbeitsmethoden*, 1910, III, 783) by which creatine is isolated from urine as its zinc chloride double salt.
F. M. G. M.

Some Complex Compounds of Platinous Chloride with Aminoacetal. J. Tschugaev and B. Orelkine (*Compt. rend.*, 1912, **155**, 1021—1023).—An endeavour to prepare two isomeric substances of the type, $[Pt(NHMe_2)_2Cl_2]$, prepared by Jörgensen (A., 1906, i, 338), replacing the dimethylamine by aminoacetal. On adding aminoacetal to a dilute solution of potassium platinosochloride, a yellow, crystalline compound is deposited, crystallising from alcohol in needles,

m. p. 133°. It has the composition ($Pt2ACl_2$), where A stands for the aminoacetal molecule, $NH_2\cdot CH_2\cdot CH(OEt)_2$. This substance is a very feeble electrolyte, and is almost unacted on by silver nitrate in alcoholic solution. In benzene solution it polymerises as shown by cryoscopic molecular weight determinations. The mother liquors from its preparation on evaporation yield a colourless, crystalline *compound*, $(Pt4A)Cl_2$, m. p. 130·5°, the chlorine of which is immediately precipitated by silver nitrate. With potassium platinosochloride it yields a *salt*, $(Pt4A)PtCl_4$, pink needles, m. p. 127°, which is not acted on by Reiset's chloride I.

An attempt was made to prepare the two isomerides having the constitution $(Pt2A2NH_3)Cl_2$, but it only yielded gummy products which with potassium platinosochloride gave the same *salt*,

$$(Pt2A2NH_3)PtCl_4,$$

lilac needles, m. p. 151°. W. G.

The Nitrile and Sulphonamide of Thiodiacetic Acid. NILS VON ZWEIGBERGK (*Ber.*, 1912, **45**, 3337—3338).—Dry hydrogen sulphide and ammonia are led into an ethereal solution of chloroacetonitrile until the solution, which first becomes warm, begins to cool. After collecting the precipitated ammonium chloride and concentrating the filtrate, white, rhombic tablets of the *nitrile* of thiodiacetic acid, $S(CH_2\cdot CN)_2$, are obtained, m. p. 45·5—46·5°. Acetone may be used instead of ether as solvent. The substance cannot be obtained by the action of phosphoric oxide on ammonium thiodiacetate.

If, instead of proceeding as above, an ammoniacal, alcoholic solution of chloroacetonitrile is saturated with hydrogen sulphide, yellowish-white leaflets of the *sulphonamide* of thiodiacetic acid, $S(CH_2\cdot CS\cdot NH_2)_2$, m. p. 124—125°, are obtained. T. S. P.

Constitution of the Compound known as Phorononitrile, and on Some Other Derivatives of Phoronic and Mesitylic Acids. J. MILIKAN (*Rec. trav. chim.*, 1912, **31**, 287—298).—The true nitrile of phoronic acid should have the formula $C_{11}H_{16}ON_2$, whereas the so-called nitrile discovered by Pinner (A., 1881, 796) has the formula $C_{11}H_{18}O_2N_2$. Applying the conclusions drawn by Anschütz in the case of mesitonic acid (A., 1888, 1272) to the present question, the relation of these nitriles to phorone shou d be represented thus: Phorone, $CMe_2\!:\!CH\cdot CO\cdot CH\!:\!CMe_2$. Nitrile, $CN\cdot CMe_2\cdot CH_2\cdot CO\cdot CH_2\cdot CMe_2\cdot CN$. Amide,

$$NH_2\cdot CO\cdot CMe_2\cdot CH_2\cdot CO\cdot CH_2\cdot CMe_2\cdot CO\cdot NH_2.$$

So-called nitrile, $\begin{array}{l} CMe_2\cdot CH_2\cdot C\cdot CH_2\cdot CMe_2. \\ | \qquad\quad \diagup \diagdown \qquad | \\ CO\text{———}NH\ \ NH\text{—}CO \end{array}$

As the direct addition of hydrogen cyanide to such an unsaturated ketone as phorone would be extremely difficult, an attempt has been made to prepare the amide. *Methyl phoronate*, $C_{13}H_{22}O_5$, obtained in white needles, m. p. 30°, by the action of methyl alcohol and sulphuric acid on phoronic acid, was heated for some hours with alcoholic ammonia in a sealed tube, when, instead of the expected amide, the so-called phorononitrile was the product, m. p. 326—327°.

As the amide group is in the favourable γ position with respect to the ketone group, it is assumed that the expected amide has lost water and that the phorononitrile is a di-lactam or an anhydrodiamide of the above constitution. It is possible to replace the hydrogen attached to the nitrogen in compounds of this structure, and, in fact, *diacetylanhydrophoronodiamide*, $C_{15}H_{22}O_4N_2$, m. p. 89—90°, has been obtained by the action of acetic anhydride. The compound is also very stable and dissolves in cold concentrated nitric acid, yielding a crystalline mass which is probably an additive product with the acid, and from which, water recovers the material unchanged.

Analogous anhydrodiamides are the imidopimelimide of Marckwald (A., 1888, 677; compare also Volhard, A., 1892, 433) and the ketodi-imide of β-acetylglutaric acid of Emery (A., 1897, i, 325).

Pinner's phoronimide (*loc. cit.*) also yields the anhydrodiamide on heating with ammonia, and, accepting Anschütz's di-lactone structure for the parent substance phoronic anhydride, it is probable that the imide is a lactone-anhydroamide of the constitution

$CMe_2{\cdot}CH_2{\cdot}C{\cdot}CH_2—CMe_2$
CO——NH O——CO.

Methyl phoronate and the di-lactone have also been heated with methylamine, the product being *anhydrophoronodimethyldiamide*, $C_{13}H_{22}O_2N_2$, m. p. 136—137°, which is much less stable than the unsubstituted anhydrodiamide, since it readily loses methylamine on warming with potassium hydroxide. The *product* of the action of methylamine on the di-lactone in the cold has the formula $C_{13}H_{26}O_4N_2$ and m. p. 116—118°, and from analogy to the fact that ammonia forms with hydrochelidonodi-lactone (Volhard, *loc. cit.*) and with β-acetylglutarodilactone (Emery, *loc. cit.*) ammonium salts of amino-acids, it probably has the constitution

$CMe_2{\cdot}CH_2{\cdot}CO{\cdot}CH_2.CMe_2$
$OC{\cdot}NHMe$ $OC{\cdot}OH,NH_2Me$.

It decomposes at its melting point, and the *product*, $C_{12}H_{19}O_3N$, m. p. 110°, is, most likely, the lactone of anhydrophoronomethylamide,

$CMe_2{\cdot}CH_2{\cdot}C{\cdot}CH_2{\cdot}CMe_2$
OC——NMe O—CO.

Methyl mesitylate, $C_9H_{15}O_3N$, has also been prepared in colourless needles, m. p. 119—120°. J. C. W.

The Formation of Metallic Nitrides from Thiocyanates and Cyanides. ALEXANDER C. VOURNASOS (*Zeitsch. anorg. Chem.*, 1912, **77**, 191—196. Compare A., 1911, ii, 600).—Aluminium, in the form of an impalpable powder, reduces many organic nitrogen compounds, with formation of the nitride; thus, with thiocarbamide, the reaction is $CS(NH_2)_2 + 2Al = Al_2N_2 + H_2S + H_2 + C$.

Potassium and ammonium thiocyanates, dried and mixed with aluminium powder, react if placed in a covered crucible and heated by the blowpipe according to the equation: $2KCNS + 2Al = {}_2S_2 + Al_2N_2 + 2C$, but a secondary reaction occurs to some extent between

the aluminium nitride, carbon, and potassium sulphide: $2K_2S_2 + Al_2N_2 + 2C = Al_2S_3 + 2KCN + K_2S$. Washing the product with alcohol gives a residue consisting of aluminium and carbon. Boron reacts in a similar manner.

Magnesium reacts violently with thiocyanates, more quietly with cyanides: $2KCN + 3Mg = Mg_3N_2 + 2K + 2C$, the product containing free potassium, whilst some carbide is formed at higher temperatures.

Glucinum reacts quantitatively with cyanides: $3Gl + Hg(CN)_2 = Gl_3N_2 + Hg + 2C$, and calcium reacts in a similar manner. C. H. D.

The Supposed Case of Isomerism with Potassium Ferricyanide. OTTO HAUSER and E. BIESALSKI (*Ber.*, 1912, **45**, 3516—3521).—The supposed green isomeride of potassium ferricyanide (compare Locke and Edwards, A., 1899, i, 407; Bellucci and Sabatini, A., 1911, i, 430) is simply the ordinary salt containing some Prussian-blue as impurity; the aqueous solution contains the Prussian-blue in collodial solution. An artificial mixture of potassium ferricyanide and Prussian-blue answers to all the reactions of the supposed green isomeride, and gives the same absorption and ultramicroscopic phenomena. The non-formation of the ferri-imido-ester (compare Bellucci and Sabatini, *loc. cit.*) from the green isomeride, or at all events its formation to a limited extent, is due to the catalytic effects of the decomposition product.

The above agrees with Piutti's observation (A., 1912, ii, 712) that the red and green forms have exactly the same absorption spectrum.

T. S. P.

Complex Compounds of Iron and the Formation of Nitroprusside. PAUL SCHWARZKOPF (*Abhandl. deut. naturwiss-med. Ver. Böhmen*, 1911, **3**; Reprint 55 pp.).—The assumption that the formation of nitroprusside occurs according to two consecutive reversible reactions:

$$K_4FeCy_6 + NaNO_2 \rightleftharpoons K_3Na(FeCy_5NO_2) + KCN \text{ and}$$
$$K_3Na(FeCy_5NO_2) + H_2O \rightleftharpoons K_2(FeCy_5NO) + KOH + NaOH$$

has been tested by titrimetric estimation of the alkali present after equilibrium is reached, and the results when substituted into an equation derived to represent the conditions of the equilibrium, yield good constants. Considering the reactions from the ionic point of view, $(FeCy_6)'''' + (NO'_2) \rightleftharpoons (FeCy_5NO_2)'''' + Cy'$ and $(FeCy_5NO_2)'''' + H_2O \rightleftharpoons (FeCy_5NO)'' + 2OH''$, the first stage seems to imply a dissociation of the ferrocyanide ion into $(FeCy_5)'''$ and Cy'; this is quite probable as mercuric chloride in not too dilute solution of potassium ferrocyanide precipitates an iron ferrocyanide apparently indicative of a series of dissociations finally reaching the ferrous ion; similarly formaldehyde which is well known to combine with hydrocyanic acid, acts on a warm solution of potassium ferrocyanide, forming a deposit consisting of a mixture of ferrous and ferric hydroxides with a complex ferrocyanide. The power of mercuric chloride to remove cyanide ions from a solution should therefore accelerate the formation of nitroprusside by withdrawing the cyanide ion produced in the first stage of the action, and experimental investigation shows that it effects a very

considerable acceleration. It was not found possible to prepare compounds in which more than one (CN) group of potassium ferrocyanide is replaced by (NO).

It is also discovered that nitrous acid exerts an incomplete oxidising action on an acidic solution of potassium ferrocyanide and an incomplete reducing action on acidic solutions of potassium ferricyanide; in a similar manner it causes the oxidation of an ordinary ferrous salt and the reduction of a ferric one. D. F. T.

Preparation and Properties of Scandium Platinocyanide. N. A. Orlov (*Chem. Zeit.*, 1912, **36**, 1407—1408).—The compounds of scandium which have hitherto been obtained leave it doubtful whether scandium must be classed with the cerium group or with the yttrium group of the rare earths. The double sulphate with potassium sulphate resembles the double sulphates of the cerium metals, whilst the weak basic properties of scandium, and the fact that copious precipitates are obtained when the salts are boiled with solutions of sodium thiosulphate or hydrofluosilicic acid, indicates its resemblance to the yttrium metals. The platinocyanides of the cerium metals are yellow, whilst those of the yttrium metals are red, and this should give a method of classifying scandium. Scandium platinocyanide was obtained by concentrating the solution obtained after collecting the precipitate of barium sulphate formed on mixing equivalent solutions of scandium sulphate and barium platinocyanide. Yellow crystals, which are very similar in appearance to cerium platinocyanide, separate from the solution, but a red, crystalline crust forms on the sides of the vessel. On drying, the yellow crystals become reddish- or orange-coloured. If the solution is evaporated to dryness on the water-bath a yellow residue is obtained, which becomes red on cooling. The reverse change from red to yellow takes place on heating. The yellow crystals have a composition corresponding with the formula $Sc_2(PtC_4N_4)_3,18H_2O$, whilst the red crystals have the formula

$$Sc_2(PtC_4N_4)_3,21H_2O.$$

T. S. P.

Some Metallic Salts and Complex Metallic Derivatives of Cyano-carboxylic Acids and their Esters. Lizzie Petterson (*J. pr. Chem.*, 1912, [ii], **86**, 458—471).—An account of the preparation and properties of some metallic salts and derivatives of cyanoacetic and α-cyanopropionic acids.

By triturating cuprous oxide with a hot concentrated aqueous solution of cyanoacetic acid in the absence of air, a *cuprous* salt,

$$CN{\cdot}CH_2{\cdot}CO_2Cu,3CN{\cdot}CH_2{\cdot}CO_2H,H_2O$$

is obtained in small, white needles, which become green and melt at 119—120° when rapidly heated.

The *ferric* salt, $Fe_3(CO_2{\cdot}CH_2{\cdot}CN)_7(OH)_2,6H_2O$, prepared by the addition of ferric sulphate to a solution of barium cyanoacetate, forms deep, garnet-red prisms, m. p. 107°; the *cobalt*, *cupric*, and *silver* salts are also mentioned.

Hydroxymercuricyanoacetic acid, $OH{\cdot}Hg{\cdot}CH(CN){\cdot}CO_2H$, is obtained as a white, crystalline precipitate by shaking mercuric oxide for two days with an aqueous solution of cyanoacetic acid; the *sodium* and

barium salts are prepared in a similar manner from the corresponding salts of cyanoacetic acid; the *potassium* salt is prepared by the addition of potassium hydroxide to an aqueous solution of mercuric cyanide and potassium cyanoacetate.

The *methyl* and *ethyl* esters are formed by the interaction of mercuric acetate and the corresponding esters of cyanoacetic acid in methyl alcoholic solution.

Mercuric acetate reacts with ammonium cyanoacetate in aqueous solution, yielding the *compound*, $O<\begin{matrix}Hg\cdot CH(CN)\cdot CO_2\\Hg\cdot CH(CN)\cdot CO_2\end{matrix}>Hg$, as a white, flocculent precipitate.

a-Hydroxymercuri-a-cyanopropionic acid, $OH\cdot Hg\cdot CMe(CN)\cdot CO_2H$, is a yellowish-white, crystalline substance obtained by the addition of α-cyanopropionic acid to a solution of mercuric oxide in excess of dilute acetic acid. F. B.

The Benzene Problem. KURT GEBHARD (*J. pr. Chem.*, 1912, [ii], 86, 540—545).—A repetition of the author's views on the structure of the benzene ring (A., 1912, ii, 242), together with a criticism of a recent paper by Liebig on this subject (A., 1912, i, 686). F. B.

Chemical Action of Light. III. Oxidation of Benzene Hydrocarbons. HERMANN SUIDA (*Monatsh.*, 1912, 33, 1255—1285).—The fact that the most easily isolable products of the autoxidation in light of benzene homologues are carboxy-acids is attributed to the relative instability of the intermediate products.

The most satisfactory source of light used was a quartz lamp, used at a distance of about 10 centimetres from the specimen of substance. The velocity of the first stage of the oxidation could be approximately measured by the amount of peroxide formation; this was estimated by the action on a solution of potassium iodide acidified with dilute sulphuric acid with titration of the liberated iodine some hours afterwards. The parallel formation of carboxylic acids was estimated previously by titration with $N/30$-potassium hydroxide solution; it appears that the amount of acid formed cannot be entirely due to the decomposition of the peroxide.

The results indicate that pure benzene is practically passive, but that the presence of thiophen causes peroxide formation. Methyl substituted benzenes undergo autoxidation when illuminated, and the action is accelerated by the presence of small quantities of nitrobenzene or of one of the nitrotoluenes. The oxidation of xylene occurs more than twice as rapidly as that of the toluenes, and *p*-xylene oxidises more rapidly than the ortho-isomeride. The oxidation of 4-nitro-*m*-xylene under the influence of light resembles that of *p*-nitrotoluene, but is feebler; this accords with the behaviour of these substances towards chromic acid; *p*- and *o*-nitrotoluenes are oxidisable by this reagent to the corresponding aldehydes, but 4-nitro-*m*-xylene in acetic anhydride solution containing sulphuric acid is oxidised, according to the conditions, to *4-nitro-m-tolualdehyde*, small, yellow rods, m. p. 64° (*phenylhydrazone*, m. p. 108°), or the corresponding *diacetate*,

$NO_2 \cdot C_6H_3Me \cdot CH(OAc)_2$, yellow needles, m. p. 80—82°, together with some 4-nitro-*m*-toluic acid, m. p. 219—220°.

The results are discussed in relation to their theoretical bearing.

D. F. T.

Rational Preparation of Benzene Homologues. FRANZ KUNCKELL and GEORG ULEX (*J. pr. Chem.*, 1912, [ii], **86**, 518—520. Compare Rennie, T., 1881, **41**, 33).—In the preparation of the homologues of benzene by the Friedel-Craft reaction, the alkyl haloids may be replaced with advantage by the esters of chlorocarbonic acid.

When aluminium chloride is added to a mixture of the aromatic hydrocarbon and chloro-ester, several alkyl groups are simultaneously introduced, whilst if the ester is added to a cooled mixture of the hydrocarbon and aluminium chloride, the main product consists of a hydrocarbon in which only one alkyl group has been substituted.

The preparation of toluene and xylene from methyl chlorocarbonate and benzene, of trimethylbenzene from toluene, and of diethylbenzene and diethyltoluene, is described.

The *iso*butyl and amyl esters of chlorocarbonic acid give better yields than the lower homologues. F. B.

α-Phenyl-ββ-dimethylpropane, a New Amylbenzene. ARTUR BYGDÉN (*Ber.*, 1912, **45**, 3479—3483).—The interaction of magnesium benzyl chloride and *tert.*-butyl bromide in boiling ether leads to the formation of *α-phenyl-ββ-dimethylpropane*, $CMe_3 \cdot CH_2Ph$, b. p. 185·6—186·0°, $D_4^{18\cdot3}$ 0·8581, $n_D^{18\cdot3}$ 1·48837, a colourless liquid having a pleasant, aromatic odour resembling that of anisole. C. S.

Influence of Light on the Rate of Polymerisation of Phenylbutadiene. HANS STOBBE and FRITZ REUSS (*Ber.*, 1912, **45**, 3496—3498).—The formation of bisphenylbutadiene by different methods has been recorded by several investigators. The authors have performed parallel experiments, in darkness and in ordinary daylight, on phenylbutadiene in an atmosphere of carbon dioxide. The course of the polymerisation is followed by measuring the change in the refractive index. It is found that the polymerisation proceeds in the dark, but is considerably accelerated by light. Assuming that the quantity of the bimolecular form is proportional to the refractive index, the unexposed hydrocarbon contains 12—13% of bisphenylbutadiene and the insolated specimen 75—76%, after two and a-half months. The polymerisation appears to be complete after seven months. C. S.

Action of Aniline on 1 : 3 : 5-Tribromo-2 : 4 : 6-tri-iodobenzene. CONSTANTIN I. ISTRATI and M. A. MIHAILESCU (*Chem. Zentr.*, 1912, ii, 1275; from *Bul. Soc. Stiinte Bucareşti*, 1912, **21**, 23—26).—When this tribromotri-iodobenzene is heated with aniline it undergoes more extensive substitution than is the case with hexachlorobenzene (compare *ibid.*, **20**, 621), and the resulting polyamines are more easily oxidised. Alcohol extracts from the product a *tribromoiodobenzene*, needles, m. p. 154—156°, the *aniline* salt of *glyoxylic*

acid, $C_8H_{11}O_4N$, yellowish-white leaflets, m. p. 173°, and also aniline hydrobromide and iodide, whilst the amorphous, dark blue, insoluble residue has the composition of an iodopenta-anilinobenzene.

J. C. W.

Rule of the Conservation of the Type in Benzene Substitutions. ARNOLD F. HOLLEMAN (*Rec. trav. chim.*, 1912, **31**, 267—280).—When reviewing the introduction of further substituents into benzene rings which have already been once or twice substituted, only a few doubtful cases were found which were contrary to the rule that the position occupied is independent of the nature of the substituent. It is now shown that the bromination and the nitration of *o*-iodotoluene, the bromination of *o*-chlorotoluene, and the chlorination of *o*-chloronitrobenzene are no longer to be regarded as exceptions to the rule.

Hirtz (A., 1896, i, 531) assigned to the product obtained by brominating *o*-iodotoluene, "by analogy," the constitution

$$Me:I:Br = 1:2:4,$$

whereas Reverdin (A., 1898, i, 180) showed conclusively that the chief nitration product was $Me:I:NO_2 = 1:2:5$. The latter compound has now been reduced by means of iron powder, yielding the *iodotoluidine*, $Me:I:NH_2 = 1:2:5$, as unstable, white leaflets, m. p. 42°, which were diazotised with difficulty in hydrobromic acid solution, and converted into bromoiodotoluene, $Me:I:Br = 1:2:5$, b. p. 262—265°, $n_{14} = 1{\cdot}6484$. On the other hand, the direct bromination of *o*-iodotoluene (compare Hirtz, *loc. cit.*) was accomplished in the presence of iron powder, but the product was of a very complicated nature, although the main fraction boiled at 260—265°. Direct comparison of such liquids being impossible, it was sought to obtain crystalline nitro-derivatives of them. The preparation from *o*-iodonitrotoluene, when heated with fuming nitric acid, gave 5-bromo-2 : 6-dinitrotoluene, m. p. 103°. The mixture from the direct bromination, when nitrated in acetic acid, gave a small number of yellowish-green crystals, a *bromoiododinitrotoluene*, m. p. 178—181°, which was the principal product when the highest fraction, b. p. 270—275°, was separately treated. The larger portion, however, remained in solution, and on dilution with water a product was obtained, m. p. 92—93°, which was shown to be a eutectic mixture of the above bromoiododinitrotoluene and the 5-bromo-2 : 6-dinitrotoluene. Assuming that only the 1 : 2 : 5-compound loses iodine on nitration, an estimation of the hydrogen iodide showed that this isomeride formed about 40% of the mixture. The 5-position is therefore entered to a preponderating extent by both the nitro-group and the bromine atom.

In the analogous case of the bromination of *o*-chlorotoluene it is most likely that the product is a mixture of all the possible isomerides, although it is not proved that the prevailing one is the 1 : 2 : 5. This one, however, predominates in the case of the nitration of *o*-chlorotoluene, as Wibaut will soon describe.

Cohen and Bennet (T., 1905, **87**, 323) obtained by the chlorination of *o*-chloronitrobenzene the isomerides $Cl_2:NO_2 = 1:4:2$ and $1:6:2$, and a further product which melted at 31° was said by them to be the 1 : 5 : 2 compound. The entry of chlorine into a position meta to

chlorine and para to a nitro-group is contrary to the conservation of type, and it is now shown that the doubtful product is most probably a eutectic mixture of the 1 : 4 : 2 and 1 : 6 : 2 isomerides. J. C. W.

Nitro-derivatives of 2 : 6-Dibromotoluene. JAN J. BLANKSMA (*Chem. Weekblad*, 1912, **9**, 968—972. Compare A., 1912, i, 982).—A number of nitro-derivatives of 2 : 6-dibromotoluene have been prepared. The parent substance is obtained by replacing the amino-group in 6-bromo-*o*-toluidine (compare Friedländer, Bruckner, and Deutsch, A., 1912, i, 318) by bromine by the Sandmeyer method, and forms colourless crystals, m. p. 2°, and not as stated by Nevile and Winther (T., 1880, **37**, 429). By the action of nitric acid (D 1·45) this substance is converted into 2 : 6-*dibromo*-3-*nitrotoluene*, pale yellow crystals, m. p. 50°, and not 2 : 6-dibromo-4-nitrotoluene as stated by Nevile and Winther. Its constitution was proved by its formation from 6-bromoacet-*o*-toluidide. On nitration, this substance yields 6-*bromo*-3-*nitroacet*-o-*toluidide*, yellow crystals, m. p. 199°, converted by concentrated sulphuric acid into 6-*bromo*-3-*nitro*-o-*toluidine*, orange-yellow crystals, m. p. 144°. Exchange of the amino-group of this compound for bromine by the Sandmeyer reaction yields 2 : 6-dibromo-3-nitrotoluene, identical with the product obtained by nitration of 2 : 6-dibromotoluene. Potassium permanganate does not oxidise it to the corresponding benzoic acid derivative. Further nitration converts it into 2 : 6-*dibromo*-3 : 5-*dinitrotoluene*, colourless crystals, m. p. 161°. Heating with alcoholic ammonia at 100° yields 6-bromo-3 : 5-dinitro-*o*-toluidine, yellow crystals, m. p. 200°; its acetyl derivative forms colourless crystals, m. p. above 300°; at 150° the product is 3 : 5-*dinitro*-1 : 2 : 6-*tolylenediamine*, light brown crystals, m. p. 298°; the corresponding acetyl derivative forms colourless crystals, decomposing above 300°. At 150° an alcoholic solution of methylamine converts 2 : 6-dibromo-3 : 5-dinitrotoluene into 3 : 5-*dinitro*-1 : 2 : 6-*tolylenedimethyldiamine*, orange-red crystals, m. p. 216°.

Nitration of 2-bromoaceto-*p*-toluidide produces 2-*bromo*-5-*nitroaceto*-p-*toluidide*, pale yellow needles, m. p. 120°, converted by concentrated sulphuric acid into 2-*bromo*-5-*nitro*-p-*toluidine*, orange-red needles, m. p. 165°, which is converted by diazotisation into 2-bromo-5-nitrotoluene, identical with that obtained from 6-bromo-3-nitro-*o*-toluidine.

Replacement of the amino-group in 2-bromo-5-nitro-*p*-toluidine by bromine by the Sandmeyer reaction yields 2 : 4-*dibromo*-5-*nitrotoluene*, colourless needles, m. p. 85°. Nitration with nitric and sulphuric acids converts this substance into 2 : 4-dibromo-3 : 5-dinitrotoluene, m. p. 130° (compare Davis, T., 1902, **81**, 873), which with alcoholic ammonia at 150° yields 3 : 5-dinitro-1 : 2 : 4-tolylenediamine (compare A., 1904, i, 566). A. J. W.

Preparation of Anthracenemonosulphonic Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 251695).—The preparation of anthracenemonosulphonic acids has previously been

attended with difficulty; it is now found to proceed smoothly if the sulphonation is carried out in the presence of glacial acetic acid.

A solution of anthracene (300 parts) in acetic acid (600 parts) is cooled and slowly treated with chlorosulphonic acid (200 parts), the mixture is rapidly heated to 95°, and maintained at this temperature during five hours; the clear olive-green solution is treated with water (5000 parts), and the insoluble residue subsequently treated with more water (4500 parts) at 40°. The anthracene-α-sulphonic acid (in 50% yield) is precipitated from the filtrate with salt, whilst the residue on treatment with a large volume of hot water furnishes anthracene-β-sulphonic acid in over 30% yield. F. M. G. M.

Tridiphenylylmethyl. JULIUS SCHMIDLIN (*Ber.*, 1912, **45**, 3171—3183).—The tridiphenylylmethyl discovered earlier (Schlenk, Weickel, and Herzenstein, A., 1910, i, 236) is a mixture of two isomerides.

By a modification of the method of the earlier workers good yields of the tridiphenylylcarbinol could be obtained. 4-Bromodiphenyl in ethereal solution was converted by the action of magnesium and successive quantities of iodine into the corresponding organomagnesium compound which reacted with *p*-bisdiphenylyl ketone, producing a mixture of α- and β-tridiphenylylcarbinol, together with some *p*-tridiphenylylmethane and *p*-bisdiphenyl. p-*Tridiphenylylmethane*, obtainable also by the reduction of the mixture of α- and β-tridiphenylylcarbinols, forms colourless crystals, m. p. 241—242° (corr.), and when recrystallised from benzene tenaciously retains benzene of crystallisation even to the m. p.; p-*bisdiphenyl* forms inodorous leaflets, m. p. 318—319° (corr.).

The isomeric carbinols, the relative proportions of which varied considerably in different experiments, could be separated by fractional recrystallisation of the mixture from ether, or by converting into a mixture of the chlorides and then recrystallising from benzene. α-*Tridiphenylylmethylcarbinol*, the less soluble isomeride, has m. p. 212° (corr.), whilst the β-compound forms leaflets, m. p. 199—200° (corr.); both carbinols, at a concentration of 1 : 60,000, in a mixture of acetic and sulphuric acids give an absorption band from 440 to 510 μμ. The action of acetyl chloride or, better, of hydrogen chloride on the benzene solution converts the carbinols into the corresponding chlorides; α-*tridiphenylylmethyl chloride*, needles, m. p. 200° (corr.); β-*chloride*, m. p. 187—188° (corr.). The two chlorides are convertible by the action of copper powder on the benzene solution into the corresponding tridiphenylylmethyls; α-*tridiphenylylmethyl*, $C(C_6H_4Ph)_3$, is a dark green, crystalline powder, the solution of which is brownish-red, and at a concentration of 1 : 5000 shows an absorption band from 430 μμ to the ultra-violet; the molecular weight in benzene solution was 499, the theoretical being 471.

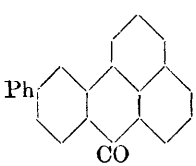
β-*Tridiphenylylmethyl* forms dark green needles, and gives a deep blue solution, which shows an absorption band (at a concentration 1 : 6000) extending from 600 to 640 μμ; the molecular weight in benzene was 518. The two tridiphenylylmethyls easily undergo

atmospheric oxidation, producing the α- and *β-tridiphenylylmethyl peroxides*, m. p. 213° (corr.) and 198° respectively.

Experiments were made to ascertain whether so-called triphenylmethyl can be observed to dissociate into the unimolecular condition. Gomberg and Cone (A., 1904, i, 658) obtained molecular weights in phenol solution indicating a dissociation, but this result was due to chemical interaction between solvent and solute with the formation of *p*-hydroxytetraphenylmethane, m. p. 282°, and triphenylmethane. By determining the alteration of m. p. and b. p. successively with the same benzene solution, it is now shown that the molecular weight is the same at both temperatures, and is only a little lower than that calculated for the bimolecular condition. The alteration in the colour of solutions of triphenylmethyl on warming is, therefore, probably not due to dissociation. D. F. T.

Phenyldiphenylylnaphthylmethyl. JULIUS SCHMIDLIN and ANTONIO GARCIA-BANÙS (*Ber.*, 1912, 45, 3183—3188).—The authors have succeeded in preparing triarylmethane compounds containing an asymmetric carbon atom.

p-*Diphenylyl α-naphthyl ketone*, $C_6H_4Ph{\cdot}CO{\cdot}C_{10}H_7$, obtained by the action of naphthoyl chloride on diphenyl in carbon disulphide solution under the influence of aluminium chloride, forms plates, m. p. 142° (corr.); when heated with aluminium chloride at 140—145°, it condenses to *phenylbenzanthrone* (annexed formula), golden-yellow plates, m. p. 178—179° (corr.), which gives a fluorescent red solution in concentrated sulphuric acid. The above diphenylyl naphthyl ketone reacts



with magnesium phenyl iodide giving *phenyl*-p-*diphenylyl-α-naphthylcarbinol*, $C_{10}H_7{\cdot}CPh(C_6H_4Ph){\cdot}OH$, prisms (with ether of crystallisation), m. p. 115—116° (corr.), m. p. when ether-free 164—165° (corr.), together with a small amount of a *substance*, m. p. 197—198°, possibly phenyl-*p*-diphenylyl-α-naphthylmethane. The carbinol, which dissolves in concentrated sulphuric acid to a violet solution, reacts in benzene solution with hydrogen chloride with the formation of *phenyl*-p-*diphenylyl-α-naphthylmethyl chloride*, a colourless, crystalline powder, m. p. 198—199° (corr.). In an atmosphere of carbon dioxide the chloride is reduced by copper powder to *phenyl*-p-*diphenylyl-α-naphthylmethyl*, an apparently homogeneous product (compare preceding abstract); this dissolves in benzene to a brown solution, and from the fact that the solution, after most of its colour has been destroyed by atmospheric oxidation, recolorises to some extent, it is suggested that, unlike tridiphenylmethyl, the present substance is not completely dissociated into the active unimolecular condition; the fresh solution (concentration 1 : 5000) shows a broad absorption band from the violet end of the spectrum to 480μμ, and a small band in the yellow; the fresh solution of the corresponding phenyl-*p*-diphenylyl-α-naphthylcarbinol in sulphuric acid gives an absorption spectrum with a band extending from 480μμ half way into the green. Solutions of the above phenyl-*p*-diphenylyl-α-naphthylmethyl are

oxidised by the atmosphere to the *peroxide*, $(C_{29}H_{21})_2O_2$, a colourless, crystalline powder, m. p. 158° (corr., decomp.).

Although triphenylmethyl chloride, by the action of menthol in pyridine solution, can be converted into *triphenylmethyl* l-*menthyl ether*, m. p. 137—138° (corr.), similar treatment of phenyl-*p*-diphenylyl-α-naphthylmethyl chloride produced only the corresponding carbinol. It was also found impossible to prepare the camphorate or camphor-sulphonate. The chloride of the carbinol will not react with nicotine or coniine, and the product obtained by replacing the halogen by the amino-group is not basic in properties. The most promising method for the resolution of the asymmetric carbinol into its enantiomorphous constituents appears to depend on the active *amyl ether* which has been obtained in the crystalline state. D. F. T.

Reduction of Aromatic Alcohols with Aliphatic Alcohols. JULIUS SCHMIDLIN and ANTONIO GARCIA-BANÚS (*Ber.*, 1912, **45**, 3188—3193 *).—By using sulphuric acid as solvent, the reduction of aromatic secondary and tertiary carbinyl chlorides by aliphatic alcohols, already observed in special cases (for example, Kauffmann and Fritz, A., 1909, i, 99), becomes a fairly general reaction. Triphenylcarbinol and triphenylmethyl chloride, in a mixture of equal volumes of alcohol and sulphuric acid, undergo reduction to triphenylmethane, the action being represented : $CPh_3{\cdot}SO_4H + EtOH = CHPh_3 + CH_3{\cdot}CHO + H_2SO_4$; the ethyl alcohol can be replaced by methyl alcohol. In a similar manner tridiphenylylmethane and diphenylmethane can be obtained from tridiphenylylmethyl chloride or tridiphenylylcarbinol and benzhydrol respectively. The reaction fails with the naphthalene-carbinols, and also in cases where the sulphuric acid itself can cause dehydration or other effects, as, for example, with αβ-diphenylethyl alcohol, which yields stilbene.

The reduction of triphenylmethyl in ethereal solution by hydrogen and platinum black produces only triphenylmethane.

The oxidation of triphenylmethane to the corresponding carbinol can be quantitatively effected by boiling nitric acid, D 1·33 (compare Schwarz, A., 1909, i, 561).

A diagram is given for an apparatus designed for the preparation of fairly large quantities of triphenylmethyl and analogous compounds.

Endeavours to prepare a "mixed" ethane derivative by the interaction of magnesium triphenylmethyl chloride and tridiphenylylmethyl chloride produced only a mixture of triphenylmethyl and tridiphenylylmethyl; also no crystalline product could be obtained from the same Grignard reagent and phenylfluorenyl chloride. D. F. T.

Valency of Carbon, Arsenic, and Silicon. WILHELM SCHLENK (*Annalen*, 1912, **394**, 178—223).—[With LEOPOLD MAIR.]—The deepening of the colour of a solution of triphenylmethyl by warming has been attributed to the shifting of the equilibrium of the system $CPh_3{\cdot}CPh_3 \rightleftarrows 2CPh_3$ from left to right. Gomberg has shown by the cryoscopic method that triphenylmethyl in cold benzene exists almost entirely as hexaphenylethane. The authors now show by the ebullio-

* and *Anal. Fis. Quim.*, 1212, **10**, 449—454.

scopic method that at its b. p. the solution contains about 25% of triphenylmethyl.

Since triphenylmethyl peroxide and diphenylenephenylmethyl oxide (diphenylfluorene ether; Kliegl, A., 1905, i, 187) are comparatively stable substances, the authors hoped to prepare triphenylmethyl oxide, $(CPh_3)_2O$, from chlorotriphenylmethane by the action of silver oxide or of the sodium derivative of triphenylcarbinol. The products in both cases, however, are triphenylcarbinol and resinous substances.

[With C. BORNHARDT.]—The same products are also obtained by the oxidation of triphenylmethyl in glacial acetic acid or acetone by chromic acid or potassium permanganate.

After keeping triphenylmethyl and sulphur in carbon disulphide in darkness for six to eight weeks, the hydrocarbon is completely converted into an inseparable mixture of triphenylmethyl polysulphides.

A benzene solution of triphenylmethyl and an alcoholic ethereal solution of diazomethane react to form *hexaphenylpropane*,

$$CPh_3\cdot CH_2\cdot CPh_3,$$

a more complete description of which is promised.

[With JULIUS RENNING.]—By heating a benzene solution of phenylxanthenol chloride, prepared by Gomberg's method (A., 1910, i, 56), with copper-bronze on the water-bath, *phenylxanthyl*,

$$C_6H_4<{CPh \atop O}>C_6H_4,$$

is obtained. It forms brown crystals which disintegrates to a yellow powder at 60° in carbon dioxide, and is shown to be present in the unimolecular form to the extent of about 82% in boiling 1—2% benzene solution by the ebullioscopic method. *Phenylthioxanthyl*, $C_6H_4<{CPh \atop S}>C_6H_4$, prepared in a similar manner from phenylthioxanthenol chloride (Gomberg, A., 1910, i, 869), is a brownish-red, crystalline powder, and is present in the unimolecular form to the extent of about 14% in cold benzene. *Phenylanthronyl*,

$$C_6H_4<{CPh \atop CO}>C_6H_4,$$

is a yellow, crystalline powder; a 1—2% benzene solution contains in the cold about 33% of the unimolecular form. *Diphenyl-α-naphthylmethyl*, $C_{10}H_7\cdot CPh_2$, obtained by boiling *chlorodiphenyl-α-naphthylmethane*, m. p. 163°, with copper bronze in petroleum, b. p. 60—75°, in an atmosphere of carbon dioxide, is a greyish-black powder; a 2—3% solution in cold benzene contains about 59% of the unimolecular form. *Phenyl-*p*-diphenylyl-α-naphthylmethyl*,

$$C_6H_4Ph\cdot CPh\cdot C_{10}H_7,$$

prepared in a similar manner from *chlorophenyldiphenylyl-α-naphthylmethane*, m. p. 194·5°, is an olive-brown powder; a 1—3% solution in cold benzene contains the unimolecular form almost entirely.

[With LEOPOLD MAIR.]—p-*Anisyldiphenylenecarbinyl chloride*,

$${C_6H_4 \atop C_6H_4}>CCl\cdot C_6H_4\cdot OMe,$$

m. p. 149—151°, prepared by treating fluorenone with magnesium *p*-anisyl iodide in ether, decomposing the product in the usual manner,

and saturating a cold ethereal solution of the resulting carbinol with hydrogen chloride, reacts with copper-bronze in boiling benzene in an atmosphere of carbon dioxide to form *di*-p-*anisylbisdiphenylene-ethane*, $C_{40}H_{30}O_2$, m. p. 170—190° (decomp.) in open tube, 227—230° in carbon dioxide in a closed tube. It is a white, crystalline powder, stable in air, and forms solutions which become brown by warming and almost colourless again by cooling; its solution in benzene absorbs oxygen and yields the *peroxide*, $C_{40}H_{30}O_4$, m. p. 192°, colourless prisms.

[With ANNA HERZENSTEIN.]—The formation of triarylmethyls by the action of metals on solutions of triarylcarbinyl chlorides bears some resemblance to the elimination by one metal of another from a solution of its salts. In fact, when equal molecular quantities of triphenylmethyl and of phenyldidiphenylylcarbinyl chloride are brought together in benzene, the colour of the solution quickly darkens in consequence of the liberation of red phenyldidiphenylylmethyl by the yellow triphenylmethyl. Still more striking is the reaction which occurs when a benzene solution of phenylnaphthyldiphenylylcarbinyl chloride is added slowly to a solution of triphenylmethyl; each drop produces, with the rapidity of an ionic reaction, the deep reddish-brown coloration of phenyldiphenylylnaphthylmethyl.

[With GEORG RACKY and C. BORNHARDT.]—Attempts to prepare tervalent carbon derivatives containing radicles other than aryl groups show that such substances are not formed or usually exist in the dimolecular state; thus Wieland's benzpinacone diphenyl ether exists as such; only at high temperatures does it change to phenoxy-diphenylmethyl (A., 1911, i, 851). The action of metals on chlorides of the type CAr_2RCl should yield hydrocarbons CAr_2R. When R is methyl or other alkyl group containing CH, however, the chloride cannot be isolated, since it spontaneously loses hydrogen chloride with the formation of diarylolefines. *Diphenyl*-tert.-*butylcarbinyl chloride*, $CPh_2Cl\cdot CMe_3$, m. p. 103—106°, large, colourless crystals, can be obtained by the interaction of magnesium phenyl bromide and ethyl trimethylacetate in ether, the product, isolated in the usual manner being saturated in ether with hydrogen chloride and finally boiled with acetyl chloride. By boiling in xylene with sodium, the chloride yields *diphenyldi*-tert.-*butylethane*, $CMe_3\cdot CPh_2\cdot CPh_2\cdot CMe_3$, which has no tendency to dissociate into the tervalent carbon derivative. *ββß-Trichloro-α-bromo-αα-diphenylethane*, $CPh_2Br\cdot CCl_3$, m. p. 87·5° colourless crystals, obtained by treating the trichlorodiphenylethane with an excess of bromine, loses chlorine and bromine by treatment with metals.

By treatment with liquid nitrogen peroxide, tetraphenylethylene in chloroform yields *pp'-dinitrotetraphenylethylene*,

$$NO_2\cdot C_6H_4\cdot CPh{:}CPh\cdot C_6H_4\cdot NO_2,$$

m. p. 180—190°, citron-yellow crystals. In boiling nitrobenzene the two substances do not react. Bis-diphenylene-ethylene in chloroform and nitrogen peroxide yield *dinitrobisdiphenylene-ethane*,

$$\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!\!>C(NO_2)\cdot C(NO_2)<\!\!\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix},$$

colourless crystals, which is stable, but decomposes by melting (178°) and yields fluorenone and nitric oxide, whilst by heating with phenol it yields nitrophenol and bisdiphenylene-ethylene.

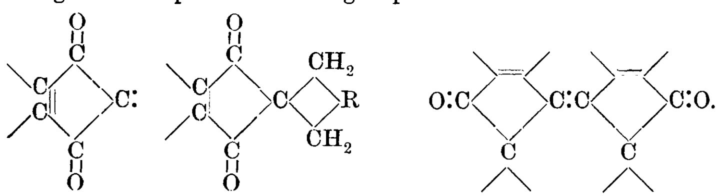
Tetradiphenylylethylene, which is obtained readily by boiling *diphenylyl ketochloride*, $CCl_2(C_6H_4Ph)_2$. m. p. 136°, in xylene with copper bronze, reacts with nitrogen peroxide in chloroform to form a blue substance, which rapidly decomposes, yielding diphenylyl ketone.

[With GEORG RACKY.]—The vapour density of arsenic disulphide at about 900° corresponds with the formula As_2S_2. The authors' experiments on the molecular weight of arsenic di-iodide in boiling benzene lead conclusively to the formula As_2I_4 (compare Hewitt and Winmill, T., 1907, **91**, 962). The molecular weight of tetraphenylcacodyl in boiling benzene corresponds with the formula As_2Ph_4. Consequently there is no evidence of the existence of bivalent arsenic compounds.

[With JULIUS RENNING.]—Silicon tetrachloride in ether is treated with magnesium phenyl bromide (2 mols.) and subsequently with magnesium methyl iodide. After treatment with water, the mixture is fractionally distilled, whereby *diphenylsilicoethylene*, $SiPh_2{:}CH_2$, is obtained. It is a colourless, odourless liquid, b. p. 266—268°/720 mm., which does not react with bromine or decolorise alkaline potassium permanganate. C. S.

Spirans. VI. Some Properties of the Spiran Carbon Atom. DAN RADULESCU (*Chem. Zentr.*, 1912, ii, 1363—1366; from *Bul. Soc. Ştiinţe Bucureşti*, **21**, 32—58. Compare A., 1912, i, 179).—The influence of the spiran carbon atom on the stability of, and on the conditions for the formation of, the two rings which it connects, and also on the reactivity of single members of the rings, is discussed. No steric hindrance exists which prevents the closing of spiran rings; in fact, spirans with five or six atoms in the ring are more stable than analogous compounds with open chains, so that the tendency is to form closed rings. The behaviour of the spiran carbon atom in strained ring systems has been studied in the case of *cyclo*propane-*cyclo*pentane-2 : 5-dione-1 : 1-spiran-3 : 4-dicarboxylic acid and its derivatives. The stability of the trimethylene ring is scarcely lessened by the spiran carbon atom.

The chromophoric properties of the rings are also affected by the quaternary system of the spiran carbon atom; the two spiran bonds in one ring act like a double link on the other ring. The group II is a stronger chromophore than the group I.

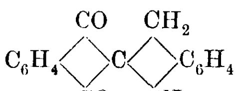


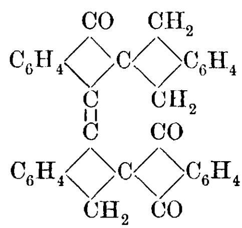
(I.) (II.) (III.)

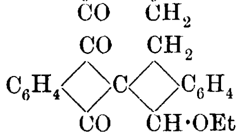
Anhydro-derivatives of the type III give yellow solutions which

with strong alkalis become blue. Carminic acid develops the same colour with very concentrated, strong bases, and has an absorption spectrum which is almost identical with that of compounds of this type.

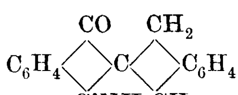
Fecht's indan-1 : 3-dione-indan-2 : 2-spiran (xylylenediketohydrindene) (A., 1907, i, 906) is found to be impure. Repeated solution in benzene and precipitation with light petroleum separates from it *anhydrobisindan*-1 : 3-*dioneindan*-2 : 2-*spiran*, $C_{34}H_{22}O_3$, (V), in pale yellow flakes, m. p. 256—257°, which give with phenylhydrazine the brownish-red hydrazone of Fecht's spiran. A very dilute alcoholic solution develops an intense indigo colour with a drop of concentrated potassium hydroxide, whereas the pure indan-1 : 3-dione-indan-2 : 2-spiran (IV) gives no coloration. The latter forms golden-yellow, thick prisms, m. p. 149°, and gives a violet colour to concentrated sulphuric acid. The ethereal mother liquors from this compound still contain *indan*-1 : 3-*dione*-1-*ethoxyindan*-2 : 2-*spiran*, $C_{19}H_{16}O_3$, (VI), which forms yellow prisms, m. p. 199—200°, and imparts a red colour to sulphuric acid, but is not affected by alkalis.

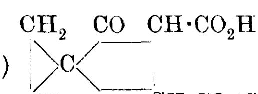
(IV.) 

(V.) 

(VI.) 

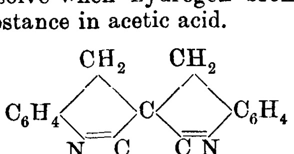
1-*Imino*-3-*indanoneindan*-2 : 2-*spiran*, $C_{17}H_{13}ON$, (VII), obtained by heating the spiran (IV) with alcoholic ammonia, separates in brick-red flakes.

(VII.) 

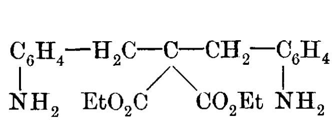
(VIII.) 

cyclo*Propane*cyclo*pentanedione*-1 : 1-*spiran*-3 : 4-*dicarboxylic acid*, (VIII), from ethyl *cyclo*propane-1 : 1-dicarboxylate, ethyl succinate, and sodamide, is converted at 180—200° or by heating with acetic anhydride into the *anhydride*, $C_9H_6O_5$, small, white needles.

Bisdihydroxyquinoline-3 : 3-*spiran* (*bisdihydrocarbostyrylspiran*), $C_{17}H_{14}O_2N_2$, (IX), from the reduction of ethyl di-*o*-nitrobenzylmalonate, sublimes above 360° in colourless, shining flakes, which dissolve when hydrogen bromide is passed into a suspension of the substance in acetic acid.



(IX.)



(X.)

When the mother liquors from the reduction are treated with

ammonia, the reddish primary product of the reaction, the *amino*-ester (X), separates out. It readily loses alcohol, forming the spiran.

Ethyl di-p-*nitrobenzylmalonate*, $C(CH_2\cdot C_6H_4\cdot NO_2)_2(CO_2Et)_2$, white needles, m. p. 171°, is the chief product when ethyl dibenzylmalonate is nitrated by fuming nitric acid in glacial acetic acid.

J. C. W.

Stereochemistry of Quinquevalent Nitrogen. I. Formation and Decomposition of the Quaternary Ammonium Bases and Salts. SHIGERU KOMATSU (*Mem. Coll. Sci. and Eng., Kyoto Imp. Univ.*, 1912, 3, 371—426).—The author has prepared a long series of quaternary ammonium compounds, and finds m. p.'s for the iodides which generally show considerable divergence from those previously stated by Jones and by Wedekind. In the thermal decomposition of the hydroxides it is observed that in the series $HO\cdot NPh(CH_2Ph)XY$ the benzyl group is always the one to be eliminated; with the series $HO\cdot NPh(C_3H_5)XY$, if X and Y are smaller groups than the allyl, the last undergoes scission, but if one is larger and the other smaller than the allyl, the smaller of X and Y becomes removed. Apart from these two classes it is found that, as a general rule, the smallest group is always left attached to the nitrogen atom.

The following tertiary bases and derivatives were obtained. Dimethylaniline gives a *picrate*, needles, m. p. 154—155°, and combines with mercuric chloride giving a yellow *compound*, crystallising in needles, also a basic *compound*, $O(Hg\cdot NMe_2PhCl)_2$, pearly scales, and a *double* salt, $NMe_2Ph,HCl,HgCl_2$, colourless needles. Methylethylaniline gives a *picrate*, prisms, m. p. 121—122°; *ferrocyanide*, colourless crystals, and combines with mercuric chloride producing a colourless, scaly basic *compound*, $O(Hg\cdot N\cdot PhMeEtCl)_2$, and a *double* salt, colourless needles. Methylallylaniline forms a picrate, m. p. 81—82°, and *ferrocyanide*, colourless crystals. Methylpropylaniline gives a *picrate*, m. p. 103—104°; *ferrocyanide*, colourless. Methyl-*n*-butylaniline, b. p. 225—230°, forms a *picrate*, rhombic needles, m. p. 141—142°; *ferrocyanide*, light green, crystalline powder. Methyl*iso*butylaniline yields a *picrate*, plates, m. p. 99—100°, and *ferrocyanide*, colourless. Methyl*iso*amylaniline forms a *picrate*, m. p. 93—94°, and *ferrocyanide*, light green. Benzylmethylaniline gives a *picrate*, rhombic prisms, m. p. 101—101·5°; *ferrocyanide*, colourless; colourless *double* salt, $(NMePh\cdot CH_2Ph,HCl)_2CdCl_2$, with cadmium chloride, and with mercuric chloride a mixture of a yellow *substance* (which on exposure to air is slowly converted into a blue *substance*, m. p. about 160°), a basic *substance*, crystallising in white needles (composition analogous to that of the basic substances above), and a *double* salt, $(NMePh\cdot CH_2Ph,HCl)_2,HgCl_2$, colourless needles. Ethylallylaniline gives a *picrate*, prisms, m. p. 98—99°, and *ferrocyanide*, colourless. Ethyl-*n*-propylaniline forms a *picrate*, crystalline powder, m. p. 94—95°, and *ferrocyanide*, colourless. Ethyl-*n*-butylaniline gives a *picrate*, rhombic prisms, m. p. 89—90°, and *ferrocyanide*, colourless. Ethyl*iso*butylaniline yields a *picrate*, crystals, m. p. 91—92°, and *ferrocyanide*, light green, crystalline powder. Ethyl*iso*amylaniline forms a *picrate*, rhombic prisms, m. p. 103—104°, and

ferrocyanide, light green, crystalline powder. Benzylethylaniline gives a picrate, rhombic prisms, m. p. 110—111°; *ferrocyanide*, light green, crystalline powder, a *double* salt (colourless needles) with cadmium chloride, and with mercuric chloride a colourless, crystalline basic *substance* and a *double* salt (needles), $(NEtPh{\cdot}CH_2Ph,HCl)_2,HgCl_2$. Diethylaniline, *picrate*, m. p. 135—136°.

The m. p. of each of the above picrates, as also of most of the iodides below, was also determined by the Kuhara-Chikashigé method (A., 1900, ii, 260), the results differing occasionally by several degrees from those obtained by the ordinary method.

The following quaternary compounds were examined:

Phenylbenzyldimethylammonium iodide, m. p. 141—142° (compare Jones, T., 1903, **83**, 1409), obtained from dimethylaniline and benzyl iodide; *platinichloride*, needles, m. p. 164—165°; the *hydroxide* when heated decomposes, giving dimethylaniline. Phenylbenzylmethylethylammonium iodide, m. p. 135—136° (compare Jones, T., 1904, **85**, 224; Fröhlich, A., 1910, i, 375), from methylethylaniline and benzyl iodide; *platinichloride*, needles, m. p. 160·5—161°; the *hydroxide* decomposes, giving methylethylaniline. Phenylbenzylmethylallylammonium iodide, rhombic prisms, m. p. 128—129° (compare Jones, T., 1905, **87**, 1721; Wedekind, A., 1899, i, 351), obtained from methylallylaniline and benzyl iodide, or from benzylmethylaniline and allyl iodide; *platinichloride*, needles, m. p. 133—134°; the *hydroxide* when decomposed yields methylallylaniline. Phenylbenzylethyl-*n*-propylammonium iodide, prisms, m. p. 143°, from methyl-*n*-propylaniline and benzyl iodide; *platinichloride*, needles, m. p. 159—160°; the *hydroxide* on decomposition gives methyl-*n*-propylaniline. Phenylbenzylmethyl*iso*butylammonium iodide, prisms, m. p. 124—125°, obtained from methyl*iso*butylaniline and benzyl iodide; *platinichloride*, needles, m. p. 147—148°; the *hydroxide* on decomposition gives methyl*iso*butylaniline. *Phenylbenzylmethyl*-n-*butylammonium iodide*, needles, m. p. 132—133°, obtained from methyl-*n*-butylaniline and benzyl iodide; *platinichloride*, needles, m. p. 139—140°; the *hydroxide* on decomposition gives methyl-*n*-butylaniline. Phenylbenzylmethyl*iso*amylammonium iodide, from methyl*iso*amylaniline and benzyl iodide, needles, m. p. 137—138° (compare Thomas and Jones, T., 1906, **89**, 280); *platinichloride*, needles, m. p. 149—150°; the *hydroxide* on decomposition gives methyl*iso*amylaniline. Phenyldibenzylmethylammonium iodide, m. p. 105—106° from benzylmethylaniline and benzyl iodide (compare Jones, T., 1903, **83**, 1410); *platinichloride*, needles, m. p. 131—132°; the *hydroxide* on decomposition yields benzylmethylaniline. *Phenylbenzylethyl*-n-*propylammonium iodide* from ethyl-*n*-propylaniline and benzyl iodide, prisms, m. p. 105—106°; *platinichloride*, needles, m. p. 146—147°; the *hydroxide* on decomposition yields ethyl-*n*-propylaniline.

Phenylbenzylethylallylammonium iodide, obtained from ethylallylaniline and benzyl iodide, prisms, m. p. 106·5°; *platinichloride*, m. p. 138—139°. Phenyldimethylallylammonium iodide, from dimethylaniline and allyl iodide, prisms, m. p. 84—85°; the *hydroxide* on decomposition gives dimethylaniline. *Phenyldiethylallylammonium*

iodide from ethylallylaniline and ethyl iodide, or from diethylaniline and allyl iodide; *platinichloride*, needles, m. p. 158—159°; the *hydroxide* on decomposition gives diethylaniline. Phenylmethyl-*n*-propylallylammonium iodide, prisms, m. p. 119—120°, from methyl-*n* propylaniline and allyl iodide, or as a gummy mass from methylallylaniline and *n*-propyl iodide; *platinichloride*, needles, m. p. 157—158°; the *hydroxide* on decomposition gives *n*-propylallylaniline. Phenylmethyl*iso*butylallylammonium iodide from methyl*iso*butylaniline and allyl iodide, needles, m. p. 124°; *platinichloride*, needles, m. p. 156—157°; the *hydroxide* on decomposition yields *iso*butylallylaniline. Phenylmethyl*iso*amylallylammonium iodide, prisms, m. p. 126—127°, from methyl*iso*amylaniline and allyl iodide; *platinichloride*, needles, m. p. 154—155°; the hydroxide on decomposition gives *iso*amylallylaniline.

Phenylmethylethyl-n-*butylammonium iodide*, prisms, m. p. 72—73°, obtained from methylethylaniline and *n*-butyl iodide, also from ethyl-*n*-butylaniline and methyl iodide; *platinichloride*, needles, m. p. 195—196°, was obtained also from the gummy reaction product of methyl-*n*-butylaniline and ethyl iodide; the *hydroxide* on decomposition gives methyl-*n*-butylaniline. *Phenylmethylethyl*iso*amylammonium iodide*, needles, m. p. 154°, was obtained from ethyl*iso*amylaniline and methyl iodide, also from methylethylaniline and *iso*amyl iodide, and from methyl*iso*amylaniline and ethyl iodide; *platinichloride*, m. p. 191—192°; the *hydroxide* on decomposition gives methyl*iso*amylaniline.

Phenylmethyl-n-*propyl*iso*butylammonium iodide*, a viscous mass, from methyl*iso*butylaniline and *n*-propyl iodide, and also from methyl-*n*-propylaniline and *iso*butyl iodide; *platinichloride*, needles, m. p. 200—201°; the *hydroxide* on decomposition yields methyl-*n*-propylaniline.

Phenylmethyl-n-*propyl*iso*amylammonium iodide*, obtained as a gummy mass from methyl*iso*amylaniline and *n*-propyl iodide and also from methylpropylaniline and *iso*amyl iodide; platinichloride, needles, m. p. 183—183·5°; the hydroxide on decomposition gives methyl-*n*-propylaniline. *Phenylmethyl*-n-*butyl*iso*amylammonium iodide*, obtained as a gummy mass from methyl*iso*amylaniline and *n*-butyl iodide, and also from methyl-*n*-butylaniline and *iso*amyl iodide; *platinichloride*, needles, m. p. 191—192°; the hydroxide on decomposition gives methyl*iso*amylaniline. D. F. T.

Esters Derived from Cyclanols and Acids of the Formic Acid Series. JEAN B. SENDERENS and JEAN ABOULENC (*Compt. rend.*, 1912, **155**, 1012—1014).—By a method previously described (A., 1912, i, 694) a series of esters has been prepared from *cyclo*hexanol and the three methyl *cyclo*hexanols and formic, acetic, propionic, butyric, *iso*butyric, and *iso*valeric acids. They are all colourless liquids with a pleasant odour, and are not affected by light, save the *o*-methyl*cyclo*hexyl esters, which turn slightly yellow on prolonged exposure. The following physical constants were determined. The b. p.'s are all at 750—753 mm.:

	*cyclo*Hexyl.		Methyl*cyclo*hexyl. Ortho.			Meta.			Para.		
	b. p.	D_4^0.	b. p.	D_4^0.	n_D^{18}.	b. p.	D_4^0.	n_D^{18}.	b. p.	D_4^0.	n_D^{18}.
Formate	162·5°	1·0057	173·0°	0·9813	—	176·5°	0·9775	—	177·5°	0·9761	—
Acetate	174·0	0·9854	184·5	0·9636	—	187·5	0·9592	—	188·5	0·9578	—
Propionate ...	193·0	0·9718	203·0	0·9548	1·444	206·0	0·9509	1·442	207·0	0·9492	1·4425
Butyrate	212·0	0·9572	221·5	0·9443	1·445	224·5	0·9403	1·4435	225·5	0·9386	1·443
*iso*Butyrate...	204·0	0·9489	212·5	0·9364	1·441	215·0	0·9318	1·440	216·0	0·9304	1·4395
*iso*Valerate...	223·0	0·9425	231·5	0·9316	1·444	234·0	0·9275	1·4425	235·0	0·9262	1·4425

In passing up the acid series there is an increase of 18·5—19° in the b. p. from one homologue to the next higher, except in the case of the formates, whilst the densities decrease, but in an irregular manner.

W. G.

Esterification of Cyclanols by Aromatic Acids. JEAN B. SENDERENS and JEAN ABOULENC (*Compt. rend.*, 1912, **155**, 1254—1256).—Applying the method used for fatty acids (A., 1912, i, 694) to aromatic acids having the carboxyl group attached to the benzene nucleus, in no case was an ester obtained, but the *cyclo*hexanol was always converted into *cyclo*hexene. If, however, the carboxyl group is in the side-chain, condensation readily occurred, and the following esters were prepared:

cyclo*Hexyl phenylacetate*, b. p. 180·5°, D_4^0 1·0535, n_D^{13} 1·518.

cyclo*Hexyl phenylpropionate*, b. p. 193·5°, D_4^0 1·0432, n_D^{13} 1·515.

o-*Methyl*cyclo*hexyl phenylacetate*, b. p. 186°, D_4^0 1·0374, n_D^{13} 1·512; the meta-*isomeride*, b. p. 188°, D_4^0 1·0323, n_D^{13} 1·510; and the para-*isomeride*, b. p. 188·5°, D_4^0 1·0316, n_D^{13} 1·509.

o-*Methyl*cyclo*hexyl phenylpropionate*, b. p. 198·5°, D_4^0 1·0286, n_D^{13} 1·510; the meta-*isomeride*, b. p. 200°, D_4^0 1·0235, n_D^{13} 1·508; and the para-*isomeride*, b. p. 200·5°, D_4^0 1·0225, n_D^{13} 1·507.

Menthyl phenylacetate, an oily liquid, b. p. 205·5°/25 mm., D_4^{17} 0·9887.

Menthyl phenylpropionate, needles, m. p. 28·5°, b. p. 216°/25 mm.

W. G.

Action of Potassium Hydroxide on *cyclo*Hexanol; Synthesis of *cyclo*Hexyl*cyclo*hexanol and of Di*cyclo*hexyl*cyclo*hexanol. MARCEL GUERBET (*Compt. rend.*, 1912, **155**, 1156—1159. Compare A., 1912, i, 67, 154).—*cyclo*Hexanol, like other secondary alcohols, undergoes condensation when heated at 230° with potassium hydroxide, some oxidation also occurring with the formation of potassium salts of acids. The following products were obtained by this method:

2-cyclo*Hexyl*-3-cyclo*hexanol*, $\begin{array}{l}CH_2\cdot CH_2\cdot CH\cdot C_6H_{11}\\ CH_2\cdot CH_2\cdot CH\cdot OH\end{array}$, a colourless, oily liquid, b. p. 178—180°/55 mm., D_4^0 0·9950, which yields an *acetate*, a colourless liquid with a pleasant odour, b. p. 188—190°/52 mm. On oxidation with chromic acid the alcohol is converted into 2-cyclo-

hexyl-3-cyclo*hexanone*, $C_6H_{11}\cdot C_6H_9O$, a colourless liquid, b. p. 176—178°/54 mm., yielding an *oxime*, m. p. 102°, and a *semicarbazone*, m. p. 149—150°.

A product of further condensation is 2-*di*cyclo*hexyl*-3-cyclo*hexanol*, $\begin{array}{l} CH_2\cdot CH_2\cdot CH\cdot C_6H_{10}\cdot C_6H_{11} \\ CH_2\cdot CH_2\cdot CH\cdot OH \end{array}$, prismatic crystals, m. p. 124°.

The acids obtained due to a secondary reaction are hexoic acid, b. p. 204—207°, and cyclo*hexyl*cyclo*hexanoic acid*, $C_6H_{11}\cdot C_6H_{11}O_2$ (?), a colourless, oily liquid, b. p. 218—220°/69 mm., D_4^0 1·010, yielding a *barium* salt, crystallising from alcohol. W. G.

Catalytic Action. V. Comparison of the Action of Various Catalysts. III. Acetylation of *o*-Nitrophenol, Carbazole, and Diphenylamine, and Some Observations on *o*-Nitroaniline and Tribromophenol as well as their Acyl Derivatives. JACOB BÖESEKEN (*Rec. trav. chim.*, 1912, **31**, 350—366. Compare A., 1911, i, 22).—Further acetylations have been studied in order to find a simple reaction on which quantitative researches on the influence of catalysts may be based. As a rule, the acetylation of primary amines is too complicated, for both mono- and di-acyl compounds are often produced; thus when *o*-nitroaniline is warmed for a quarter of an hour with acetic anhydride and a trace of sulphuric acid or aluminium chloride, the resulting diaceto-*o*-nitranilide contains a little of the mono-derivative.

The case of *s*.-tribromophenol has already been studied by Smith and Orton (T., 1909, **95**, 1063), but their method is criticised, for the acetic acid employed may have influenced the catalysts and their estimation of the final products does not seem to have been trustworthy, since the acetate is somewhat saponified on boiling with water. Titration of the alkali required to saponify the acetate is also found unsatisfactory. The solidification points of mixtures of tribromophenol (m. p. 92·5°) with the acetate (m. p. 82°) have therefore been plotted, but the curve is irregular, and indicates the formation of molecular compounds with m. p. about 65°.

In the case of *o*-nitrophenol, however, a simple solidification curve has been obtained, and found to provide the best means of estimating a mixture of the two compounds. The product of the reaction is washed with ice water, extracted with benzene, and the extract is dried and allowed to evaporate at 50°. By this means it is found that *o*-nitrophenol is acetylated by acetic anhydride at 98° to the extent of 92% in about four and a-half hours. Hydrogen chloride has only a feeble influence, for in one and a-half hours and with 50 molecules of the gas per 100, the process is only two-thirds complete, whereas 3 molecules per 100 of aluminium chloride complete the reaction in one and a-half hours, and 3 molecules per 100 of anhydrous ferric chloride do so in ten minutes.

Diphenylamine is so completely acetylated without catalytic agency on heating with acetic anhydride on the steam-bath that the present studies were carried out at 45°, again with the aid of a solidification curve. Fuming sulphuric acid, ferric chloride, aluminium chloride, and acetyl chloride have nearly equal effects, and the conclusion is drawn

that the catalysts have formed compounds with one of the systems already present, and that it is their influence that is being studied. The formation of sulphacetic acid and probably mono- and di-acetylsulphuric acids from acetic anhydride and sulphuric acid (Franchimont, A., 1881, 716) is of importance in this connexion, as well as the fact that aluminium chloride and acetic anhydride produce acetyl chloride (see this vol., i, 6).

Since carbazole is unaffected by alcoholic potash, it was found possible to analyse the mixture by titrating the alkali required for the saponification of the acyl derivative. Without a catalyst, scarcely any acetylation has taken place after five hours at 98°, but with a trace of sulphuric acid or with quite minute amounts of ferric chloride, the process is complete in half an hour. J. C. W.

Nitro-derivatives of Diphenylene Oxide and of Phenyl Ether. ALPHONSE MAILHE (*Bull. Soc. chim.*, 1912, [iv], **11**, 1011—1014).—An error in the calculation of nitrogen has led to the description of nitro-derivatives of phenyl ether containing more than four nitro-groups (Mailhe and Murat, A., 1912, i, 346), of penta- and hexa-nitrodiphenylene oxides, and of the disulphonic acid derivative of the latter (Mailhe, A., 1912, i, 553). These substances do not exist.

H. W.

***m*-Dithiolbenzene (Dithioresorcinol).** THEODOR ZINCKE and OTTO KRÜGER (*Ber.*, 1912, **45**, 3468—3479).—The *m*-Dithiolbenzene was prepared in the ordinary way from benzene-1 : 3-disulphonyl chloride by reduction with zinc and hydrochloric acid. In order to obtain good yields the zinc sulphinate must first be formed by the action of the zinc on the chloride in alcoholic solution, and afterwards reduced to the mercaptan by the addition of hydrochloric acid and further action of the zinc. If this method of procedure is not adopted, the free sulphinic acid and the mercaptan react with the formation of tetra- or poly-sulphides.

The following derivatives of *m*-dithiolbenzene have been prepared. *Di*-1 : 3-*phenylene disulphide*, $S_2(C_6H_4)_2S_2$, prepared by the action of perhydrol in alkaline alcoholic solution, forms a yellowish-white, amorphous powder. 4 : 6-*Dichloro*-1 : 3-*dichlorothiolbenzene*,

$$C_6H_2Cl_2(SCl)_2,$$

is obtained by chlorination in chloroform solution. It may also be prepared from the benzyl ester. It forms yellow, glistening needles, m. p. 103°, and shows the usual reactions of the arylsulphur chlorides. When warmed with acetone, it gives slender, colourless needles of 4 : 6-*dichloro*-1 : 3-*diacetonylthiolbenzene*, $C_6H_2Cl_2(S{\cdot}CH_2Ac)_2$, m. p. 97°.

On methylation with methyl sulphate, *m*-dithiolbenzene gives 1 : 3 *dimethylthiolbenzene*, $C_6H_4(SMe)_2$, a strongly refracting liquid with characteristic odour, b. p. 149°/17 mm., which on treatment with 1 : 4-nitric acid in glacial acetic acid solution yields 4-*nitro*-1 : 3-*dimethylthiolbenzene*, $NO_2{\cdot}C_6H_3(SMe)_2$, yellow, glistening needles, m. p. 114°. The disulphoxide is formed at the same time. 1 : 3-*Diethylthiolbenzene*, $C_6H_4(SEt)_2$, is similar to the dimethyl ether, and has b. p.

164°/18—19 mm. 1 : 3-*Dibenzylthiolbenzene*, $C_6H_4(S{\cdot}CH_2Ph)_2$, crystallises in leaflets, m. p. 50°.

4 : 6-*Dichloro*-1 : 3-*dimethylthiolbenzene*, $C_6H_2Cl_2(SCH_3)_2$, prepared from the dimethyl ether by chlorination in glacial acetic acid solution, crystallises in long, glistening needles, m. p. 123°. When chlorination takes place in chloroform solution, 1 : 3-*ditrichloromethylthiolbenzene*, $C_6H_4(S{\cdot}CCl_3)_2$, is obtained as crystals, having the m. p. 106°. Under the action of aniline, fission occurs with the formation of dithiolbenzene and triphenylguanidine.

When the dimethyl ether is treated with bromine in chloroform solution, stout, dark orange needles of 4 : 6-*dibromo*-1 : 3-*dimethylthiolbenzene dibromide*, $C_6H_2Br_2(SMe){\cdot}SBr_2Me$, are obtained. When shaken with sodium hydrogen sulphite solution in the presence of chloroform, 4 : 6-*dibromo*-1 : 3-*dimethylthiolbenzene* itself, $C_6H_2Br_2(SMe)_2$, is obtained as colourless, glistening needles, m. p. 142°. The same compound may be obtained from the disulphoxide by treatment with hydrogen bromide. 4 : 6-*Dibromo*-1 : 3-*diethylthiolbenzene tetrabromide*,

$$C_6H_2Br_2(SBr_2{\cdot}Et)_2,$$

results from the bromination of the diethyl ether in chloroform solution; it forms dark red, in reflected light steel-blue, needles, which readily lose bromine under the action of sodium hydrogen sulphite, giving 4 : 6-*dibromo*-1 : 3-*diethylthiolbenzene*, $C_6H_2Br_2(SEt)_2$, which crystallises in long, silky needles, m. p. 58°.

Oxidation of the dimethyl ether (1 part) with perhydrol (1·5 parts) in glacial acetic acid solution at the ordinary temperature gives white needles of *phenylene*-1 : 3-*dimethyldisulphoxide*, $C_6H_4(SOMe)_2$, m. p. 131°. The corresponding *disulphone*, $C_6H_4(SO_2Me)_2$, is obtained when 3 parts of perhydrol are used and the reaction completed on the water-bath; it crystallises in white, glistening leaflets, and has m. p. 196—197°. The following compounds were obtained in a similar manner: *Phenylene*-1 : 3-*diethyldisulphoxide*, $C_6H_4(SOEt)_2$, is a colourless, oily liquid; the *disulphone*, $C_6H_4(SO_2Et)_2$, forms colourless, clear plates, m. p. 142°. *Phenylene*-1 : 3-*dibenzyldisulphoxide*, $C_6H_4(SO{\cdot}CH_2Ph)_2$, gives colourless, glistening crystals, m. p. 131°, whilst the *disulphone*, $C_6H_4(SO_2{\cdot}CH_2Ph)_2$, forms tabular crystals, m. p. 229°. T. S. P.

4 : 4′-Dithioldiphenyl. THEODOR ZINCKE and ALEXANDER DAHM (*Ber.*, 1912, **45**, 3457—3468).—4 : 4′-Dithioldiphenyl was obtained from benzidine by Leuckart's method (A., 1890, 603), except that the decomposition of the diazoxanthate was carried out in the presence of copper powder, whereby explosions are avoided and better yields obtained. From this compound a number of derivatives have been obtained.

By the action of chlorine on the solution of the dimercaptan or of its benzyl ether in carbon tetrachloride, 4 : 4′-dichlorothioldiphenyl (A., 1911, i, 369) is obtained. This compound loses chlorine on warming with glacial acetic acid, alcohol or dilute alkali, giving a compound which is probably the tetrasulphide, $S_2(C_6H_4{\cdot}C_6H_4)_2S_2$. Oxidation with nitric acid or chlorine in glacial acetic acid solution gives the corresponding sulphonyl chloride. On heating with acetone, 4 : 4′-*diacetonylthioldiphenyl*, $C_{12}H_8(S{\cdot}CH_2Ac)_2$ is obtained in the form

of almost white needles, m. p. 165°. It can also be obtained from the dimercaptan and chloroacetone.

4 : 4′-Dimethylthioldiphenyl, $C_{12}H_8(SMe)_2$ (compare Leuckart, *loc. cit.*), is obtained by methylating the dimercaptan with methyl sulphate; m. p. 185°. The action of chlorine in glacial acetic acid solution gives the diphenyldichlorothiol, but in chloroform solution substitution occurs in the methyl groups, with the formation of 4 : *4′-di-trichloromethylthioldiphenyl*, $C_{12}H_8(S{\cdot}CCl_3)_2$, white needles, m. p. 195°. When heated with aniline, triphenylguanidine and diphenyldithol are formed from the di-trichloro-compound.

4 : 4′-Diethylthioldiphenyl, $C_{12}H_8(SEt)_2$ (compare Leuckart, *loc. cit.*), is prepared similarly to the ethyl compound. The action of chlorine in chloroform solution gives a red oil. It forms a *tetrabromide* and *hexaiodide*.

4 : *4′-Dibenzylthioldiphenyl*, $C_{12}H_8(S{\cdot}CH_2Ph)_2$, forms white, glistening, leaflets, m. p. 198—199°. Chlorination in chloroform solution gives benzylidene chloride and the dichlorothioldiphenyl.

4 : *4′-Dimethylthioldiphenyl tetrabromide*, $C_{12}H_8(SMeBr_2)_2$, is obtained as a red, crystalline precipitate by the action of dry hydrogen bromide on the corresponding sulphoxide (see later) in chloroform solution; m. p. 130° (decomp.). Thiosulphate, sodium sulphite, or concentrated alkali eliminates bromine, whilst water or very dilute alkali regenerates the sulphoxide to some extent. The *hexabromide*, $C_{12}H_8(SMeBr_2)_2,Br_2$, prepared from the dimethyl ester by direct addition of bromine in chloroform solution, forms dark red crystals, and has m. p. 90° (decomp.). It behaves similarly to the tetrabromide towards bromine-eliminating agents. The *hexaiodide*, $C_{12}H_8(SMeI_2)_2,I_2$, is prepared similarly to the hexabromide, and has m. p. 198° (decomp.); it forms almost black crystals. It can also be obtained from the disulphoxide and hydrogen iodide. Iodine is eliminated by the usual agents, but the disulphoxide cannot be obtained from it.

4 : *4′-Diphenyldimethyldisulphoxide*, $C_{12}H_8(SOMe)_2$, prepared from the dimethyl ether by oxidation with hydrogen peroxide or nitric acid (D 1·5), forms white leaflets, m. p. 195°. In glacial acetic acid solution it is reduced by hydrogen bromide or iodide, in contradistinction to its behaviour in chloroform solution (see above). Oxidation with perhydrol gives the *disulphone*, $C_{12}H_8(SO_2Me)_2$, white leaflets, m. p. 302°. The following sulphoxides and sulphones are prepared similarly: 4 : *4′-Diphenyldiethyldisulphoxide*, $C_{12}H_8(SOEt)_2$, small, colourless needles, m. p. 134°; the *disulphone*, $C_{12}H_8(SO_2Et)_2$, forms white needles, m. p. 187°. 4 : *4′-Diphenyldibenzyldisulphoxide*, $C_{12}H_8(SO{\cdot}CH_2Ph)_2$, consists of white needles, m. p. 243°, as also does the *disulphone*, $C_{12}H_8(SO_2{\cdot}CH_2Ph)_2$, m. p. 320°. T. S. P.

The Autoxidation of Trinaphthylcarbinol. JULIUS SCHMIDLIN and MAXIMILIAN BERGMAN (*Ber.*, 1912, **45**, 3203—3205).—In reply to Tschitschibabin's criticism (A., 1911, i, 969) that of the two described isomerides of trinaphthylcarbinol (Schmidlin and Massini, A., 1909, i, 563) the more stable is in reality an oxidation product of the other, it is stated that this oxidation product (α-naphthyl-di-αα-naphthafluoryl alcohol) is a distinct substance, which causes a considerable depression

of the m. p. of the stable isomeride and is more easily obtained than the latter.

It has not hitherto been possible to prepare a triarylcarbinol containing only the diphenyl and naphthyl radicles; bis-diphenylyl ketone and also esters of diphenylcarboxylic acid refuse to react with magnesium naphthyl iodide, also dinaphthyl ketone with magnesium diphenyl bromide. D. F. T.

Preparation of Acetal Condensation Derivatives from Polyhydroxy-alcohols with Aldehydes or Ketones. WALTER GERHARDT (D.R.-P. 253083. Compare Harnitzky and Mentschutkin, *Annalen*, 1865, **136**, 126).—Glycerol benzylidene ether,

$$C_6H_5\cdot CH<\genfrac{}{}{0pt}{}{O}{O}>C_3H_5\cdot OH,$$

has now been obtained with b. p. 280° and m. p. 84° (compare Fischer, A., 1894, i, 395) by heating glycerol and benzaldehyde together at 135—145°.

The *compound*, $C_{10}H_{12}O_2$, b. p. 113·5—115·5°/14 mm., is obtained from propylene glycol and benzaldehyde at 162°; and the same aldehyde with trimethylene glycol furnishes *trimethylene glycol benzylidene ether*, $C_{12}H_{10}O_2$, m. p. 50°, b. p. 121—124°/15 mm.

Chlorohydrin benzylidene ether, $C_6H_5\cdot CH{:}O_2{:}C_3H_5Cl$, b. p. 144—146°/14 mm., is prepared from chlorohydrin and benzaldehyde; glycerol and anisaldehyde yield the *compound*, $C_{11}H_{14}O_4$, b. p. 208—210°/18·5 mm., whilst the *compound*, $C_{11}H_{12}O_5$, m. p. 107—107·5°, is furnished by glycerol and piperonal; and *acetophenone glycerol*, a viscous liquid, b. p. 156°/16 mm., is obtained from glycerol and acetophenone.

F. M. G. M.

Cubebin. IV. and V. EFISIO MAMELI (*Gazzetta*, 1912, **42**, ii, 546—550, 551—566. Compare A., 1908, i, 20; 1909, i, 503).—IV. iso*Cubebin ether* is obtained when cubebin is dissolved in the least quantity of concentrated acetic acid and treated with a small quantity of concentrated sulphuric acid; on pouring the solution into water, the ether is precipitated. It forms colourless, acicular crystals, m. p. 157°, and has the composition and molecular weight required by the formula $C_{20}H_{18}O_5$. The substance is optically active, having $[\alpha]_D$ 26·02°. It reactions indicate that it is an internal ether.

Although cubebin ether is easily converted into cubebinol by reducing agents, *iso*cubebin ether resists such treatment, but it is converted into cubebinol when boiled with dilute acids.

V. This paper deals with hydroxycubebinic acid and some of its derivatives. The author has investigated the oxidation of cubebin and its derivatives by means of a large number of oxidising agents (hydrogen peroxide, bromine water, iodine water, Fehling's solution, silver oxide, Nessler's reagent, dilute nitric acid, lead nitrate, and lead peroxide, and hydrochloric acid), and has obtained in all cases results analogous to those previously obtained with other oxidising substances by himself and other observers. When, however, cubebin is suspended in strongly alkaline solution of sodium hypobromite at the ordinary temperature, a salt of a new acid, hydroxycubebinic acid, is produced.

The preparation is effected by keeping the reaction mixture in the dark for five or six days; the *sodium* salt which has separated (yield 93—96%) is collected and purified from admixed cubebin, which is insoluble in warm water. When the aqueous solution of this salt is treated with dilute sulphuric acid, the lactone, *cubebinolide*, $C_{20}H_{18}O_6$, is obtained; it forms colourless crystals, m. p. 63—64°, $[\alpha]_D$ +33·69° (in chloroform). This substance behaves in all its reactions as a lactone of a monocarboxylic acid. It dissolves with difficulty in boiling alkalis, yielding the sodium and *potassium* salts of hydroxycubebinic acid. The sodium salt, $C_{20}H_{19}O_7Na$, forms acicular crystals, which melt in their water of crystallisation at 70°; the anhydrous salt has m. p. 205—207°; the salt has no pharmacological action. The other salts were obtained from the sodium salt. The *strontium, magnesium, zinc, cadmium, iron, uranium, copper, cobalt, nickel, lead, manganese, calcium*, $Ca(C_{20}H_{19}O_7)_2$, and *barium*, $Ba(C_{20}H_{19}O_7)_2$, salts were prepared. Indications of the existence of the free acid were observed, but it was not possible to isolate it.

When cubebinolide is treated with magnesium phenyl bromide, a *diphenyl* derivative is obtained, which is to be regarded as the product of dehydration of the glycol which would be expected. This substance crystallises in colourless leaflets, m. p. 136—137°, $[\alpha]_D$ −178·78° (in chloroform), and has the probable formula $C_{32}H_{28}O_5$, although the analytical results do not agree with this very well.

When a methyl-alcoholic solution of cubebinolide is saturated with hydrogen chloride and kept in a sealed vessel, an *ester*, $C_{21}H_{21}O_6Cl$, is obtained; it crystallises in thin laminæ, m. p. 95°, $[\alpha]_D$ +13·89°. When saponified (with strong alkali) it yields a salt of hydroxycubebinic acid.

Oxidation of the lactone with dilute nitric acid gives a *dinitro*-derivative, m. p. 183—184°. The action of bromine on an alcoholic solution of the lactone yields a *dibromo*-derivative, m. p. 137°.

The author gives provisional formulæ to illustrate possible modes of origin of the compounds above described, and their bearing on the constitution of cubebin. R. V. S.

Hydrolysis of *o*-Acetoxybenzoates and the Preparation of Calcium *o*-Acetoxybenzoate. Michael Máthé (*Chem. Zentr.*, 1912, ii, 431; from *Pharm. Post*, 1912, **45**, 474—476, 481—483).—The calcium salt was prepared by suspending slaked lime in alcohol and adding *o*-acetoxybenzoic acid, when the salt separated as a coagulated mass, which was washed with alcohol and dried at 40—60°. The sodium salt decomposes in aqueous solution more quickly than the lithium salt, and the latter at first more slowly, but eventually more quickly, than the calcium salt. The lithium salt decomposes when kept in dry powder, and also the calcium salt, but the latter only to a slight extent. In water, all three salts form acetic acid and the corresponding salicylate. T. A. H.

The Action of Hydrochloric Acid and Potassium Hydroxide on the Lactam of Benzoyldehydracetic Acid. Joh. Schöttle and Pavel Iv. Petrenko-Kritschenko (*Ber.*, 1912, **45**, 3229—3231. Compare A., 1911, i, 1020; 1912, i, 128).—It has already been

observed that the action of concentrated hydrochloric acid and sodium hydroxide solutions on the lactam of benzoyldehydracetic acid produces 2 : 6-diphenyl-4-pyridone-3-carboxylic acid and 2 : 6-diphenyl-4-pyridone respectively.

The action of hydrochloric acid in dilute solution in aqueous alcohol, or of dilute solution of potassium hydroxide in alcohol, gives rise to benzoyldehydracetic acid. This easy removal of nitrogen from the ring does not militate against the structure assumed for the lactam, as the alternative possibility of the position of the nitrogen atom in the side-chain would necessitate the assumption that ammonium chloride (in the action of concentrated solution of acid or alkali) can condense with benzoyldehydracetic acid—an assumption which is not in accord with experimental evidence.

The amide of dehydracetic acid, when heated in a sealed tube with hydrochloric acid at 180°, quantitatively eliminates a molecule of ammonia. D. F. T.

Nitrogentisic Acids. ALFONS KLEMENC (*Monatsh.*, 1912, **33**, 1243—1254).—The stability of gentisic acid (2 : 5-dihydroxybenzoic acid) is so increased by esterification that it can be successfully nitrated, especially if the hydroxyl groups are previously acetylated.

The methyl ester of diacetylgentisic acid, m. p. 62—63·5°, obtained by acetylation of methyl gentisate or by the action of diazomethane on diacetylgentisic acid, when nitrated with fuming nitric acid (D 1·52) and subsequently hydrolysed produces 3-*nitrogentisic acid*, a yellow powder, m. p. 230° (decomp.); *ammonium* salt, brown; the *silver* salt, a yellow, crystalline powder, on treatment with methyl iodide produces the *methyl* ester, yellow needles, m. p. 158° (decomp.), which can also be obtained by direct esterification of the acid by a methyl-alcoholic solution of hydrogen chloride.

Methyl 2-hydroxy-5-methoxybenzoate (Graebe and Martz, A., 1905, i, 702), when nitrated in acetic acid solution with fuming nitric acid, yields *methyl* 3-*nitro*-2-*hydroxy*-5-*methoxybenzoate*, yellow needles (from methyl alcohol), which change to leaflets, m. p. 138—139°; the *potassium* salt, yellow needles, obtained by hydrolysis, on acidification gives 3-*nitro*-2-*hydroxy*-5-*methoxybenzoic acid*, yellow needles, m. p. 181°.

Diazomethane acting in ethereal solution converts 3-nitrogentisic acid, and also 3-nitro-2-hydroxy-5-methoxybenzoic acid, into the *methyl* ester (colourless needles, m. p. 71—72°) of 3-*nitro*-2 : 5-*dimethoxybenzoic acid* (yellow needles, m. p. 181—183°), the acid being obtainable by hydrolysis.

The three nitro-acids described above all give characteristic colours when dissolved in potassium hydroxide solution. D. F. T.

Preparation of Anthraquinonecarboxylic Acids. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 250742).—Anthraquinonecarboxylic acids can be readily prepared by oxidising the corresponding methyl-anthraquinones with nitrous fumes (NO_2 or N_2O_3) at a high temperature in the presence of a suitable solvent, whilst some nitroanthraquinones can be converted by the action of chlorine into the

corresponding chloroanthraquinones with elimination of the nitro-group.

1-*Chloroanthraquinone-2-carboxylic acid*, yellow needles, is obtained when 1-chloro-2-methylanthraquinone (25 parts) dissolved in 200 parts of trichlorobenzene is treated at 160° with the gases generated from a mixture of arsenious and nitric acids; and the required 1-chloro-2-methylanthraquinone is prepared by treating 1-nitro-2-methylanthraquinone with chlorine at 180°.

1 : 4-*Dichloroanthraquinone-2-carboxylic acid*, citron-yellow needles, is obtained from 1 : 4-dichloro-2-methylanthraquinone, whilst 2-methylanthraquinone furnishes *anthraquinone-2-carboxylic acid*.

F. M. G. M.

Benzalacetoneoxalic Acid [Benzylideneacetylpyruvic Acid]. OTTO MUMM (*Ber.*, 1912, **45**, 3236—3237).—The condensation product of pyruvic acid with benzaldehyde described by Mumm and Bergell (A., 1912, i, 936) as benzylideneacetylpyruvic acid is in reality the isomeric ketoacetylphenylparacone, $CH_3\cdot CO\cdot CH<\begin{matrix}CO\cdot CO\\CHPh-\end{matrix}>O$ (Ruhemann, T., 1906, **89**, 1236).

It is also formed from ethyl pyruvate and benzaldehyde, either from the sodium salt of the ester or from the free ester in presence of piperidine.

E. F. A.

The Combination of Phenolcarboxylic Acids. FERDINAND MAUTHNER (*J. pr. Chem.*, 1912, [ii], **86**, 550—551).—A correction. The products obtained by hydrolysing the compounds described in previous communications (A., 1911, i, 725; 1912, i, 267) with alkalis fully confirms the constitutions there given, and, therefore, the author retracts the statements made in his last paper (A., 1912, i, 858).

F. B.

Isomeric and Tautomeric Organo-magnesium Compounds. JULIUS SCHMIDLIN and ANTONIO GARCIA-BANÙS (*Ber.*, 1912, **45**, 3193—3203).—The earlier explanation of the different behaviour of aromatic aldehydes with ordinary and previously heated solutions of magnesium triphenylmethyl chloride (Schmidlin, A., 1906, i, 392; 1907, i, 26, 601; 1908, i, 239) is adhered to in spite of the criticism of Tschitschibabin (A., 1909, i, 778). In refutation of the latter's criticism, it is stated that his experiments were not of a nature to decide the question, and it is further shown that, although magnesium benzyl chloride cannot be separated into two isomerides, the solution behaves as if it contained a tautomeric mixture of two isomerides, which, it is suggested, represent the normal and quinonoid configurations already assumed for the two forms of magnesium triphenylmethyl chloride.

When magnesium benzyl chloride solution in ether is treated with benzaldehyde, the latter being added in drops, the product is $\alpha\beta$-diphenylethyl alcohol, $CH_2Ph\cdot CHPh\cdot OH$. During the progress of the reaction, the Grignard reagent, which is believed to be an equilibrium mixture of the forms $CH_2:C_6H_4<\begin{matrix}H\\MgCl\end{matrix}$ and $CH_2Ph\cdot MgCl$,

has time to rearrange so as to give a theoretical yield of the diphenylethyl alcohol produced by the latter form. If, however, the Grignard reagent is gradually introduced into the ethereal solution of benzaldehyde, both forms enter into reaction, and the product is a mixture of the above diphenylethyl alcohol with 1 : 3-*diphenyl*-3 : 4-*dihydro*-2 : 1-*benzopyran* (*diphenyl*iso*chroman*),

$$C_6H_4<\begin{matrix}CHPh\cdot O \\ CH_2—CHPh\end{matrix},$$

prismatic needles, m. p. 111·5° (corr.), b. p. 237°/9 mm., which dissolve in concentrated sulphuric acid to a green solution; on oxidation with potassium permanganate it gives *o*-benzoylbenzoic acid and benzoic acid, whilst chromic acid produces anthraquinone and benzoic acid. In the preparation of the above diphenyldihydrobenzopyran, there was occasionally obtained 1 : 3-*diphenyl*-2 : 1-*benzopyran* (*diphenyl*iso*chromene*), $C_6H_4<\begin{matrix}CHPh\cdot O \\ CH{=}CPh\end{matrix}$, colourless needles, m. p. 125—126° (corr.); this decolorises bromine and potassium permanganate solutions, and gives a colourless solution in sulphuric acid; chromic acid gives the same oxidation products as with the dihydro-compound, whilst reduction by hydrogen and platinum-black produces the dihydro-derivative.

With other reagents, the magnesium benzyl chloride undergoes reaction merely through one of its isomerides; thus the action of carbon dioxide affects only the normal compound, whereas the formation of *o*-tolyl alcohol from formaldehyde (Tiffeneau and Delange, A., 1904, i, 48) depends on the reaction taking place with the quinonoid isomeride. D. F. T.

The Action of Ultraviolet Light on *o*-, *m*-, and *p*-Nitrobenzaldehyde and on Benzaldehyde. ANTON KAILAN (*Monatsh.*, 1912, 33, 1305—1327).—Under the action of ultraviolet light, *o*-nitrobenzaldehyde, both in alcoholic and benzene solutions, is slowly transformed into *o*-nitrosobenzoic acid (compare Ciamician and Silber, A., 1901, i, 547), the reaction taking place quicker in quartz than in glass vessels. The formation of acid from benzaldehyde takes place similarly. With both aldehydes the acid formation takes place more rapidly in benzene than in alcoholic solutions. The velocity of reaction increases with increase in concentration of the aldehyde, but proportionality does not exist, the increase in velocity being less than would be expected. Under similar conditions the amount of acid formed from the *o*-nitrobenzaldehyde is about twice as great as from the benzaldehyde. When the distance between the source of ultraviolet light (a mercury lamp) and the reaction vessel is increased, the diminution in reaction velocity is greater than would be expected from the inverse-square law. During the reaction a very considerable portion of the active rays is absorbed.

m- and *p*-Nitrobenzaldehydes, either as the solids or in solution, are hardly affected by ultraviolet light, the formation of acid being extremely small. Both solid *o*-nitrobenzaldehyde and liquid benzaldehyde are acted on to a considerable extent, in one case 87% of the benzaldehyde being converted into benzoic acid.

The formation of acid is due principally to oxidation by the oxygen of the air, or by ozone formed by the ultraviolet light; the reaction expressed by the equation: $2Ph{\cdot}COH + H_2O = Ph{\cdot}CH_2OH + Ph{\cdot}CO_2H$, if it takes place at all, plays only a subsidiary part.

In absolute alcoholic solution benzoic acid is not esterified to any appreciable extent under the conditions of experiment, nor does it have any accelerating action on the oxidation of the benzaldehyde, although hydrions, when present in great concentration, may exert such an action.

The temperature-coefficient of the above reactions is very small, as is usually the case in photochemical actions. T. S. P.

New Synthesis of *o*-Aldehydophenylnitrosohydroxylamine. OSKAR BAUDISCH (*Ber.*, 1912, **45**, 3429—3430).—A solution of *o*-nitrobenzaldehyde in 96% alcohol (10 vol.) is diluted with 5 vol. of water, treated with 3 vol. of amyl nitrite and 3 vol. of concentrated aqueous ammonia, and then gradually with zinc dust. The reaction is complete after about fifteen minutes. The mixture is treated with an excess of aqueous copper sulphate, and dilute hydrochloric acid is added carefully with cooling. From the still alkaline solution is obtained a brown, flocculent precipitate, which is removed. The filtrate is rendered distinctly acid, whereby the copper derivative of *o*-aldehydophenylnitrosohydroxylamine is precipitated. After being washed with acetone, the copper salt is converted by aqueous alcoholic potassium hydroxide into the potassium salt, from which *o*-aldehydophenylnitrosohydroxylamine, m. p. 52·5°, is liberated by metaphosphoric acid.

C. S.

Chemical Action of Light. II. Photo-Oxidation of the Aldehyde Group. I. Terephthalaldehyde. HERMANN SUIDA (*Monatsh.*, 1912, **33**, 1173—1187. Compare A., 1912, i, 117).—Although terephthalaldehyde is very stable in the solid state and in solution in benzene in the dark, its solution undergoes rapid atmospheric oxidation when illuminated by a mercury lamp, and a white, crystalline deposit is formed; the deposit consists of terephthalaldehydic acid to the extent of roughly two-thirds, the remainder being terephthalic acid; the solution from which the crystals have separated gives a peroxide reaction with acidified potassium iodide solution. This oxidation of terephthalaldehyde appears not to occur at all if light is excluded, and it is not accelerated by the presence of nitrobenzene, this substance, indeed, exerting a hindering effect; a comparison with benzaldehyde seems to indicate that, assuming the supply of oxygen by diffusion to be more than sufficient, the oxidation velocity of each aldehyde group in terephthaldehyde is considerably diminished by the presence of a similar group in the para-position. By interposing solutions of potassium chromate and of quinine sulphate between the solution and the source of light, it is discovered that the effect is mainly due to the ultra-violet rays, but that yellow and red light can cause the oxidation to occur, although only very feebly. Spectrographic examination indicates that the effective rays are from 400 to $300\mu\mu$.

D. F. T.

Catalytic Reduction. VII. The Preparation and Application of Colloidal Platinum Metals. ALADAR SKITA and W. A. MEYER (*Ber.*, 1912, **45**, 3579—3589).—When submitted to the action of free hydrogen, an aqueous alcoholic solution containing an unsaturated aldehyde or ketone with a little palladious chloride and gum arabic undergoes reduction; colloidal palladium is first formed, which then catalytically accelerates the hydrogenation of the ethylenic linking (Skita, A., 1909, i, 479). If the ethylenic substance does not contain a ketonic or aldehydic group, colloidal palladium is not obtained, but precipitated metal, which, however, is sufficient to aid the reduction of camphene to dihydrocamphene, and of β-phenylvinyl acetate to *β-phenylethyl acetate*, b. p. 109—112°/13 mm., although it fails to reduce double bonds in aromatic nuclei. This action of the carbonyl group in aiding the formation of colloidal palladium is probably due to the formation of a double compound of the ketone or aldehyde with the greater portion of the metallic chloride present (compare Zeisse, *Annalen*, 1840, **33**, 29); under such conditions it is probable that colloidal particles are first formed which can cause the separation of the rest of the metal in the same form. This is confirmed by the behaviour at the ordinary temperature of a solution of palladious chloride and gum arabic, which, after the addition of a little colloidal palladium, is rapidly reduced by hydrogen to the colloidal metal, whereas if treated directly with hydrogen the metal is slowly precipitated in an insoluble form; this effect is not merely due to the prevention of supersaturation (Zsigmondy, A., 1906, ii, 679), but is also in part catalytic.

A colloidal solution of palladium can also be obtained by the action of hydrogen on a hot aqueous solution of palladious chloride containing gum arabic; when a mixture of this solution with an alcoholic feebly acid solution of piperine was treated with hydrogen, tetrahydropiperine (Skita and Franck, A., 1911, i, 1017) was produced.

Solutions of palladious chloride and of potassium platinosochloride containing gum arabic, when treated with sodium carbonate, give palladious and platinous hydroxides in a colloidal condition; careful evaporation in a vacuum, after dialysis, gives a residue of brown palladious hydroxide or black platinous hydroxide consisting of scales, which readily dissolve in water again. These colloidal hydroxides are well suited to reduction processes, for example, hydrogen reduced an aqueous alcoholic solution of pinene containing a little palladium hydroxide to pinane, and a solution of phorone containing a little platinum hydroxide readily absorbed an amount of hydrogen corresponding with two ethylenic linkings.

Colloidal palladium hydroxide solutions when shaken with hydrogen are reduced to colloidal palladium, and on evaporation in a vacuum black scales are obtained which readily re-dissolve in water; black scales of colloidal platinum can be similarly obtained. These, which can also be prepared directly by reduction of the corresponding chlorides, are again suitable for reduction experiments, *o*-nitroacetophenone and nitrobenzene being easily reduced to the corresponding amino-compounds.

The most satisfactory method for the hydrogenation of an un-

saturated compound is to add to the solution of platinum chloride and gum arabic a trace of a colloidal palladium or platinum solution, and then to act with hydrogen; the unsaturated substance which may be present from the commencement or introduced later is then easily reduced, for example, quinine yields dihydroquinine, whilst diacetylmorphine gives *diacetyldihydromorphine*, needles, m. p. 158° (*hydrochloride*, needles, m. p. above 300°), and cinnamic acid yields β-phenylpropionic acid. D. F. T.

Catalytic Reduction. VIII. Hydrogenation of Aldehydes and Ketones, and of Aromatic and Heterocyclic Substances in Colloidal Solutions. ALADAR SKITA and W. A. MEYER (*Ber.*, 1912, **45**, 3589—3595. Compare preceding abstract).—It has already been observed that hydrogenation occurs more readily in certain solvents than in others (Fokin, A., 1907, i, 819), and that acetic acid is so suitable that in the presence of platinum black even aromatic substances can be reduced (Willstätter and Hatt, A., 1912, i, 545). By using a colloidal solution of platinum, prepared by one of the methods described (preceding abstract), and applying acetic acid as solvent, it is found possible with hydrogen under an additional pressure of one atmosphere, to reduce toluene to methyl*cyclo*hexane, benzoic acid to *cyclo*hexanecarboxylic acid, naphthalene to decahydronaphthalene, pyridine to piperidine, heptaldehyde to heptyl alcohol, dihydro*iso*phorone to *trans*-dihydro*iso*phorol, and benzene to *cyclo*hexane; in the last two cases only a trace of colloidal platinum was taken with a solution of the substance for reduction, together with chloroplatinic acid, so that the treatment with hydrogen first produced the catalyst, and then reduced the organic substance; the reduction processes generally occupied one to three hours. Quinoline, however, required longer treatment with a rather higher pressure of hydrogen for reduction to decahydroquinoline, and by checking the reduction at the right stage, tetrahydroquinoline could be obtained. A description of the apparatus employed is given.

It was not found possible to replace gum arabic satisfactorily by any other protecting colloid. D. F. T.

Condensation Products of Cyclic Ketones with Acetone. OTTO WALLACH and W. VON RECHENBERG (*Chem. Zentr.*, 1912, ii, 923—924; from *Nachr. K. Ges. Wiss. Gött.*, 1912, 442—445).—Further investigation of the condensation of acetone with 1 : 3-methyl*cyclo*hexanone (A., 1896, i, 572; 1897, i, 425) shows that condensation takes place between the O-atom of the cyclic ketone and hydrogen from the acetone, with the production of compounds having a :CO group in the side-chain, which can be reduced to saturated ketones of the type $R\cdot CH_2\cdot COMe$, where R is a cyclic radicle. The position of the ethylenic linking is uncertain, but it is probably cyclic.

1 : 3-*Methyl*cyclo*hexylacetone*, b. p. 211·5—212°, $D^{21\cdot5}$ 0·8915, $n_D^{21\cdot5}$ 1·4496, obtained by reducing the methyl*cyclo*hexenylacetone produced by condensing 1-methyl*cyclo*hexan-3-one with acetone (*loc. cit.*), is lævorotatory, resembles other extra-cyclic ketones in aroma, gives a *semi-*

carbazone, m. p. 154°, and on oxidation with sodium hypobromite yields 1 : 3-methyl*cyclo*hexylacetic acid. 1 : 4-*Methyl*cyclo*hexenylacetone*, b. p. 216—217°, D^{21} 0·916, n_D^{21} 1·4672, has an anise odour, gives a *semicarbazone*, m. p. 122—123°, and a liquid *oxime*. On reduction it yields 1 : 4-*methyl*cyclo*hexylacetone*, b. p. 214—215°, D^{21} 0·8930, n_D^{21} 1·4499. The latter gives a *semicarbazone*, m. p. 166°, and is oxidised by sodium hypobromite to 1 : 4-methyl*cyclo*hexylacetic acid. T. A. H.

Action of an Alcoholic Solution of Potassium Hydroxide on Ketones. II. PIETER J. MONTAGNE and JACOB MOLL VAN CHARANTE (*Rec. trav. chim.*, 1912, **31**, 298—349. Compare A., 1908, i, 988).—The action of alcoholic potash on further derivatives of benzophenone is described. It is found that the introduction of an amino-group into any position in the ring entirely prevents the reduction to a benzhydrol, but that the presence of methyl, chlorine, or bromine in the *para*-position, or of chlorine in the *ortho*-position, is without influence on the reduction. In the case of the bromo-derivatives it was previously found that 2 : 4 : 6-tribromobenzophenone is not only reduced, but that it also loses the bromine atoms in 2 and 6 (A., 1910, i, 42). Studying this detaching influence of the –COPh group further, it is found that the elimination of bromine occurs readily in the case of *o*-bromobenzophenone, to a slight extent with the para-compound, and to a still smaller extent, but certainly, with the meta-derivative. The –CHPh·OH group, on the contrary, has no such detaching influence, the substituted benzhydrols remaining entirely unchanged when heated with alcoholic potash; only in the case of the 4 : 4′-dibromobenzhydrol was there any trace of halogen removed. The following benzophenones have been studied: 2-, 3-, and 4-chloro-, 4 : 4′-dichloro-, 2-, 3-, and 4-bromo-, 2 : 4-, 2 : 6-, and 4 : 4′-dibromo-, 4-iodo-, 2-amino-, 2 : 2′-diamino-, 4 : 4′-didimethylamino- (Michler's ketone), 2- and 3-methyl-. Many of these have been described by Montagne and Koopal (see Koopal, Thesis).

2 : 4-Dibromobenzophenone was obtained by the action of benzoyl chloride and aluminium chloride on 1 : 3-dibromobenzene (Boeseken, A., 1908, i, 189) and also synthesised as follows: Acetanilide was converted into 2 : 4-dibromoacetanilide, not by Chattaway's method (A., 1900, i, 152), since that yielded only *p*-bromoacetanilide, but according to Mannino and Donato (A., 1908, i, 826). This was saponified by 10% potassium hydroxide, and the 2 : 4-dibromoaniline diazotised. With amyl nitrite, nitrous acid, or sodium nitrite and dilute sulphuric acid, a varying quantity of 2 : 4 : 2′ : 4′-tetrabromodiazoaminobenzene crystallised out, but on warming with water the mixture gave a good yield of 1 : 3-dibromobenzene. When mixed with potassium nitrite and added to concentrated nitric acid, the formation of a diazoamino-compound was prevented (compare O. N. Witt, A., 1909, i, 855), and on warming the diluted diazotised liquid with a mixture of copper sulphate and potassium cyanide the 2 : 4-dibromobenzonitrile was obtained. This was saponified and the acid converted into the chloride, which with benzene and aluminium chloride gave the 2 : 4-dibromobenzophenone. From the mother liquors of this compound a small amount of 2 : 6-dibromobenzo-

phenone was recovered, the two bromine atoms exerting no steric hindrance, which confirms the author's experience that the Friedel and Crafts's reaction on halogenated benzenes gives rise to ortho- as well as to para-substitution.

2 : 6-Dibromobenzophenone was also synthesised. Sulphanilic acid was converted into dibromoaniline (Orton and Pearson, T., 1908, **93**, 735), and this was diazotised as above and converted into 2 : 6-dibromobenzonitrile, which was saponified by 65% sulphuric acid. The amide, m. p. 208·5°, was further treated with 90% sulphuric acid, and the 2 : 6-dibromobenzoic acid was converted into 2 : 6-dibromobenzoyl chloride and this into 2 : 6-*dibromobenzophenone*, $C_6H_3Br_2$·COPh, which crystallises in very long needles, m. p. 121·5°, b. p. 381°.

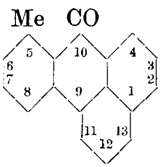
4-Aminobenzophenone, m. p. 124°, obtained by the reduction of 4-nitrobenzophenone (Shröter, A., 1909, i, 773) was found to remain unchanged by acetic acid, and was thus distinguished from 4-aminobenzhydrol, m. p. 121°, since the latter gives an acetyl compound, m. p. 153° (Doebner, A., 1882, 507). New benzhydrols obtained by the action of alcoholic potash on the benzophenones are 3-*bromobenzhydrol*, C_6H_4Br·CHPh·OH, m. p. 43°, and 3-*methylbenzhydrol*, C_6H_4Me·CHPh·OH, slender needles, m. p. 53°.

Detailed crystallographic measurements of the following substances have been made: 4-bromoacetanilide, 2 : 4-dibromoacetanilide, 2 : 4-dibromoaniline, 2 : 4-dibromobenzophenone, 2 : 6-dibromobenzamide, and 2-nitrobenzophenone. J. C. W.

Conversion of Distyryl Ketone into 2 : 6-Diphenylpyrone. DANIEL VORLÄNDER and G. A. MEYER (*Ber.*, 1912, **45**, 3355—3358).—Distyryl ketone tetrabromide (Claisen and Claparède, A., 1882, 511) when heated in alcoholic solution with a quadrimolecular quantity of potassium hydroxide is converted into a viscous oil, probably the diethoxy-compound, CO(CH:CPh·OEt); the substance gives a blood-red solution in sulphuric acid and a gradual brownish-black coloration with ferric chloride solution. When it is heated with hydrochloric acid (D 1·1) under reflux condenser for several hours a mixture of 2 : 6-diphenylpyrone, needles, m. p. 139—140°, with much resinous matter is produced. D. F. T.

Elimination of Hydrogen from Aromatic Nuclei and Union of the Latter by means of Aluminium Chloride. ROLAND SCHOLL and CHRISTIAN SEER (*Annalen*, 1912, **394**, 111—177).—Isolated instances of the union of aromatic nuclei by means of aluminium chloride at elevated temperatures are known, for example, the formation of perylene from 1 : 1′-dinaphthyl (Scholl, Seer, and Weitzenböck, A., 1910, i, 616), of flavanthrene from 2-aminoanthraquinone (Scholl, A., 1907, i, 540), and of *meso*-naphthadianthrone from *meso*-benzdianthrone (Scholl and Mansfeld, A., 1910, i, 494). The authors have now examined this reaction more fully, and find that, by means of anhydrous aluminium chloride at 80—140°, aromatic nuclei can be very satisfactorily united, particularly in the case of aromatic

ketones, where the elimination of the hydrogen is accompanied by the formation of new rings; thus, 1 : 9-benzanthrone is obtained in 76% yield by heating phenyl α-naphthyl ketone and anhydrous aluminium chloride (5 pts.) at 150° during two and a-half hours. In a similar manner, *o*-tolyl α-naphthyl ketone yields 5-*methyl*-1 : 9-*benzanthrone* (annexed formula), m. p. 167—168°, yellow needles; *m*-tolyl α-naphthyl ketone yields 6-*methyl*-1 : 9-*benzanthrone*, m. p. 169·5°, yellow needles; *p* tolyl α-naphthyl ketone yields 7-*methyl*-1 : 9-*benzanthrone*, m. p. 158—159°, yellow needles; *p*-diphenylyl α-naphthyl ketone yields 7-*phenyl*-1 : 9-*benzanthrone*, m. p. 170—171°, yellowish-brown leaflets; phenyl α-4-hydroxynaphthyl ketone yields 2-*hydroxy*-1 : 9-*benzanthrone*, m. p. 304°, dark red needles (*benzoyl* derivative, m. p. 236°, golden-yellow needles). In the last preparation, 2-*hydroxydihydro*-1 : 9-*benzanthrone*, m. p. 142—143°, yellowish-brown needles, is first formed; it is converted into 2-hydroxy-1 : 9-benzanthrone by prolonged heating or by passing oxygen through its solution in hot aqueous sodium hydroxide.



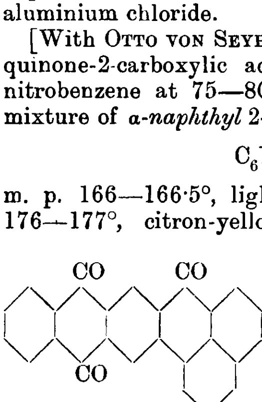
The interaction of naphthalene, *o*-toluoyl chloride, and aluminium chloride in carbon disulphide leads to the formation of o-*tolyl* α-*naphthyl ketone*, $C_{10}H_7\cdot CO\cdot C_6H_4Me$, m. p. 64°, b. p. 365—375°. By similar methods, m-*tolyl* α-*naphthyl ketone*, m. p. 74—75°, and p-*tolyl* α-*naphthyl ketone*, m. p. 85°, have been prepared. p-*Diphenylyl* α-*naphthyl ketone*, $C_{10}H_7\cdot CO\cdot C_6H_4Ph$, m. p. 136—137°, is obtained in a similar manner from α-naphthoyl chloride and diphenyl, or from naphthalene and the *chloride*, m. p. 114—115°, colourless needles, of diphenyl-4-carboxylic acid. *Phenyl* α-4-*hydroxynaphthyl ketone*, $OH\cdot C_{10}H_6\cdot COPh$, m. p. 164—165°, is obtained from α-naphthol and benzoyl chloride by Doebner's method.

o-α-Naphthoylbenzoic acid yields naphthanthraquinone, not the expected 1 : 9-benzanthrone-5-carboxylic acid, by heating with aluminium chloride.

[With Otto von Seybel.]—The interaction of the chloride of anthraquinone-2-carboxylic acid, naphthalene, and aluminium chloride in nitrobenzene at 75—80° for ten hours leads to the formation of a mixture of α-*naphthyl* 2-*anthraquinonyl ketone*,

$$C_6H_4{<}{\textstyle{CO \atop CO}}{>}C_6H_3\cdot CO\cdot C_{10}H_7,$$

m. p. 166—166·5°, light brown leaflets, and the β-*isomeride*, m. p. 176—177°, citron-yellow needles, which is separated by repeated crystallisation from glacial acetic acid and from pyridine. By heating with aluminium chloride at 100—140° for one hour and again at 140—145° for another hour, the former yields 6 : 7-*phthaloyl*-1 : 9-*benzanthrone* (annexed formula), m. p. 325—326°, dark yellow needles, which, unlike the α-naphthyl anthraquinonyl ketone, forms with alkaline sodium hyposulphite a dark green vat producing on unmordanted cotton green tones changing to yellow in air. The constitution of the

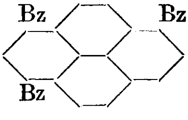


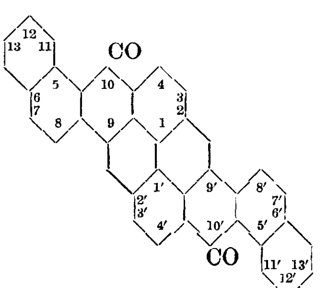
phthaloylbenzanthrone is proved by oxidation with chromic acid, whereby 2 : 3-*phthaloylanthraquinone-5-carboxylic acid*,

$$C_6H_4<^{CO}_{CO}>C_6H_2<^{CO}_{CO}>C_6H_3\cdot CO_2H,$$

m. p. 338° (decomp.), microcrystalline, yellow needles, is obtained, which is converted by sublimation into Philippi's 2:3-phthaloylanthraquinone (A., 1911, i, 793). Phthaloylanthraquinonecarboxylic acid forms a greenish-yellow *sodium* salt, which forms with hot alkaline sodium hyposulphite a violet, and finally an orange, solution, changing to blue in air; this solution produces on unmordanted cotton a blue colour which becomes red by treatment with acids.

The interaction of pyrene, benzoyl chloride (rather more than 1 mol.), and aluminium chloride in carbon disulphide for twelve hours at the ordinary temperature, and then for an equal period on the water-bath, leads to the formation of 3-*benzoylpyrene*, m. p. 124—125°, yellow crystals, which is purified by means of the *picrate*, $C_{29}H_{17}O_8N_3$, m. p. 157°, orange needles. By using two or more mols. of benzoyl chloride, a mixture of di- and tri-benzoylpyrene is obtained, which is separated readily owing to the slight solubility of the latter in glacial acetic acid. 3 : 5 : 8-*Tribenzoylpyrene* (annexed formula), m. p. 239—240°, crystallises in yellow needles. 3 : 8-*Dibenzoylpyrene*, m. p. 158—160°, slender, yellow needles, yields pyrenequinone by oxidation with aqueous potassium dichromate and sulphuric and acetic acids, and is converted into pyranthrone when mixed with aluminium chloride, placed in a bath previously heated to 155—160°, and kept there for one hour (if the heating is effected gradually, the benzoyl groups are eliminated before the benzanthrone rings are formed). This formation of pyranthrone establishes the direct relation of the substance to pyrene, and also proves the orientation of the benzoyl groups in the dibenzoylpyrene. 3 : 5 : 8-Tribenzoylpyrene is converted into 3-*benzoylpyranthrone*, reddish-brown, metallic needles, in a similar manner; at a slightly higher temperature, 165—170°, the benzoyl group is eliminated and pyranthrone is formed. The interaction of pyrene, α-naphthoyl chloride, and aluminium chloride in carbon disulphide leads to the formation of a nearly quantitative yield of a mixture of 3 : 8- and 3 : 10-di-α-naphthoylpyrene, which is separated by boiling glacial acetic acid, in which the former is insoluble. 3 : 8-*Di-α-naphthoylpyrene*, $C_{38}H_{22}O_2$, m. p. 271·5—273°, crystallises in microscopic, yellow leaflets; the 3 : 10-*isomeride*, m. p. 219—220°, in yellow leaflets. The former and aluminium chloride at 140° for forty minutes yield 5 : 6 : 5′ : 6′-*dibenzpyranthrone* (annexed formula), a brown powder, which forms in hot alkaline sodium hyposulphite a sparingly soluble vat, by which unmordanted cotton is dyed blue, changing to orange-

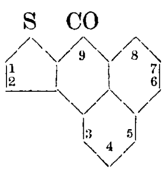




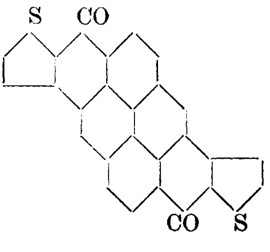
red in air. In a similar manner, pyrene, β-naphthoyl chloride, and aluminium chloride yield 3 : 10-*di-β-naphthoylpyrene*, m. p. 195·5—197°, yellow crystals (purified by means of the orange-yellow *picrate*), and 3 : 8-*di-β-naphthoylpyrene*, m. p. 289°, flattened, yellow needles. The latter and aluminium chloride at 145—155° yield 7 : 8 : 7′ : 8′-*dibenzpyranthrone*, a brown, indistinctly crystalline powder with green shimmer, which forms a vat behaving like that of the preceding isomeride.

It will be noticed that the action of the preceding acyl chlorides on pyrene in the presence of aluminium chloride yields in each case a pair of diacylpyrenes. One of these is undoubtedly the 3 : 8-diacylpyrene, since it is converted into benz-(or dibenz-)pyranthrone by aluminium chloride. It is known that hydrocarbons such as anthracene and phenanthrene, which are easily oxidised to quinones, are attacked in the Friedel-Crafts reaction by the acid chloride or anhydride in the same positions as by the oxidising agent in the formation of the quinone. Consequently it is probable that pyrene, which forms 3 : 8-diacylpyrenes in the Friedel-Crafts reaction, yields 3 : 8-pyrenequinone, not 3 : 10-pyrenequinone (Goldschmiedt, A., 1907, i, 310), by oxidation.

The constitution of violanthrone (Bally's violanthrene, A., 1905, i, 237) has been proved by the formation of the substance from 4 : 4′-dibenzoyl-αα-dinaphthyl and aluminium chloride at 95—100°.



The interaction of naphthalene, pyromucyl chloride, and aluminium chloride in carbon disulphide leads to the formation of (impure) *α-furyl α-naphthyl ketone*, $C_4OH_3 \cdot CO \cdot C_{10}H_7$, b. p. 360—365°, which reacts with aluminium chloride to form a brown substance from which individual products have not been isolated. In a similar manner, naphthalene and the chloride of thiophen-2-carboxylic acid, or thiophen and α-naphthoyl chloride, yield *α-thienyl α-naphthyl ketone*, $C_4SH_3 \cdot CO \cdot C_{10}H_7$, m. p. 68—69°, b. p. 383°, almost colourless needles, which is converted by aluminium chloride at 140—144° into *benzthiophanthrone*-9 (annexed formula), a brown, crystalline powder; this sinters at 210°, but is not fused at 250°, and yields by fusion with alcoholic potassium hydroxide a dye which is probably the analogue, $C_{30}H_{12}O_2S_2$, of violanthrone.

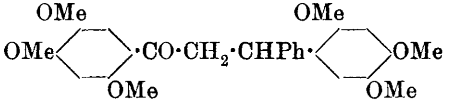


The interaction of pyrene, the chloride of thiophen-2-carboxylic acid, and aluminium chloride in carbon disulphide leads to the formation of 3 : 8-*di-α-thiophenoylpyrene*, $C_{26}H_{14}O_2S_2$, m. p. 278—279°, elongated, yellow leaflets, and 3 : 10-*di-α-thiophenoylpyrene*, m. p. 191—192°, yellow leaflets; the former and aluminium chloride at 150—158° yield *pyrthiophanthrone* (annexed formula), microscopic, reddish-brown needles. C. S.

Chalkones and Hydrochalkones. II. Guido Bargellini and Mina Finkelstein (*Gazzetta*, 1912, 42, ii, 417—426. Compare Bargellini and Bini, A., 1912, i, 118).—The present paper describes

the reduction of four chalkones to the corresponding hydrochalkones by means of hydrogen in the presence of platinum black or palladium black.

2′ : 4′ : 5′-Trimethoxychalkone (compare Bargellini and Avrutin, A., 1911, i, 68) is conveniently prepared by the original method of preparation of chalkones (Stockhausen and Gattermann, A., 1893, i, 163). If, however, the heating of the mixture of hydroxyquinol trimethyl ether, cinnamyl chloride, and aluminium chloride is prolonged to ten or twelve hours, the principal product is a *substance*, $C_{27}H_{30}O_7$, which forms colourless needles, m. p. 127—128°. This compound dissolves in concentrated sulphuric acid, giving a pale yellow coloration, and does not react with bromine; it probably has the annexed constitution.



2′ : 4′ : 5′-*Trimethoxyhydrochalkone*, $C_{18}H_{20}O_4$, crystallises in colourless needles, m. p. 105—107°; it dissolves in concentrated sulphuric acid, giving a pale yellow coloration.

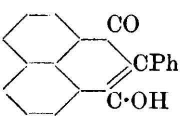
3 : 4 : 2′ : 4′ : 5′-*Pentamethoxyhydrochalkone*, $C_{20}H_{24}O_6$, forms colourless needles, m. p. 115—117°; it dissolves in concentrated sulphuric acid, giving a pale yellow coloration.

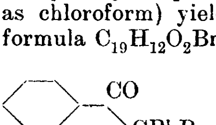
2′-*Hydroxy*-4 : 4′-*dimethoxyhydrochalkone*, $C_{17}H_{18}O_4$, crystallises in colourless needles, m. p. 58—60°.

2′-*Hydroxy*-3 : 4 : 4′-*trimethoxyhydrochalkone*, $C_{18}H_{20}O_5$, crystallises in colourless needles, m. p. 78—79°, and dissolves in concentrated sulphuric acid, giving a pale yellow coloration.

Attempts to reduce esperitin were unsuccessful, possibly owing to the hindering action of the free phenolic hydroxyl groups, or perhaps owing to some influence of the solvent. R. V. S.

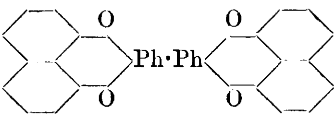
Phenylhydroxyketoperinaphthindene. MARCELLO CESARIS (*Gazzetta*, 1912, **42**, ii, 453—472).—When phenylacetic acid, naphthalic anhydride, and potassium acetate are heated at 230° for two hours, 1-hydroxy-3-keto-2-phenylperinaphthindene (annexed formula) is formed; it crystallises in iridescent, orange-yellow scales, m. p. 218°, and dissolves in concentrated sulphuric acid, giving an intense yellow coloration. The substance dissolves in alkalis, and is reprecipitated by acids. The *acetyl* derivative, $C_{19}H_{11}O_2Ac$, forms deep yellow needles, m. p. 172—175°. Bromination of hydroxyketophenylperinaphthindene in anhydrous solvents (such as chloroform) yields an unstable *additive product* of the probable formula $C_{19}H_{12}O_2Br_2,HBr$. By the action of water on this compound, or by bromination in aqueous solvents, 2-*bromo*-1 : 3-*diketo*-2-*phenylperinaphthindene* (annexed formula) is obtained; it forms prisms or needles, m. p. 198°. The *anilide*, $C_{19}H_{11}O_2\cdot NHPh$, prepared from the bromo-derivative, crystallises in golden-yellow scales, m. p. 225—227°. When the bromo-derivative is treated with alkalis, hydroxyketophenylperinaphthindene





is obtained. The action of hydrogen bromide on hydroxyketophenylperinaphthindene (in chloroform) yields an unstable *compound*, $C_{19}H_{12}O_2HBr$, which begins to melt at 90° and is completely melted at 210°.

Cautious oxidation of hydroxyketophenylperinaphthindene with permanganate yields naphthalic acid, benzoic acid, and traces of an *acid* crystallising in colourless needles, m. p. about 200—202°. Oxidation with potassium dichromate in acetic acid yields a neutral substance, $C_{38}H_{22}O_4$, to which the annexed structure of *bis-diketophenylperinaphthindene* is ascribed; it is a straw-coloured, crystalline powder, m. p. about 235—236° (decomp.), and it dissolves in concentrated sulphuric acid, giving an intense orange-red coloration. R. V. S.



Preparation of α-Chloroanthraquinone. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 252578).—When α-nitroanthraquinone (or its derivatives) is treated with chlorine, this element displaces the α-nitro-group. Moreover, when 1-nitro-2-methylanthraquinone is similarly treated at high temperatures it furnishes ω-di- with some ω-mono- and ω-tri-chloro-derivatives. 1-Chloroanthraquinone is obtained (in satisfactory yield) when 1-nitroanthraquinone (80 parts) in 400 parts of trichlorobenzene is treated at 160—165° with a stream of chlorine; 1 : 5-dinitroanthraquinone at 190° furnishes 1 : 5-dichloroanthraquinone, and at 160—180° 1-nitro-2-methylanthraquinone yields chiefly ω-1-trichloro-2-methylanthraquinone. F. M. G. M.

Preparation of Condensation Products of the Anthracene Series Containing Sulphur. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 251115).—When negatively substituted anthraquinones which in addition contain one or more auxochrome groups are condensed with arylmercaptols they yield compounds which can be employed as pigments, or for the preparation of dyes.

The *compound* obtained when an alcoholic solution of 4-chloro-1-hydroxy-2-methylanthraquinone (54 parts) containing 13 parts of potassium hydroxide is heated at 100° with *p*-tolyl mercaptan (25 parts) is a crystalline, violet powder. The following *compounds* obtained in a similar manner are described in the original; from *p*-tolyl mercaptan with (1) 4-chloro-1-amino-2-methylanthraquinone a glistening, bronze, crystalline powder; (2) with 4-bromo-1-methylaminoanthraquinone, glistening, violet needles; (3) with 1-chloroaminoanthraquinone an orange, crystalline powder; whilst 2-bromo-1-amino-4-hydroxyanthraquinone furnishes 1-*amino*-4-*hydroxyanthraquinone* 2-p-*tolyl thioether*, violet-brown bronze needles, and 2:3-dichloro-1 : 4-diaminoanthraquinone yields 1 : 4-*diaminoanthraquinone* 2 : 3-*dithio*-p-*tolyl ether*, blue needles. F. M. G. M.

Preparation of Anthracene Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 252530. Compare A., 1907, i, 1067).—An account of the preparation of *compounds* of cœrthionium type by heating the following anthraquinone thio-ethers with concentrated sulphuric acid at 150—160°: αα′-dianthraquinonyl thioether; αβ-dianthraquinonyl thioether; 4 : 4′- or 5 : 5′-dibenzoyldi-

amino-1 : 1′-dianthraquinonyl thioether, whilst the condensation of 1 : 5-dichloroanthraquinone (1 mol.) with 2 mols. of anthraquinone-2-mercaptol (compare A., 1907, i, 1067) furnishes 1 : 5-*anthraquinonedimercaptol-di-2′-anthraquinonyl thioether.* F. M. G. M.

Binuclear Quinones of the Anthraquinone Group. HANS MEYER, RICHARD BONDY, and ALFRED ECKERT (*Monatsh.*, 1912, 33, 1447—1468).—The supposed oxidation of dihydrodianthrone by amyl nitrite (Padova, A., 1909, i, 167, 655) to dianthrone is apparently a mistake, as the product is a mixture of anthraquinone with unchanged dihydrodianthrone. *Dianthrone*,

$$CO<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>C{=}C<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>CO,$$

can, however, be easily obtained by the oxidation of dianthranol in alkaline solution with potassium persulphate or hydrogen peroxide; the product, a crystalline powder, is preceded by an intermediate labile green *substance.* If a solution of dianthrone in acetic acid is exposed to sunlight or to the rays from a mercury lamp or an electric arc, it deposits yellow needles of *meso*-naphthadianthrone, $CO<\begin{matrix}C_6H_3\\C_6H_3\end{matrix}>C{=}C<\begin{matrix}C_6H_3\\C_6H_3\end{matrix}>CO$ (compare Scholl, Mansfield, and Potschiwauscheg, A., 1910, i, 494); the different properties of the substance described earlier are shown to be due to impurity, as the purified substances give practically identical absorption spectra. The substance gives an orange vat, it dissolves in sulphuric acid to a red fluorescent solution, and is oxidised by chromic acid to anthraquinone. The hydrogen liberated during the above conversion of dianthrone into *meso*-naphthadianthrone is probably largely oxidised by oxygen dissolved in the solvent; also, if an atmosphere of carbon dioxide is used, it is observed that some carbon monoxide is formed; only 95% of the original substance is obtained as *meso*-naphthadianthrone, whilst the solvent is found to contain afterwards about 2% of a volatile *hydrocarbon*, leaflets, m. p. 62—63°, possibly hexahydroanthracene, and also a little anthraquinone.

When anthraquinone is submitted in acetic acid to the action of nascent hydrogen (tin and hydrochloric acid) in intense light, the usual products, anthranol and dianthryl, are accompanied by a considerable quantity of dihydroanthracene.

By stopping the action of light on dianthrone at an early stage, dianthranol is found to be present, and is presumably the primary product from which the other substances above are subsequently formed; this idea is supported by the plentiful formation of diacetyldianthranol when a hot solution of dianthrone in acetic anhydride is exposed to light. Diacetyldianthranol in boiling solution when exposed to light for a considerable time is converted largely into a crystalline *substance*, m. p. circa 300°, and a little *meso*-naphthadianthrone.

Helianthrone (Scholl and Mansfield, *loc. cit.*), dissolved in acetic acid and exposed to light, deposits rhombic leaflets of a substance which on crystallisation from nitrobenzene separates in the characteristic needles of *meso*-naphthadianthrone; the identity of

the product was proved by its absorption spectrum. The yield was over 90%, and was accompanied by a brown, amorphous substance possessing the properties of a hydro-derivative of helianthrone.

D. F. T.

Preparation of Borneol and *iso*Borneol Esters. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 252158).—*Borneyl cinnamate*, b. p. 215°/10 mm., when treated with bromine (in carbon tetrachloride solution) yields *borneyl dibromo-β-phenylpropionate*, colourless, glistening crystals, m. p. 73°; this ester can also be prepared by the action of dibromo-β-phenylcinnamoyl chloride on borneol in the presence of pyridine; the corresponding iso*borneyl* ester forms colourless, glistening leaflets, m. p. 69°.

When *borneyl phenylpropiolate*, b. p. 230—235°/19 mm., is treated with bromine it furnishes *borneyl bromocinnamate*, colourless crystals, m. p. 76°, which is also procurable from borneol and bromocinnamoyl chloride.

Borneyl o-*chlorocinnamate*, colourless crystals, m. p. 102—108° (probably a mixture of two isomerides), on bromination yields *borneyl* o-*chloro-αβ-dibromophenylpropionate*, colourless prisms, m. p. 91°.

αβ-Dibromo-m-*methoxy-β-phenylpropionyl chloride*, m. p. 189°, yields a *borneyl* ester, m. p. 63—64°; *borneyl dibromocinnamate* has m. p. 65°, and *borneyl αβ-dibromo-β*-p-*tolylpropionate*, m. p. 90—91°.

These esters are of therapeutic value. F. M. G. M.

Preparation of Odourless or Faintly Odorous Esters from Valeric Acid and Therapeutically Powerful Alcohols. J. D. RIEDEL (D.R.-P. 252157).—iso*Valerylglycylborneyl* ester, a viscous liquid, b. p. 181°/12 mm., D^{20} 1·027, is prepared by stirring together borneyl chloroacetate and sodium valerate until the separation of sodium chloride is complete; the corresponding iso*borneyl* ester has b. p. 182—183°/12 mm. and D^{15} 1·0318, whilst the iso*valerylglycylmenthyl* ester has b. p. 197°/19 mm. and D^{16} 0·986. F. M. G. M.

Δ^4-Menthen-3-one. OTTO WALLACH, RUD. MÜLLER, and FR. HENJES (*Chem. Zentr.*, 1912, [ii], 922—923; from *Nachr. K. Ges. Wiss. Gött.*, 1912, 431—436).—In order to confirm the description and constitution already assigned to Δ^4-menthen-3-one (A., 1908, i, 813), the authors have prepared it from (*a*) Δ^4-menthene, made from 1 : 4-*cyclo*hexanone, and (*b*) *d*-menthene, obtained from menthol, and find that the characters of these two preparations are the same as those already given. The active specimen had $[\alpha]_D^{18}$ $-67·46°$ in methyl alcohol. The low boiling point of the ketone is probably due to the position of the *iso*propyl side-chain between a :CO group and an ethylenic linking. The latter probably renders reactive the hydrogen atom in position 6, whilst the :CO group confers reactivity on the neighbouring H-atom (position 2), and this joint action explains the formation of a dibenzylidene derivative from this ketone. No thymol is produced on oxidation with ferric chloride in acetic acid. T. A. H.

Hydrogenation with Platinum Metals as Catalyst. VI. ALADAR SKITA (*Ber.*, 1912, **45**, 3312—3318. Compare A., 1911, i, 1017).—Azobenzene in alcoholic solution is readily reduced by

hydrogen under a pressure of two atmospheres in the presence of colloidal palladium with gum arabic as the protecting colloid. The reduction to hydrazobenzene takes place rapidly, whereas the reduction of the hydrazobenzene to aniline proceeds comparatively slowly.

[With W. A. MEYER and JULIUS VON BERGEN.]—Under conditions similar to those used with azobenzene, α-ionone is reduced to *dihydro-α-ionone*, $C_{13}H_{22}O$, which is a liquid, b. p. 121—122°/14 mm., possessing a slight odour of cedar wood, but the characteristic odour of the α-ionone has disappeared. Similarly, β-ionone gives *dihydro-β-ionone*, b. p. 126—129°/12 mm., possessing properties resembling those of the α-compound. Both the dihydro-compounds on further reduction give the same *tetrahydroionone*, $C_{13}H_{24}O$, b. p. 126—127°/13 mm., showing that it is the ethylene linking in the side-chain which is first reduced.

Tiemann (A., 1898, i, 376) has expressed the opinion that ionone acts as a perfume because of the αβ-ethylene linking in the side-chain. If this is so, a dihydroionone which has been hydrogenised in the nucleus, and still contains an αβ-ethylene linking in the side-chain should still be a perfume. To prepare such a compound, dihydro*cyclo*citral was acetylated in tartaric acid solution by a method similar to that used in preparing ψ-ionone from citral and acetone. The *dihydroionone*, $C_{13}H_{22}O$, thus obtained was a pale yellow liquid, b. p. 124—125°/14 mm., and having an odour similar to that of ionone. Since only the latter compound possesses the character of a perfume, the authors propose that the name dihydroionone should be retained for it, whilst the dihydro-compounds obtained from the α- and β-ionones should be termed 1 : 1 : 3-trimethyl-Δ^3- and 1 : 1 : 3-trimethyl-Δ^2-*cyclo*hexenylethyl methyl ketones respectively.

ψ-Ionone when hydrogenised gives *tetrahydro-ψ-ionone*,

$$CMe_2{:}CH{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}[CH_2]_2{\cdot}COMe,$$

b. p. 126—127°/14 mm.

In the unsaturated aldehydes and ketones hitherto examined, with the exception of mesityl oxide (A., 1910, i, 71) and phorone (A., 1909, i, 479), the hydrogenation does not affect the carbonyl group. Acraldehyde also forms an exception, giving allyl alcohol together with propaldehyde.

[With FRIEDRICH NORD.]—The following alkaloids have been hydrogenised by method similar to that used with quinone and cinchonine (A., 1911, i, 1017), the protecting colloid not being used. Quinidine gives *dihydroquinidine*, $C_{20}H_{26}O_2N_2,H_2O$, m. p. 165°, $[\alpha]_D^{20}$ +265·3°; the *methiodide*, $C_{22}H_{27}O_2N_2I$, forms slender, light yellow needles, m. p. 224—225°, and the *phosphate*, $C_{20}H_{29}O_6N_2P$, decomposes at 212°. Cinchonidine gives *dihydrocinchonidine*, $C_{19}H_{24}ON_2$, m. p. 229°, $[\alpha]_D^{20}$ −97·5°, the *methiodide*, $C_{20}H_{27}ON_2I$, and *phosphate*, $C_{19}H_{27}O_3N_2P$, of which have the m. p.'s 248° and 113° respectively. The dihydroquinidine is identical with the naturally-occurring hydroconquinine, and the dihydrocinchonidine with hydrocinchonidine. T. S. P.

[Glycuronic Acids Produced by the Coupling of Alicyclic Compounds in the Organism.] JUHO HÄMÄLÄINEN (*Skand. Arch. Physiol.*, 1912, 27, 141—226).—See this vol., i, 133.

The Simultaneous Action of Catalysts. VLADIMIR N. IPATIEV (*Ber.*, 1912, **45**, 3205—3218. Compare A., 1911, i, 31).—[With N. MATOV.]—In order to prepare fenchane from fenchone, the latter was first heated with hydrogen under pressure (110 atmos.) for twenty hours at 240°, whereby fenchenol, b. p. 196°/752 mm. and D^{20} 0·9554, was obtained. Attempts to prepare fenchene, which could then be hydrogenised to fenchane, from fenchenol by the fission of water under the catalytic action of alumina at temperatures varying from 210° to 255° gave only very small yields, and the use of the bromo-compound gave no better results. When, however, fenchenol was heated at 215° for twelve to fourteen hours with hydrogen under a pressure of 110 atmos., in the presence of a mixture of nickel oxide and alumina as catalysts, fenchane was obtained directly; $[\alpha]_D$ − 19·83°, D^{17} 0·8766, D^{20} 0·8733, n^{17} 1·45409.

The hydrogenisation of commercial camphene (m. p. 48·5°, b. p. 160—165°/761 mm.) in the presence of nickel oxide at 240° gives *iso*camphane, m. p. 53·5—57°, b. p. 162·5—163·5°/758 mm., D^{19} 0·8457.

Attempts to prepare camphene by the dehydration of borneol in the presence of alumina at 350—360° gave only small yields of a liquid camphene, together with large quantities of oxidation products, the reaction being a very slow one. When, however, borneol (m. p. 208—210°, b. p. 215°, $[\alpha]_D$ + 30·21°) is hydrogenised at 215—220° under 110 atmos. pressure in the presence of a mixture of nickel oxide and alumina, *iso*camphane is obtained, m. p. 63—64·5°, b. p. 164°/757 mm., D^{70} 0·84157, $[\alpha]_D$ − 8·50°. Under similar conditions, *iso*borneol (m. p. 209°, b. p. 211°, $[\alpha]_D$ − 1·82°) also gives rise to *iso*camphane, m. p. 62·5—64°, b. p. 164—164·5°/756·1 mm., D^{70} 0·84293, $[\alpha]_D$ − 2·81°. When heated with alumina alone at 350—360°, *iso*borneol yields small quantities of crystalline camphene, together with considerable quantities of condensation products.

The transformation of cyclic ketones into the saturated hydrocarbons by the combined action of reduction and dehydration catalysts takes place readily, at much lower temperatures than in the reduction of the alcohols. In the presence of a mixture of nickel oxide and alumina at 200°, carvomenthone is readily reduced to menthane by hydrogen under pressure. Similarly, camphor (m. p. 174·5—176°, b. p. 203·5°/743·2 mm., $[\alpha]_D$ + 33·20°) at 200° gives *iso*camphane (m. p. 64·5—65·5, b. p. 164—165°/757 mm., D^{70} 0·8462, $[\alpha]_D$ − 3·95°). Comparison of the physical properties of the various *iso*camphanes prepared from camphene, borneol, *iso*borneol, and camphor shows that they are very similar to each other.

When a mixture of alumina and copper oxide is used instead of alumina and nickel oxide as catalyst, terpene alcohols give rise to unsaturated hydrocarbons. The temperature of dehydration is much lower, being 220° instead of 360°, and in consequence of this lower temperature there is no hydrogenisation of the double linking in the presence of the copper oxide. Under such conditions borneol at 200—220° and a hydrogen pressure of 50 atmos., gives a mixture of solid and liquid camphene, the former having m. p. 60—62·5°, b. p. 156—159°/763 mm., D^{70} 0·85075, and the latter b. p. 155—160°/

763 mm., D^{16} 0·8688, $[\alpha]_D$ 1·61°, n^{16} 1·45819. This liquid camphene yields a chloride, m. p. 140°, and when hydrogenised in the presence of nickel oxide gives liquid *iso*camphane, b. p. 160—165°, D^{18} 0·85204, n^{18} 1·45009.

Under the same conditions as with borneol, *iso*borneol gives rise only to a solid camphene, m. p. 53·5°, b. p. 162—167°/766 mm., D^{70} 0·85092, n^{60} 1·44244.

[With O. ROUTALA.]—At 240°, in the presence of a mixture of alumina and copper oxide and under a hydrogen pressure of 20 atmos., 1-methyl*cyclo*hexan-2-ol yields methyl-Δ^1-*cyclo*hexene (compare A., 1911, i, 25), b. p. 107·5—108·5°/759·5 mm., D_4^{18} 0·8063, n^{18} 1·44094. The *nitrosochloride*, C_7H_{12}·NOCl, m. p. 102°, is very unstable, decomposing in a desiccator with the formation of the *oxime*, C_7H_{10}:NOH. The *nitrosate*, $C_7H_{12}O_4N_2$, has m. p. 115°. By the addition of hydrogen bromide in acetic acid solution, 1-*bromomethyl*cyclo*hexane* is obtained as a colourless liquid, b. p. 156—160°, D^{18} 1·2544, n^{18} 1·48168. The action of silver oxide on this compound gives rise to small quantities only of the alcohol, the methyl*cyclo*hexene being regenerated for the most part. With silver acetate, however, the *acetic* ester, $C_9H_{16}O_2$, is readily obtained, b. p. 182—187°, D^{18} 0·9536, n^{18} 1·43862, which, on saponification with alcoholic alkali gives 1-*methyl*cyclo*hexan*-1-*ol*, $C_7H_{14}O$, b. p. 159—164°/759 mm., D^{18} 0·9417, n^{18} 1·45179.

Attempts to prepare the bromide from 1-methyl*cyclo*hexan-2-ol by the action of phosphorus tribromide were unsuccessful, owing to the ready fission of hydrogen bromide.

To explain the greater catalytic effect of the combined catalysts, it is assumed that a labile complex, for example, NiO,Al_2O_3, is formed as an intermediate product, and then decomposes, giving the components in the nascent state. The combined action of the catalysts is called "hydrolytic reduction." T. S. P.

Constituents of Ethereal Oils. The Sesquiterpene Selinene and its Derivatives. FRIEDRICH W. SEMMLER and FELIX RISSE (*Ber.*, 1912, **45**, 3301—3307. Compare Schimmel, A., 1910, i, 328).—Selinene, $C_{15}H_{24}$, the sesquiterpene from celery seed oil, which has b. p. 128—132°/11 mm., D^{20} 0·9190, n_D 1·5092, $[\alpha]_D$ + 61°36′, is shown to be a bicyclic doubly unsaturated hydrocarbon. On reduction with hydrogen in presence of finely divided platinum, or of the dihydrochloride with sodium and alcohol, *tetrahydroselinene*, $C_{15}H_{28}$, is obtained, b. p. 126—128°/10·5 mm., D^{20} 0·8881, n_D 1·48259, $[\alpha]_D$ + 7°.

When selinene dihydrochloride is treated with calcium hydroxide, one halogen atom is eliminated as hydrogen chloride, and the other replaced by hydroxyl, the alcohol *selinenol*, $C_{15}H_{26}O$, being obtained; it has b. p. 155—163°/19 mm., D^{20} 0·9627, n_D 1·50895, $[\alpha]_D$ + 52°36′. On reduction, *dihydroselinenol*, crystallising in colourless needles, m. p. 86—87°, is obtained. The preparation of this compound is the best method of detecting selinene. E. F. A.

Extraction of Coffee Oil. VIKTOR GRAFE (*Monatsh.*, 1912, **33**, 1389—1406. Compare Erdmann, A., 1902, i, 551).—From a comparison with ordinary coffee beans and beans which have been previously deprived of caffeine, it is found that the latter give less coffee oil, the

shortage being especially in the furfuryl alcohol of the mixture. Beans freed from skin and wax gave practically the same results as ordinary beans, so that the parent substance of the coffee oil must have been still present. It is believed that the treatment preceding the extraction of the caffeine diminishes the content of fibrous matter, and causes partial decomposition of the chlorogenic and coffalic acids; these acids are regarded as the source of the valeric acid in coffee oil, whilst the fibrous matter is the origin of the furfuryl alcohol.

D. F. T.

Desulphuration of Vulcanised Rubber. PAUL ALEXANDER (*Chem. Zeit.*, 1912, **36**, 1289—1291, 1340—1342, 1358—1359).—The author has stated previously (*ibid.*, 1910, **34**, 789) that it is impossible to remove the combined sulphur from vulcanised rubber without destroying the rubber substance. The work of Hinrichsen and Kindscher (A., 1912, i, 706) having placed this conclusion in doubt, the author has repeated and extended this work.

Para rubber was vulcanised by mixing it with varying quantities (5 to 20 parts) of sulphur and heating at 143° under 4 atmospheres pressure. The products (A—E) were then treated in benzene solution with (1) alcoholic sodium hydroxide; (2) alcoholic sodium hydroxide in presence of zinc, magnesium or calcium, and the materials (A_1A_2, B_1B_2, C_1C_2, etc.) thus obtained examined in comparison with the original products. The results are too numerous to quote, but the most interesting are the "vulcanisation-coefficients" arrived at in three different ways: (1) calculated from the total sulphur, less the sum of the sulphur in the ash and that in the "matter soluble in acetone"; (2) calculated from the sulphur in the "matter insoluble in acetone," less the sulphur in the ash, and (3) the sulphur in the nitrosite prepared from the product under examination. From the whole of his results the author draws the conclusion that the last method gives the true vulcanisation-coefficient, that is, the amount of sulphur which combines with 100 parts of pure rubber. The following general conclusions are drawn: The methods described, which are those of Hinrichsen and Kindscher, do not remove combined sulphur from vulcanised rubber, but actually increase the amount in combination when insufficient sodium hydroxide to combine with all the free sulphur is used. The metals used exert no action in this direction. The whole of the free sulphur is not removed from vulcanised rubber by extraction with acetone, probably because part of it at the temperature of vulcanisation is converted into a modified form, which is insoluble in acetone, but dissolves in alcoholic sodium hydroxide. The products (A_1A_2, etc.) referred to above contain "depolymerised rubber," which is soluble in acetone; this material is produced by the heat applied, and not by the action of the alkali hydroxide or the metals or solvents used. The rest of the paper is polemical in favour of Loewen (A., 1912, ii, 914, 915) against Hinrichsen and Kindscher (A., 1912, i, 1007).

T. A. H.

Resin of Pinus Halepensis. L. REUTTER (*J. Pharm. Chim.*, 1912, [vi], **6**, 497—500).—This resin has m. p. 83—85°, acid number

180·75—182·74, saponification number 196·5—199·3, ester number 15·7—16·5, and gives colour reactions similar to those of cholesterol. The portion soluble in ether yields to aqueous ammonium carbonate, *helepinic acid*, $C_{21}H_{40}O_4$, m. p. 73·5—74·5°, and subsequently to aqueous sodium carbonate: (1) *helepinolic acid*, $C_{40}H_{56}O_5$, m. p. 144·2—145·5°, which is crystalline and yields a *silver* salt; (2) *a-helepinolic acid* $C_{34}H_{50}O_4$, m. p. 80·5—81·5°, which is soluble in alcohol, but yields a lead salt insoluble in that solvent; (3) *β-helepinolic acid*, $C_{18}H_{28}O_4$, m. p. 80·5—82°, which is soluble in alcohol and yields a *lead* salt also soluble in alcohol, and (4) *heleponic acid*, $C_{18}H_{28}O_2$, m. p. 156—157°, separating from methyl alcohol in crystals. The resin also contains 14·4% of volatile oil (compare Tschirch and Schulz, A., 1907, i, 544).

T. A. H.

The Resinous Exudation of Pinus Pinea. L. REUTTER (*J. Pharm. Chim.*, 1912, [vi], 6, 494—497).—The portion of the oleo-resin soluble in ether yielded on extraction with (1) aqueous ammonium carbonate, *pineic acid*, $C_7H_{14}O_4$, m. p. 99—99·5°, and (2) aqueous sodium carbonate, *pineolic acid*, $C_{18}H_{28}O_3$, m. p. 86°, and a very small amount of a substance giving a precipitate with alcoholic lead acetate. The portion insoluble in ether on steam distillation yielded *pinearesen*, $C_9H_{13}O_4$, m. p. 85°, and a volatile oil, which had an odour recalling that of turpentine, and when kept deposited colourless crystals, m. p. 204°, with an odour similar to that of borneol.

T. A. H.

Chemical Composition of Dulcamara. GEORGES MASSON (*Chem. Zentr.*, 1912, ii, 366—367; from *Bull. Sci. Pharm.*, 1912, 19, 283—289. Compare Desfosses, *Jahresb.*, 1820, 2, 114; Davis, A., 1902, ii, 686).—The aërial portion of dulcamara is free from solanine, but contains in addition to proteins, gums, and reducing sugars, dulcamaretic acid, dulcamaric acid, and solacein (1%). The two acids are both soluble in alcohol, but the first only is soluble in ether, and they can be separated by the use of this solvent.

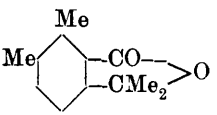
Dulcamaric acid is a glucosidic saponoid; it forms a greenish-brown powder, m. p. 190° (decomp.), and yields brown, amorphous salts with alkalis. On hydrolysis with 7% sulphuric acid in alcohol it furnishes (1) *dulcamarigenic acid*, m. p. 160°, and (2) a reducing sugar, which gives a *phenylosazone*, m. p. 196—197°, crystallising from boiling water in slender needles.

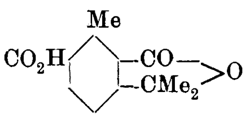
Dulcamaretic acid, m. p. 90—92°, is a non-glucosidic saponoid; it forms a green buttery mass, giving green, amorphous alkali salts. It could not be hydrolysed.

Solacein, m. p. 236—237°, is a nitrogenous glucoside; it forms a colourless, amorphous mass, soluble in alcohol, but insoluble in ether or water, and reduces auric chloride or silver nitrate on warming, but not Fehling's solution. It yields a yellow *platinichloride*, a stable *sulphate*, and a gelatinous *hydrochloride*. On hydrolysis by acids it furnishes solanidine, m. p. 190°, and a sugar from which a *phenylosazone*, m. p. 171—172°, crystallising in needles from methyl alcohol, was prepared.

Dulcamarin is regarded as an alkali compound of the two acid saponoids. T. A. H.

Picrotoxin. FRANCESCO ANGELICO (*Gazzetta*, 1912, 42, ii, 540—545. Compare A., 1911, i, 1003).—When the ketone, $C_{14}H_{16}O_3$ (obtained by the action of hydriodic acid and red phosphorus on picrotoxin, as already described), is heated with concentrated alcoholic potassium hydroxide, a new *compound*, $C_{12}H_{14}O_2$ is obtained in good yield. This substance crystallises in large, colourless needles, m. p. 81°, b. p. 290°; it is volatile with steam and has an odour of celery like the phthalides. It is stable towards oxidisers and reducers, but when heated at 260—280° with three times its weight of powdered potassium hydroxide, it yields acetone and 2:3-dimethylbenzoic acid, the barium salt of which gives *o*-xylene when distilled with barium oxide. When the phthalide, $C_{12}H_{14}O_2$, is oxidised with nitric acid, it yields an *acid*, $C_{12}H_{14}O_4$, of the probable constitution II, whilst when it is oxidised with alkaline potassium permanganate it yields an *acid*, $C_{12}H_{10}O_6,H_2O$, of the probable formula III. This acid gives a fluorescein with resorcinol, and when fused with potassium hydroxide yields acetone and 1:2:3-benzenetricarboxylic acid. The acid, $C_{12}H_{10}O_6,H_2O$, loses H_2O at about 130°, and gives potassium and silver salts. In view of these reactions, the compound, $C_{12}H_{14}O_2$, probably has the structure indicated in formula I.


(I.)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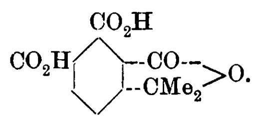
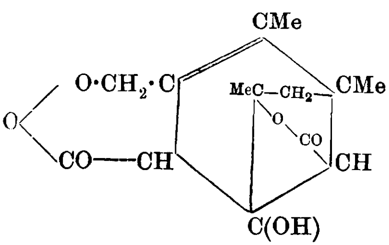
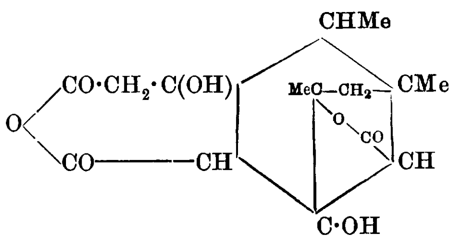

(III.)

The phthalide has been obtained by other means (but not identified) by Sielisch (A., 1912, i, 886).

The ketone, $C_{14}H_{16}O_3$, from which the phthalide is obtained, also loses acetone when fused with potassium hydroxide, and probably contains the keto-methylenic grouping, since the action on it of amyl nitrite and sodium ethoxide gives an oximino-compound, m. p. 215° (decomp.), which is converted by hydroxylamine into a dioxime. In consequence of these results and of those formerly published, the author regards picrotoxinine and picrotin, not as hydronaphthalene derivatives, but as hydrobenzene derivatives, related to *cyclo*hexene and *cyclo*hexane respectively. He suggests, therefore, the following provisional formulæ for the two substances:





R. V. S.

Picrotinic Acids. PAUL HORRMANN (*Ber.*, 1912, **45**, 3434—3437).—Angelico has given the formula $C_{15}H_{18}O_8$ to α-picrotinic acid and $C_{17}H_{24}O_8$ to its ethyl ester (A., 1910, i, 404). One or other of these formulæ must be wrong. The author shows that α-picrotinic acid has the formula $C_{15}H_{20}O_8$, decomp. 258°, and is identical with Horrmann and Seydel's δ-picrotinic acid (A., 1912, i, 1008). It is not an oxidation product of picrotin, but is produced merely by the addition of water. C. S.

Tannin. KARL FEIST (*Arch. Pharm.*, 1912, **250**, 668—683).—The author has stated previously that "Turkish" galls contain glucogallic acid and a tannin, which yields dextrose on hydrolysis by acids (A., 1912, i, 566, 888). These two substances are now described.

"Turkish" galls were extracted in turn with chloroform, benzene, and dry ether. The chloroform extract contained chlorophyll, *cyclo*-gallipharic acid, and gallic acid. Benzene removed nothing of importance. The ether extract consisted of glucogallic acid and a little tannin. The former was isolated by dissolving the dry extract in acetone, allowing the latter to evaporate, and pouring off the mother liquor as long as amorphous matter separated. Eventually *glucogallic acid* separated in rosettes of greyish needles. It can be prepared in like manner from commercial tannin derived from "Turkish" galls. Glucogallic acid, m. p. 233° (decomp. anhydrous), $[\alpha]_D^{17}+10{\cdot}6°$ in acetone, contains when air-dry about 12% of water, and has a molecular weight, when dry, of about 318 as determined by titration (assuming 1 CO_2H group) or by the b. p. method. On hydrolysis by boiling with N-sulphuric acid it yields dextrose and gallic acid. It reduces Fehling's solution on boiling, and yields a semi-crystalline *methyl* derivative, m. p. 79°, which, unlike the acid itself, gives no coloration with ferric chloride, and does not reduce Fehling's solution. Glucogallic acid is not decomposed by emulsin, so that it is probably an α-glucoside; it probably does not contain a free ·CHO group.

The partly exhausted galls were next extracted with hot acetone. The *tannin* (designated "Turkish" tannin to distinguish it from that obtained from "Chinese" galls) had $[\alpha]_D+28{\cdot}6°$ to $+31°$, and molecular weight 615—746 (b. p. method). On treatment with diazomethane in ether, part of it dissolved and was methylated (compare Herzig and Tscherne, A., 1905, i, 354). On hydrolysis the tannin yields dextrose and gallic acid; no glucogallic acid could be obtained as an intermediate product in this hydrolysis (compare Fischer and Freudenberg, A., 1912, i, 471, 887).

The tannin of "Chinese" galls (A., 1912, i, 888) has a molecular weight 899—1045, and is partly methylated on treatment with diazomethane in ether. T. A. H.

Action of Nitric Acid and Silver Nitrate on Tannin. ROGER DOURIS and A. WIRTH (*Chem. Zentr.*, 1912, ii, 1360; from *Bull. Sci. Pharmacol.*, 1912, **19**, 403—407).—When a solution of tannin is boiled with nitric acid and silver nitrate, silver cyanide is precipitated, the maximum yield occurring with the proportions 2 grams of silver nitrate, 10 c.c. of nitric acid (40° Bé.), and 2 grams of tannin, made up

to 100 c.c. with water. With a mixture of twice this concentration, a very violent reaction results in the formation of oxalic acid. Gallic acid has the same effect, but with pyrogallol or quinol the product is masked by the large amount of reduced silver which is also formed.

J. C. W.

Ratanhine. GUIDO GOLDSCHMIEDT (*Monatsh.*, 1912, **33**, 1379—1388).—Ratanhine occurs only exceptionally in ratanhin extract (compare Kreitmair, A., 1874, 1038).

A specimen which came into the author's possession had the composition $C_{10}H_{13}O_3N$, m. p. 252° (decomp.); *hydrochloride*, monoclinic crystals [$a:b:c = 1{\cdot}0283:1:0{\cdot}5111$, $\beta = 103{\cdot}77°$]; *copper* salt, deep violet prisms; *methyl* ester, m. p. 116—117°, monoclinic prisms [$a:b:c = 0{\cdot}8096:1:0{\cdot}8107$, $\beta = 116{\cdot}32°$]. On fusion with potassium hydroxide, ratanhine yielded *p*-hydroxybenzoic acid, whilst decomposition by heat gave a *base*; *hydrochloride*, $C_{19}H_{13}ON,HCl$, colourless prisms.

D. F. T.

Degradation of Bilirubin and Bilirubic Acid. HANS FISCHER and HEINRICH RÖSE (*Ber.*, 1912, **45**, 3274—3280).—Previously only traces of bases have been obtained on reduction of bilirubin. On boiling for fourteen to sixteen hours with acetic acid and hydrogen iodide, cryptopyrrole, $NH<\begin{matrix}CH{=}CMe\\ CMe{:}CEt\end{matrix}$, is readily obtained. It is left undecided whether hæmopyrrole and phyllopyrrole are also present. The second degradation product, the isomeric phonopyrrolecarboxylic acid, was isolated in relatively considerable quantity. It is readily esterified by means of methyl alcohol and dry hydrogen chloride, a method which is also applicable to phonopyrrolecarboxylic acid. This ester forms a dark brownish-red picrate, whereas the picrate of the isomeric ester is a normal yellow colour.

Bilirubic acid when reduced in a similar manner yields cryptopyrrole in small quantity together with a large proportion of the isomeric phonopyrrolecarboxylic acid; a considerable amount of the bilirubic acid remains unattacked. The results are interpreted as in favour of the formula:

$$\begin{matrix}CEt{\cdot}CMe\\ CMe{\cdot}NH\end{matrix}>C{\cdot}O{\cdot}C<\begin{matrix}CMe{\cdot}C{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H,\\ NH{-}CMe\end{matrix}$$

for bilirubic acid.

Methyl phonopyrrolecarboxylate crystallises in colourless, flat needles, m. p. 57—58°. The *picrate* forms reddish-brown needles with a marked lustre, m. p. 121—122°. The *picrate* of the isomeric *methyl phonopyrrolecarboxylate* crystallises in slender, yellow, concentrically-grouped needles, m. p. 107—108°. The free *ester* obtained from the picrate forms crystals, m. p. 47—48°.

E. F. A.

Bile Pigments. IV. HANS FISCHER and HEINRICH RÖSE (*Zeitsch. physiol. Chem.*, 1912, **82**, 391—405).—In part already abstracted (preceding abstract). On oxidation of bilirubin after reduction with sodium amalgam, methyl ethylmaleinimide and the oxime of phonopyrrole

carboxylic acid are obtained. This observation makes the existence of a third pyrrole complex in bilirubin probable.

Methylethylmaleinimide is also obtained on oxidation of bilirubic acid together probably with the oxime of phonopyrrolecarboxylic acid.

E. F. A.

Transformation of an Alcohol into a Sulphide or a Peroxide by Hydrogen Sulphide or Hydrogen Peroxide. ROBERT FOSSE (*Compt. rend.*, 1912, 155, 1019—1020).—Xanthhydrol reacts with hydrogen sulphide or hydrogen peroxide as does a basic hydroxide, giving rise respectively to a sulphide and a peroxide.

On passing a stream of hydrogen sulphide into a solution of xanthhydrol in acetic acid a white, microcrystalline deposit of *xanthyl sulphide*, $\left(O<\substack{C_6H_4 \\ C_6H_4}>CH\right)_2S$, is obtained, which is decomposed by hydrochloric acid, giving hydrogen sulphide and unstable xanthyl chloride. *Xanthyl peroxide*, $\left(O<\substack{C_6H_4 \\ C_6H_4}>CH\right)_2O_2$, is similarly prepared by the addition of hydrogen peroxide to the acetic acid solution of xanthhydrol. On boiling it with fuming hydrochloric acid, chlorine is evolved and a pyrryl salt is produced. The peroxide gives an orange-yellow solution in a mixture of acetic and hydrochloric acids, which with chlorides or bromides of gold or uranium yields double xanthyl metallic chlorides or bromides.

W. G.

Triphenylmethyl. XXI. Quinocarbonium Salts of the Hydroxyxanthenols. MOSES GOMBERG and C. J. WEST (*J. Amer. Chem. Soc.*, 1912, 34, 1529—1569).—In an earlier paper (A., 1911, i, 737) it was stated that hydroxy- and methoxy-xanthenols yield colourless carbinyl chlorides which are capable of uniting with a metal haloid, a halogen, or hydrogen haloid to form coloured quinocarbonium salts (compare Gomberg and Cone, A., 1910, i, 55, 869). A study has now been made of the salts of *p*-, 1-, 2-, 3-, and -4-hydroxy- and -methoxy-phenylxanthenol and of 3 : 6-dihydroxyphenylxanthenol.

It has been found that the hydroxy- and methoxy-groups cause a deepening of the colour of the quinonoid derivatives from the yellow of phenylxanthenol to deep red except in the case of the 3-derivatives which are yellow. The presence of these groups increases the stability of the quinonoid compounds, but diminishes that of the benzenoid salts; it also increases the reactivity of the xanthones. The influence of acetoxy- and benzoxy-groups diminishes the tendency of the compounds to tautomerise into the quinonoid form. The constitution of the compounds is discussed.

I. p-*Hydroxyphenylxanthenol Compounds*.—p-*Anisylxanthenol*,

$$OMe\cdot C_6H_4\cdot C(OH)<\substack{C_6H_4 \\ C_6H_4}>O,$$

m. p. 120—121°, prepared by adding xanthone to the product of the action of magnesium on *p*-anisyl iodide, separates from benzene in white, prismatic crystals, containing $\frac{1}{2}C_6H_6$, and from ether or acetone in large, monoclinic prisms. p-*Anisylquinoxanthenol chloride*

hydrochloride, $\begin{matrix} HCl,CHCl\cdot CH:C\text{---------}O \\ CH{=}CH{-}C:C(C_6H_4\cdot OMe) \end{matrix}>C_6H_4$, m. p. 110—115° (decomp.), prepared by saturating a benzene solution of the xanthenol, to which a little acetyl chloride has been added, with hydrogen chloride, forms dark red crystals. If this salt is suspended in benzene or light petroleum and a current of air passed through the mixture, the hydrogen chloride is removed, and p-*anisylxanthenol chloride*, $OMe\cdot C_6H_4\cdot CCl<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>O$, m. p. 95—96°, is produced, which forms colourless crystals. When a solution of the chloride in benzene is shaken with molecular silver, an unsaturated compound, analogous to triphenylmethyl, is formed, which on exposure to the air is converted into the *peroxide*, $\left[O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>C(C_6H_4\cdot OMe)\right]_2O_2$, m. p. 214° (decomp.), obtained as a white, crystalline powder. The following additive compounds of the chloride are described: *ferrichloride*, m. p. 198—199°; *zincichloride*, m. p. 240—241°; *mercurichloride*, m. p. 185—186°; *perbromide*, m. p. 159—163° (decomp.); and *periodide*. p-Anisylxanthenol *ethyl ether*,

$$O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>C(OEt)\cdot C_6H_4\cdot OMe,$$

m. p. 156—157°, and *methyl ether*, m. p. 129—130°, form colourless crystals.

p-*Anisylquinoxanthenol bromide hydrobromide* is a dark brown, crystalline substance. The *bromide*, $OMe\cdot C_6H_4\cdot CBr<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>O$, forms colourless crystals; its *zincibromide* has m. p. 224—225°; *mercuribromide*, m. p. 192—194°; *perbromide*, m. p. 174—175°, and *periodide*, m. p. 187—189°. *p*-Methoxyphenylxanthenol *perchlorate*, m. p. 192—193°; hydrogen sulphate, m. p. 117—118°, and *phosphate*, m. p. 124—125°, are described.

p-*Hydroxyphenylxanthenol*, $O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>C(OH)\cdot C_6H_4\cdot OH$, m. p. 149—150° (decomp.), prepared from *p*-anisylxanthenol by Baeyer's method (A., 1910, i, 251), crystallises in rosettes of colourless needles. The *perchlorate* has m. p. 255—256°, and the *hydrogen sulphate*, m. p. 240—245°. p-*Hydroxyphenylquinoxanthenol chloride hydrochloride*, $O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>C:C_6H_4<\begin{matrix}OH\\Cl,HCl\end{matrix}$ or

$$O<\begin{matrix}C_6H_4\text{------}\\C_6H_4(Cl,HCl)\end{matrix}>C\cdot C_6H_4\cdot OH,$$

m. p. 235—240°, forms dark red, iridescent plates. p-*Hydroxyphenylquinoxanthenol chloride*, m. p. 235—245° (decomp.), is obtained as a red powder by heating the hydrochloride in a vacuum at 130°; its *ferrichloride* has m. p. 156—157°; *zincichloride*, m. p. 222—223°; *mercurichloride*, m. p. 215—216°, and *perbromide*, m. p. 230—235°; the *periodide* is purple. p-*Hydroxyphenylquinoxanthenol bromide*, m. p. 258—260° (decomp.), is a red, crystalline powder. When *p*-hydroxyphenylxanthenol is heated at 110—120° for two hours, it loses a molecule of water and is converted into *xanthylene-*

quinomethane, $O<\substack{C_6H_4\\C_6H_4}>C<\substack{CH:CH\\CH:CH}>CO$, m. p. 287—288°, which has a green colour, and is readily hydrolysed by dilute acid or alcoholic potassium hydroxide with regeneration of *p*-hydroxyphenylxanthenol. If the quinone is treated with hydrogen chloride, *p*-hydroxyphenylquinoxanthenol chloride hydrochloride is produced, whilst by the action of hydrogen bromide, *p*-hydroxyphenylquinoxanthenol bromide is obtained. Acetic anhydride converts the qninone into *p*-acetoxyphenylxanthenol. The quinone unites with 1 mol. of methyl sulphate to form a red additive compound which yields *p*-anisylxanthenol on hydrolysis. By the action of phosphorus pentachloride the quinone is converted into *p*-chlorophenylxanthenol chloride (Gomberg and Cone, A., 1910, i, 57).

p-*Acetoxyphenylxanthenol*, $O<\substack{C_6H_4\\C_6H_4}>C(OH)\cdot C_6H_4\cdot OAc$, m. p. 145—146°, obtained by the action of acetic anhydride and sodium acetate on *p*-hydroxyphenylxanthenol, crystallises in long, slender, colourless needles. p-*Acetoxyphenylquinoxanthenol chloride hydrochloride*, $O<\substack{C_6H_4\text{———}\\C_6H_4(Cl,HCl)}>C\cdot C_6H_4\cdot OAc$, m. p. 118—122° (decomp.), forms light red crystals. p-*Acetoxyphenylxanthenol chloride*,

$$O<\substack{C_6H_4\\C_6H_4}>CCl\cdot C_6H_4\cdot OAc,$$

is obtained in colourless crystals; its *ferrichloride* has m. p. 182°; *zincichloride*, m. p. 194°; *stannichloride*, m. p. 188°, and *mercurichloride*, m. p. 215°; the *perbromide* has an orange colour. The *peroxide*, $\left[O<\substack{C_6H_4\\C_6H_4}>C(C_6H_4\cdot OAc)\right]_2O_2$, has m. p. 211—212° (decomp.).

p-*Benzoxyphenylxanthenol*, $O<\substack{C_6H_4\\C_6H_4}>C(OH)\cdot C_6H_4\cdot OBz$, m. p. 181—182°, forms colourless crystals. p-*Benzoxyphenylquinoxanthenol chloride hydrochloride*, m. p. 143—145° (decomp.), varies in colour from yellow to orange-red. p-*Benzoxyphenylxanthenol chloride*, m. p. 175—176°, yields additive *compounds* with ferric chloride, m. p. 204—205°, and with zinc chloride; the *perchlorate* has m. p. 235—236°. p-*Benzoxyphenylxanthenol peroxide* has m. p. 218—219° (decomp.).

II. 1-*Hydroxy*-9-*phenylxanthenol Compounds*.—Hydroxy- and methoxy-xanthones combine much more readily with metal haloids than xanthone itself. The hydrogen haloid additive compounds are very unstable, and can only be prepared in absence of water. 1-Methoxyxanthone (Tambor, A., 1910, i, 559) yields the following compounds: *stannichloride*, m. p. 135—136°; *stannibromide*, m. p. 172—173°; *mercurichloride*, m. p. 183—184°; *mercuribromide*, m. p. 167—168°; *zincichloride* and *zincibromide*, and the *hydrochloride*, m. p. 110—115°.

1-*Methoxy*-9-*phenylxanthenol*, $OH\cdot CPh<\substack{C_6H_4\text{———}\\C_6H_3(OMe)}>O$, m. p. 162—163°, prepared by adding 1-methoxyxanthone to a solution of magnesium phenyl bromide, forms lustrous, colourless needles; its *perchlorate* has m. p. 225°. 1-*Methoxy*-9-*phenylquinoxanthenol chloride*

hydrochloride, $O<\begin{matrix}C_6H_4\text{———————}\\C_6H_3\cdot OMe(Cl,HCl)\end{matrix}>CPh$, crystallises in lustrous, purple needles. 1-*Methoxy*-9-*phenylxanthenol chloride*,

$$O<\begin{matrix}C_6H_4\text{———}\\C_6H_3(OMe)\end{matrix}>CPhCl,$$

m. p. 160—161°, forms colourless crystals and yields coloured additive compounds with metal haloids. The *peroxide* has m. p. 200—201°.

1-*Hydroxy*-9-*phenylxanthenol*, $OH\cdot CPh<\begin{matrix}C_6H_4\text{———}\\C_6H_3(OH)\end{matrix}>O$, m. p. 148—150° (decomp.), forms colourless crystals, and yields a dark purple *perchlorate*, m. p. 249—250°. 1-Hydroxy-9-phenylxanthenol chloride could not be isolated, but its *ferrichloride*, m. p. 146—147°, and *stannichloride*, m. p. 185°, were prepared.

III. 2-*Hydroxy*-9-*phenylxanthenol Compounds*.—2-Methoxyxanthone furnishes the following additive compounds: *stannichloride*, m. p. 235—240°; *stannibromide*, m. p. 199—200°; *zincichloride*, m. p. 244—245°; *mercurichloride*, m. p. 200°; *mercuribromide*, m. p. 187—189°; *perchlorate*, m. p. 150—155°. 2-*Methoxy*-9-*phenylquinoxanthenol chloride hydrochloride*, m. p. 140—144° (decomp.), forms bright red crystals. 2-*Methoxy*-9-*phenylxanthenol chloride* has m. p. 198°, and yields a *ferrichloride*, m. p. 123—124°; *zincichloride*, m. p. 197—198°; *mercurichloride*; *stannichloride*, m. p. 147—149°, and *perbromide*. 2-*Methoxy*-9-*phenylquinoxanthenol bromide hydrobromide* forms deep red crystals and decomposes at 223—224°. 2-*Methoxy*-9-*phenylxanthenol bromide* is colourless, and yields coloured additive compounds with metal haloids; the *perchlorate* and *hydrogen sulphate* have m. p. 193—194° and 110—120° respectively.

2-Hydroxy-9-phenylxanthenol has m. p. 170°. 2-*Hydroxy*-9-*phenylquinoxanthenol chloride hydrochloride*, m. p. about 240°, is obtained as a dark red powder. 2-*Hydroxy*-9-*phenylxanthenol chloride* is colourless, and gives coloured additive compounds with metal haloids. 2-Hydroxy-9-phenylquinoxanthenol bromide (Kropp and Decker, A., 1909, i, 249) yields a *perchlorate*, m. p. about 260°, and *hydrogen sulphate*, m. p. 133—135°.

2-*Acetoxy*-9-*phenylxanthenol*, m. p. 151—152°, is a colourless, crystalline substance; the *perchlorate* has m. p. 180—185°. 2-*Acetoxy*-9-*phenylquinoxanthenol chloride hydrochloride*, m. p. 125—129° (decomp.), forms light orange crystals. 2-*Acetoxy*-9-*phenylxanthenol chloride* is colourless and gives coloured additive compounds with metal haloids. The *peroxide*, m. p. 128° (decomp.), forms white crystals.

2-*Benzoxy*-9-*phenylxanthenol*, m. p. 205—206°, is colourless; its *perchlorate* has m. p. 210°. 2-*Benzoxy*-9-*phenylquinoxanthenol chloride hydrochloride*, m. p. 147—148°, forms light red crystals. 2-*Benzoxy*-9-*phenylxanthenol chloride*, m. p. 190°, yields coloured additive compounds. The *peroxide* has m. p. 170° (decomp.).

IV. 3-*Hydroxy*-9-*phenylxanthenol Compounds*.—3-Hydroxyxanthone combines readily with metal and hydrogen haloids to form additive compounds. Phenyl-3-methoxyxanthenol (Decker and Fellenberg, A., 1907, i, 1065) has m. p. 125°, and its *perchlorate*, m. p. 215—217°. 3-*Methoxy*-9-*phenylxanthenol chloride* yields a *ferrichloride*, m. p.

163—164°; *zincichloride*, m. p. 200—201°, and *mercurichloride*, m. p. 190°. 3-*Methoxy*-9-*phenylquinoxanthenol bromide hydrobromide*, m. p. 112—115°, is orange-yellow and crystalline. The *zincibromide* of phenyl-3-methoxyxanthenol bromide has m. p. 150—155°.

3-*Hydroxy*-9-*phenylxanthenol* cannot be isolated, as it spontaneously loses water with formation of phenylfluorone. 3-*Hydroxy*-9-*phenylquinoxanthenol chloride hydrochloride*, prepared by the action of hydrogen chloride on phenylfluorone, forms yellow crystals. On passing dry air through a solution of this substance in benzene, 3-*hydroxy*-9-*phenylquinoxanthenol chloride*, $O<\begin{matrix}C_6H_4 \\ C_6H_3Cl(OH)\end{matrix}>CPh$, m. p. 198—200°, is produced as a yellow solid, which, when treated with molecular silver, is converted into phenylfluorone. 3-*Hydroxy*-9-*phenylquinoxanthenol bromide*, m. p. 238—240°, forms orange needles, and yields a *perchlorate*, m. p. 250°, and hydrogen sulphate, m. p. 201—202°.

V. 4-*Hydroxy*-9-*phenylxanthenol Compounds*.—4-Methoxyxanthone has m. p. 173—174°, and yields a *stannibromide*, m. p. 125—135°; *stannichloride*, m. p. 187—188°; *mercurichloride*, m. p. 204—205°; *perchlorate*, m. p. 160°; and *hydrobromide*. 4-*Methoxy*-9-*phenylquinoxanthenol chloride hydrochloride*, m. p. 144—145°, prepared from phenyl-4-methoxyxanthenol (Baeyer, A., 1910, i, 251), forms dark red, iridescent needles. 4-*Methoxy*-9-*phenylxanthenol chloride*, m. p. 237—238°, is colourless, and yields coloured additive compounds; the *ferrichloride* has m. p. 147—148°; *mercurichloride*, m. p. 205—207°; and the *zincichloride*, m. p. 240—241°. The *peroxide*, m. p. 202° (decomp.), forms colourless crystals. 4-*Methoxy*-9-*phenylquinoxanthenol bromide hydrobromide*, m. p. about 260°, separates in dark red crystals. The colourless bromide was not isolated, but the following coloured compounds were prepared: *zincibromide*, m. p. 234—235°; *mercuribromide*, m. p. 223°; *perbromide*, m. p. 188—189°.

4-Hydroxy-9-phenylxanthenol (Baeyer, *loc. cit.*) yields a *perchlorate*, m. p. 248—249°. 4-*Hydroxy*-9-*phenylquinoxanthenol chloride hydrochloride*, m. p. 210—211°, forms dark red crystals. 4-*Hydroxy*-9-*phenylquinoxanthenol chloride* has m. p. 200—201°, and the corresponding *bromide*, m. p. 261—262°.

4-*Acetoxy*-9-*phenylxanthenol*, m. p. 127—128°, crystallises in colourless needles; its *perchlorate* has m. p. 190°. 4-*Acetoxy*-9-*phenylquinoxanthenol chloride hydrochloride* is an orange-red substance, which, when left in a desiccator, loses hydrogen chloride with formation of the colourless 4-*acetoxy*-9-*phenylxanthenol chloride*, m. p. 134—135°; this compound gives a *ferrichloride*, m. p. 136—137°, and a *zincichloride*, m. p. 160—165°. 4-*Acetoxy*-9-*phenylxanthenol peroxide*, m. p. 145—146°, forms colourless crystals.

4-*Benzoxy*-9-*phenylxanthenol* has m. p. 113—115°, and yields a *perchlorate*, m. p. 157—158°. 4-*Benzoxy*-9-*phenylquinoxanthenol chloride hydrochloride*, m. p. 85—90° (decomp.), crystallises in yellow needles. 4-*Benzoxy*-9-*phenylxanthenol chloride*, m. p. 111—112°, is colourless, and gives coloured additive compounds with metal haloids.

VI. 3 : 6-*Dihydroxy*-9-*phenylxanthenol Compounds*.—3 : 6-*Dihydroxy*-

9-*phenylquinoxanthenol chloride*, $O<\substack{C_6H_4(OH)\\C_6H_3Cl(OH)}>CPh$, prepared by the action of hydrogen chloride on a solution of phenyl-3-hydroxyfluorone (Kehrmann and Dengler, A., 1908, i, 1002) in nitrobenzene or alcohol, forms yellow crystals containing 1 mol. of the solvent. The pure salt darkens at 250°, but does not melt at 275°. E. G.

The Benzeins of the Xyloquinols. FRIEDRICH KEHRMANN and TH. E. STILLER (*Ber.*, 1912, **45**, 3346—3349).—By modifying the process of preparation used for quinolbenzein chloride (Kehrmann, A., 1910, i, 408) it has been found possible to condense *o*- and *p*-xyloquinols with benzaldehyde.

o-*Xyloquinolbenzein chloride* (2 : 7-*dihydroxy*-9-*phenyl*-3 : 4 : 5 : 6-*tetramethylxanthonium chloride*), $CPh<\substack{C_6PhMe_2(OH)\\C_6HMe_2(OH)}>O{\cdot}Cl$, can be obtained by the careful action of benzaldehyde on a mixture of *o*-xyloquinol with the corresponding quinone in the presence of a mixture of equal parts of acetic acid and sulphuric acid; the *sulphate*, which separates in reddish-brown needles, when dissolved in water and treated with concentrated hydrochloric acid precipitates the chloride in brown needles or granules. The solution of the chloride when treated with sodium acetate solution deposits the free *base* in deep brownish-violet needles, for which the analysis indicates an equimolecular combination of anhydride and carbinol base (compare Kehrmann, *loc. cit.*); *platinichloride*, reddish-brown, crystalline powder. If an alkaline solution of the free base is carefully acidified with acetic acid and shaken with ether, the latter extracts the colourless carbinol base, which with more acetic acid turns yellow on account of the formation of the oxonium salt.

p-Xyloquinol was obtained by the reduction of *p*-xyloquinone prepared by the oxidation of *p*-xylidine (compare Noelting, Witt, and Forel, A., 1886, 57). The quinol was made to condense with benzaldehyde by a process similar to that which proved successful with the ortho-isomeride; the resultant p-*xyloquinolbenzein chloride* (2 : 7-*dihydroxy*-9-*phenyl*-1 : 4 : 5 : 8-*tetramethylxanthonium chloride*), deep red or blackish-brown crystals, on treatment in solution with sodium acetate precipitates the free *base* in bright yellow crystals; *platinichloride*, yellow crystalline powder. Unlike the analogous bases previously obtained, which dissolve in sodium hydroxide with a fleeting violet-colour, this base gives a yellow solution in sodium hydroxide.

D. F. T.

Ethers and Esters of Phthaleins and Benzeins of Orcinol. FREDRICH KEHRMANN [with E. ACKER, M. GUNTHER, and J. KNOP] (*Ber.*, 1912, **45**, 3505—3514).—By heating with methyl iodide, a solution of α-orcinolphthalein in dilute sodium hydroxide yields *α-orcinolphthalein dimethyl ether*,

$$O<\substack{C_6H_2Me(OMe)\\C_6H_2Me(OMe)}>C<\substack{C_6H_4\\O\text{——}}>CO,$$

m. p. above 365°, a white, crystalline powder, which exhibits a smaller

tendency than α-orcinolphthalein itself to form oxonium salts. By heating with methyl alcohol and concentrated hydrochloric acid, or by keeping for a month with methyl alcohol saturated with hydrogen chloride, it is converted into the dimethylated *methyl ester oxonium chloride*, $OCl{<}{\substack{C_6H_2Me(OMe)\\ C_6H_2Me(OMe)}}{>}C\cdot C_6H_4\cdot CO_2Me$, reddish-brown needles, which is comparatively easily hydrolysed by water and forms with cold dilute sodium hydroxide a dark blue *substance*, probably the base in the form of a quinol or quinhydrone.

β-Orcinolphthalein is much more prone than the α-isomeride to form oxonium salts, even 10% hydrochloric acid producing an orange-red chloride. By boiling with methyl alcoholic hydrogen chloride, β-orcinolphthalein yields the *methyl ester oxonium chloride*,

$$OCl{<}{\substack{C_6H_2Me(OH)\\ C_6H_2Me(OH)}}{>}C\cdot C_6H_4\cdot CO_2Me,$$

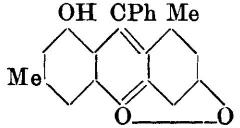
brick-red needles, whilst by treatment with methyl iodide and aqueous sodium hydroxide it yields *β-orcinolphthalein dimethyl ether*,

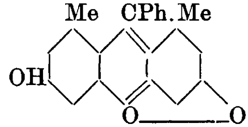
$$O{<}{\substack{C_6H_2Me(OMe)\\ C_6H_2Me(OMe)}}{>}C{<}{\substack{C_6H_4\\ O}}{>}CO,$$

m. p. 247—250°, colourless crystals, which like the dimethylated α-isomeride has little tendency to the formation of stable oxonium salts. The dimethyl ether and methyl alcoholic hydrogen chloride yield the *oxonium chloride*, $OCl{<}{\substack{C_6H_2Me(OMe)\\ C_6H_2Me(OMe)}}{>}C\cdot C_6H_4\cdot CO_2Me$, tufts of yellowish-red needles, which dissolves in cold water without hydrolysis, forming an intensely bitter, orange-yellow solution. The solution is attacked only slowly by sodium acetate or sodium hydrogen carbonate, more rapidly by alkali carbonates or hydroxides, yielding the colourless *carbinol*, from which, immediately after its formation, the orange-yellow salts can be regenerated; the *platinichloride* and *nitrate* are described.

γ-Orcinolphthalein, which is readily freed from its isomerides by means of methyl-alcoholic hydrogen chloride, whereby the pure *chloride* is precipitated in orange-yellow leaflets with a blue shimmer, is not readily etherified or esterified.

Orcinol, benzoic acid, and anhydrous zinc chloride heated at 160—170° for six to seven hours yield a mixture of β-*orcinolbenzein*, (formula I), orange-red crystals, m. p. 260—265°, and γ-*orcinolbenzein* (formula II), orange-red crystals with a bluish shimmer, m. p. about 270°, the former being isolated as the *alcoholate*, colourless prisms. A concentrated alcoholic solution of this alcoholate and concentrated hydrochloric acid yield, after short boiling, the *oxonium chloride*, $C_{21}H_{17}O_3Cl$, red crystals with a violet shimmer. α-Orcinolbenzein has not been isolated.

I. 

II. 

By heating with aqueous sodium hydroxide and methyl iodide, β-orcinolbenzein yields the *dimethyl ether*, $C_{23}H_{22}O_4$, m. p. 192--193°,

colourless crystals, which is probably the carbinol,

$$OMe\cdot C_6H_2Me\langle\begin{matrix}CPh(OH)\\ O\end{matrix}\rangle C_6H_2Me\cdot OMe.$$

C. S.

Fluorescein. HANS VON LIEBIG (*J. pr. Chem.*, 1912, [ii], 86, 472—516).—A continuation of previous work (A., 1912, i, 376).

I. *Fluorescein.*—In this section the author gives further details concerning the various modifications of fluorescein, together with an account of the alkali salts of fluorescein and a discussion of their constitution.

Of the five unimolecular yellow varieties of fluorescein, the β- and δ-forms are undoubtedly single chemical individuals, although this may not be the case with the α- and γ-modifications. β-Fluorescein is readily obtained from ordinary fluorescein by boiling (1) with alcoholic hydrogen chloride, (2) with methyl alcoholic potassium hydroxide, and extracting the solution with ether, after acidification with acetic acid. It separates from ether in crystals of the composition $C_{20}H_{12}O_5,C_4H_{10}O$, and on crystallisation from ethyl acetate yields glistening, red leaflets of the βII form, $C_{20}H_{12}O_5$, which becomes red at 280—290° and has m. p. 347°.

A *monosodium* salt of fluorescein having the composition

$$2C_{20}H_{11}O_5Na,2MeOH,H_2O$$

is produced by dissolving fluorescein in methyl-alcoholic sodium hydroxide. It crystallises in lustrous, reddish-yellow leaflets, and when heated increases enormously in volume, after the manner of Pharoah's serpents; the *monopotassium* salt, $C_{20}H_{11}O_5K,MeOH$, prepared in a similar manner, also forms reddish-yellow leaflets.

An anhydrous and alcohol-free *monosodium* salt, $C_{20}H_{13}O_6Na$, is obtained in brownish-red crystals, having a violet lustre, by heating the disodium salt of fluorescein at 220—240°, and subsequently extracting with cold water or hot alcohol; the aqueous or alcoholic extract contains δ-fluorescein, which forms with alcohol, crystals of the composition $4C_{20}H_{12}O_5,EtOH$.

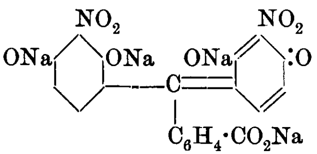
The monosodium salt containing alcohol is at once decomposed by cold water into β-fluorescein and the disodium salt, whilst the alcohol-free salt is insoluble. Further, the anhydrous salt differs from the one containing alcohol in being stable towards cold mineral acids and in yielding a dark brownish-red *sulphate*, $2C_{20}H_{12}O_5,H_2SO_4$, crystallising in leaflets, when boiled with dilute sulphuric acid; the sodium salt containing alcohol yields a *sulphate* of the same composition, but crystallising in yellow leaflets.

A marked difference in the behaviour of the mono- and di-alkali salts of fluorescein has also been observed; the monoalkali salts dissolve in excess of alkali, yielding solutions from which β-fluorescein is liberated by acids, whilst the dialkali salts when subjected to the same treatment give the red variety of fluorescein.

The preparation of a *fluorescein hydrate*, $2C_{20}H_{12}O_5,H_2O$, from the yellow monosodium salt by the action of water is also described; this forms lustrous, light- to violet-red needles, which readily lose their water at the ordinary temperature and then have m. p. 347°.

II. 4:5-*Dinitrofluorescein* (compare Hewitt and Perkins, T., 1900,

77, 1324; Baeyer, A., 1910, i, 249).—The blue tetrapotassium salt of 4 : 5-dinitrofluorescein, which the author considers to be a *p*-quinonoid salt of the annexed formula, is obtained by dissolving dinitrofluorescein in aqueous alcoholic potassium hydroxide; it forms bluish-violet needles of the composition



$C_{20}H_6O_5(NO_2)_2K_4,H_2O,EtOH$,

and yields blue aqueous solutions, which gradually become light red on dilution, owing to hydrolysis and the formation of a red mono- or di-potassium salt. The light red solutions slowly acquire a yellow colour, a change referred by the author to the loss of water and re-formation of the pyrone ring. The rupture of the ring in these yellow solutions may be effected by alkali hydroxides, but not by sodium carbonate or ammonia.

The *hydrate* of 4 : 5-dinitrofluorescein, $C_{20}H_{10}O_5(NO_2)_2,H_2O$, prepared by acidifying a fresh aqueous solution of the tetrapotassium salt, crystallises from alcohol in red prisms, m. p. 211—212°.

The *ammonium* salt, $C_{20}H_8O_5(NO_2)_2,2NH_3,H_2O,MeOH$, crystallises in large dark red prisims, m. p. 234° (decomp.); it is obtained by dissolving the dinitrofluorescein in methyl-alcoholic ammonia.

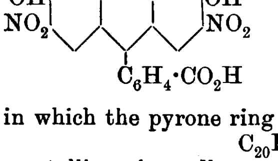
When prepared by the action of potassium hydroxide on 4 : 5-dinitrofluorescein in aqueous solution, the *dipotassium* salt,

$$C_{20}H_8O_5(NO_2)_2K_2,$$

forms a blackish-red mass of a greenish lustre; in alcoholic solution red crystals of the composition $C_{20}H_8O_5(NO_2)_2K_2,H_2O,EtOH$ are obtained.

Addition of strong aqueous ammonia to 4 : 5-dinitrofluorescein gives rise to the ammonium salt of the acridine compound described by Reverdin (A., 1897, i, 226); this crystallises in red needles of the composition $2C_{20}H_{10}O_4(NO_2)_2{:}NH,3NH_3,6H_2O$.

For the purpose of comparison, 2 : 7-*dinitrofluorescein* (annexed formula) has been prepared and its behaviour towards alkalis studied. It is obtained as a light red, crystalline powder by boiling the nitrate with water, and resembles the parent compound in forming only yellow or red salts, in which the pyrone ring remains intact. The *nitrate*,



$$C_{20}H_{10}O_5(NO_2)_2,HNO_3,H_2O,$$

crystallises in yellow needles, and is formed by the action of hot 30—35% nitric acid on fluorescein.

III. *Fluorescein Ethers* (compare A., 1912, i, 376).—In addition to the previously described colourless diethyl ether of m. p. 181°, the action of ethyl sulphate on the disodium salt of fluorescein at 100° gives rise to a new colourless *diethyl ether*, crystallising in needles or prisms, m. p. 234—235°. This resembles in its general behaviour the ether of m. p. 181°, but differs from the latter compound in that it does not form oxonium salts and does not undergo reduction in acid solution. A similar difference is shown by the colourless dimethyl ethers of m. p. 255° and 197° (*loc. cit.*); in both cases the behaviour of the ethers of higher m. p. is in better agreement with the

formula $O<\begin{matrix}C_6H_3(OR)\\C_6H_3(OR)\end{matrix}>C<\begin{matrix}-O-\\C_6H_4\end{matrix}>CO$ than that of the less fusible ethers, to which, however, this formula has already been assigned.

By hydrolysing the coloured dimethyl ether of m. p. 208° with aqueous sodium hydroxide, Fischer and Hepp (A., 1895, i, 291) obtained a coloured monomethyl ether of m. p. 262°, which closely resembles the monomethyl ether (m. p. 265°) isolated by the author (*loc. cit.*). When hydrolysed with alcoholic potassium hydroxide the dimethyl ether of m. p. 208° yields a colourless *monomethyl ether*, which probably has the constitution $O<\begin{matrix}C_6H_3(OMe)\\C_6H_3(OH)\end{matrix}>C<\begin{matrix}-O-\\C_6H_4\end{matrix}>CO$. This separates from ethyl acetate in feathery crystals, m. p. 256—257°, forms a dark red *sodium* salt, $C_{21}H_{11}O_5Na$, and on reduction with zinc and glacial acetic acid yields a *substance*, $C_{21}H_{16}O_5$, crystallising in needles, m. p. 205—206°.

The above-mentioned sodium salt corresponds to a *monomethyl ether* of m. p. 266°, which crystallises in lustrous, yellow needles, and is formed by the action of methyl sulphate on an aqueous solution of the disodium salt of fluorescein.

The monomethyl ether of m. p. 265° (or 262°) forms a *sodium* salt of the composition $C_{42}H_{32}O_{14}Na_3$, whilst a coloured *monomethyl ether*, obtained in yellowish-white crystals, m. p. 272°, by methylating fluorescein with methyl iodide and potassium hydroxide in alcoholic solution, yields a blackish-red *sodium* salt having the composition $C_{21}H_{12}O_5Na_2,H_2O$. Since the monomethyl ethers of m. p. 262°, 265°, and 272° do not yield monosodium salts, the conclusion is drawn that these compounds cannot be represented by the formula $O<\begin{matrix}C_6H_4(OMe)\\-C_6H_3(:O)\end{matrix}>C\cdot C_6H_4\cdot CO_2H$. When warmed with alcohol and hydrochloric acid and the resulting *chloride* heated at 250°, the dimethyl ether of m. p. 208° yields a small amount of the dimethyl ether of m. p. 197°. The latter compound was also obtained in an attempt to prepare a trimethyl ether of fluorescein by the oxidation of the corresponding ether of fluorescin with lead dioxide in glacial acetic acid solution.

Fluorescin trimethyl ether, $C_{23}H_{20}O_5$, prepared by warming fluorescin with strong aqueous potassium hydroxide and methyl sulphate, crystallises in small prisms or leaflets, m. p. 136°. It is accompanied by a *fluorescin monomethyl ether*, $C_{21}H_{16}O_3$, which separates with benzene (1 mol.) in crystals of m. p. 120—125°; in one instance a *substance* was obtained, which crystallised in leaflets, m. p. 204°, and resembled in its behaviour the reduction product of the dimethyl ether of m. p. 197°, mentioned below.

In addition to the dimethyl ethers of m. p. 197°, 208° and 255°, and the monomethyl ether of m. p. 266°, the action of methyl sulphate on an aqueous solution of the disodium salt of fluorescein yields the following substances: (1) a quadrimolecular *monomethyl ether*, $3C_{20}H_{12}O_5,C_{21}H_{14}O_5$, which separates from a mixture of benzene and alcohol in red or brownish-yellow crystals, which become red at 260°, or in crystals containing 4EtOH; all three modifications have m. p. 330—333°. (2) A *monomethyl* ester, $O<\begin{matrix}C_6H_3(OH)\\-C_6H_3(:O)\end{matrix}>C\cdot C_6H_4\cdot CO_2Me$, which forms

dark red crystals of a violet lustre, m. p. 282—283°. (3) A *hydrate* of the above ester, $C_{21}H_{14}O_3,H_2O$, crystallising in yellow needles, which become red and melt at 280°.

The monomethyl ester, m. p. 282—283°, is also formed by directly esterifying fluorescein with alcohol and hydrogen chloride, whilst esterification with alcohol and sulphuric acid gives rise to a monomethyl ester of m. p. 252° (compare Feuerstein and Wallach, A., 1901, i, 723).

Methylation of fluorescein by means of methyl iodide and alcoholic potassium hydroxide yields the monomethyl ethers of m. p. 256—257°, 265° and 272°, the dimethyl ether, m. p. 208°, and the quadrimolecular monomethyl ether of m. p. 330—333°.

The *hydrochloride* of the monomethyl ester of m. p. 282—283°, $C_{21}H_{14}O_5,HCl$, forms orange-yellow needles (decomp. 260°).

The monomethyl ether of m. p. 272° yields a *hydrochloride*,

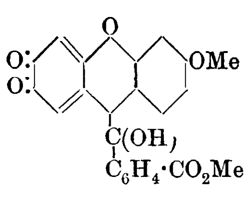
$$3C_{21}H_{14}O_5,2HCl,4H_2O,$$

crystallising in brownish-yellow needles, m. p. 250°.

The products obtained by reducing the ethers of fluorescein, containing a free carboxyl group, with zinc and glacial acetic acid form crystalline compounds with benzene, which is firmly retained until about 110°, whilst those obtained from ethers in which the carboxyl group has been esterified or undergone lactone formation readily lose their benzene below 100°.

The *substance*, $C_{21}H_{16}O_5$, obtained by reducing the monomethyl ether of m. p. 257°, forms needles, m. p. 205—206°; that from the monomethyl ether of m. p. 266° separates in crystals, which become yellow and lose their benzene at 120—125°. The monomethyl ether of m. p. 265° yields a *substance*, $C_{21}H_{16}O_5,2C_6H_6$, which has m. p. 132—133° or 169—170° accordingly as it is dried at 100° or 140°. The *substance* from the monomethyl ether of m. p. 272° has m. p. 173—174°, that from the monomethyl ester of m. p. 282° separates from alcohol in small needles of the composition $C_{21}H_{16}O_5,EtOH$, m. p. 190—191°, and from benzene in crystals which melt at 83—84°, solidifies at a higher temperature, and then melts at 190—191°. The quadrimolecular monomethyl ether on reduction yields a *substance*, $3C_{20}H_{14}O_5,C_{21}H_{16}O_5,H_2O,8C_6H_6$, which loses benzene below 100°, sinters at 220°, and melts at 237—238°.

The *substance*, $C_{22}H_{18}O_5$, obtained from the dimethyl ether of m. p. 197°, forms clusters of needles, m. p. 204°; that from the dimethyl ether of m. p. 208°, stout crystals, m. p. 165°. When oxidised with lead dioxide or hydrogen peroxide in acetic acid solution the last-mentioned reduction product yields a dark red *substance* (decomp. about 200°), which forms dark brown alkali salts, and is probably produced by the oxidation of one of the resorcinol residues, as shown in the annexed formula.

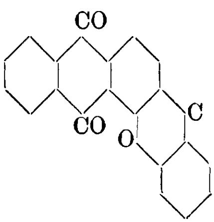


The author suggests that the above results are best explained on the assumption that the ordinary red fluorescein is a polymeride, consisting probably of various di-, ter-, and quadri-molecular combinations as in the case

of resorcinolbenzein, and that the methyl ether of m. p. 330—333°, containing one methyl group to four fluorescein molecules, represents the initial stage in the methylation of the quadrimolecular form, the further methylation resulting in a more or less complete degradation into simple molecules. F. B.

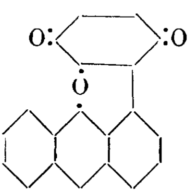
Preparation of Xanthones of the Anthraquinone Series. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 251696).—Xanthones of the anthraquinone series are readily prepared by the action of condensing agents on phenyl, naphthyl, or anthraquinonyl ethers of 1-hydroxyanthraquinone-2-carboxylic acids or their substituted derivatives.

1-*Phenoxyanthraquinone*-2-*carboxylic acid*, tablets, m. p. 272°, is prepared by the fusion of 1-chloroanthraquinone-2-carboxylic acid (10 parts) with phenol (60 parts) and potassium hydroxide (25 parts) during four hours at 150°. When this product, suspended in trichlorobenzene, is treated with phosphorus pentachloride and the temperature slowly raised, it furnishes the *xanthone* (annexed formula), which separates in yellow, glistening tablets.



1-*Naphthoxyanthraquinone*-2-*carboxylic acid*, yellow tablets, m. p. 262°, is prepared in a similar manner from β-naphthol at 130—140° during two hours; the corresponding *xanthone* is obtained as greenish-yellow leaflets, m. p. above 300°; it dissolves in alkaline hyposulphite with an intense blue, and in concentrated sulphuric acid with a brownish-red, coloration. F. M. G. M.

Preparation of Condensation Products in the Anthracene Series. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 251020).—The *compound*, $C_{20}H_{10}O_3$ (annexed formula), a black powder, is obtained when anthranol and p-benzoquinone are boiled together in nitrobenzene solution; it dissolves in concentrated sulphuric acid with a violet-red coloration.



The tinctorial properties of other analogous compounds obtained from p-benzoquinone with substituted anthranols are tabulated in the original. F. M. G. M.

Preparation of "7:7′-Diaminothioindigo." FARBWERKE VORM. MEISTER, LUCIUS & BRUNING (D.R.-P. 252771).—When "7:7′-dinitrothioindigo" (or its substituted derivatives) is reduced with sodium sulphide or dextrose it yields the corresponding "7:7′-diaminothioindigo," a black powder, whilst "5:5′-dichloro-7:7′-dinitrothioindigo" furnishes "5:5′-*dichloro*-7:7′-*diaminothioindigo*," also a black powder. F. M. G. M.

Carpiline, a New Alkaloid from Jaborandi. ÉMILE LÉGER and FERDINAND ROQUES (*Compt. rend.*, 1912, **155**, 1088—1091*).—An

* and *J. Pharm. Chim.*, 1913, [vii], **7**, 5—13.

extract of *Pilcarpus microphyllus*, after the removal of the greater portion of the bases as their hydrochlorides, yields, on precipitating from the mother liquor, the alkaloid *pilocarpiline*, $C_{16}H_{18}O_3N_2$, m. p. 184—185°, α_D +24°. It is soluble in chloroform, benzene, and boiling water, and crystallises in colourless prisms. It is a feeble base, its salts with organic acids being dissociated by alcohol, whilst those with mineral acids are stable, all having a bitter taste. It gives a *hydrochloride*, $C_{16}H_{18}O_3N_2,HCl$, colourless prisms; a *sulphate*; a *platinichloride*, $(C_{16}H_{18}O_3N_2)_2,H_2PtCl_6,5H_2O$, crystalline plates, and a *methiodide*, $C_{16}H_{18}O_3N_2,MeI$, small, pale yellow prisms. The base is saturated, since its salts do not reduce potassium permanganate in the cold.

Carpiline contains a lactone group, and thus dissolves in alkali hydroxide solutions, giving compounds of the type *potassium carpilinate*, $C_{12}H_{19}O_4N_2K$, long needles, very soluble in water. The presence of an hydroxyl group is shown by the formation of an amorphous benzoyl derivative which yields *benzoylcarpiline platinichloride*,

$$[C_{16}H_{17}O_3N_2Bz]_2,H_2PtCl_6.$$

The alkaloid on oxidation with nitric acid yields benzoic acid, and on heating with water at 140° in a sealed tube, it is decomposed, giving benzaldehyde and two amorphous bases, but no hydrogen cyanide. The alkaloid thus contains the groups CHPh:, –OH, $\begin{matrix}-CO\\ \mid\\ -O\end{matrix}$, and the group $C_8H_{11}N_2$, the constitution of which has yet to be elucidated. Carpiline is but slightly toxic, and has not the same effect as pilocarpine on the secretions. W. G.

Active Principles of Catha Edulis. RALPH STOCKMAN (*Pharm. J.*, 1912, 89, 676—678).—The leaves and twigs of this plant have long been used in Abyssinia, Somaliland, and Arabia as a stimulant-narcotic. They are now shown to contain at least three alkaloids, cathine, cathidine, and cathinine, to which the characteristic physiological action of the plant is due. By mixing a dry aqueous extract of the plant with slaked lime and extracting with dry alcohol, 0·65 and 0·75% of amorphous alkaloids are obtained from the leaves and twigs respectively. This amorphous mixture appears to consist largely of cathine and its alteration products, but no crystalline alkaloid could be isolated from it. The finely-powdered leaves were extracted completely with cold water or very dilute sulphuric or lactic acid, and the liquor made alkaline and extracted with chloroform, which removed cathine along with much impurity, from which the alkaloid was eventually separated as the sulphate. The ground, partly extracted leaves were then mixed with aqueous sodium carbonate and extracted with ether, which removed cathidine and cathinine; these were separated by taking advantage of the fact that the former is precipitated by sodium carbonate solution from aqueous solutions of its hydrochloride, whilst cathinine remains in solution along with some cathidine.

Cathine sulphate crystallises in colourless needles, is neutral in reaction, has a bitter taste, is precipitated by iodine solution, Mayer's reagent or picric acid, but not by tannin or platinic chloride. *Cathine* crystallises from chloroform and appears to be unstable in presence of

alkalis. Its physiological action on the nervous and muscular systems of the frog is similar to those exerted by morphine and caffeine; in large doses it paralyses the terminations of the motor nerves.

Cathidine is colourless and amorphous and has a bitter taste; it gives precipitates with the usual alkaloidal reagents. Cathidine is a muscle poison, and a slight stimulant to the nervous system.

Cathinine sulphate crystallises from water in rosettes of needles, has a bitter taste, and is precipitated by the usual alkaloidal reagents. The free base has only been obtained as a gummy or semi-crystalline mass. Cathinine is less depressant than cathine in its action on the brain, but has a greater stimulant effect on the spinal cord; it paralyses the terminations of the motor nerves.

All three alkaloids in mammals and man act chiefly on the cerebrum and spinal cord, causing stimulation or much excitement according to the dose; cathine produces drowsiness at first. The leaves also contain a fermentable sugar, tannin, caoutchouc, wax, and volatile oil.

T. A. H.

Preparation of Esters of Hydroquinine. VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 251936. Compare A., 1912, i, 1013). —It is found that the hydroquinine esters described previously can be most easily prepared in the presence of either finely divided metals of the platinum group or their colloidal solutions.

Hydroquinine ethyl carbonate (*loc. cit.*) is obtained when quinine ethyl carbonate (10 parts), 20% sulphuric acid (14 parts), and 80 parts of water are shaken with 0·1 part of colloidal palladium in 10 parts of water in an atmosphere of hydrogen under pressure until no further absorption of hydrogen is observed; ammonium hydroxide is added, and the product extracted with ether.

Acetylhydroquinine, large, colourless crystals, m. p. 100°, is prepared in a similar way from acetylquinine, and *p*-aminobenzoylhydroquinine (*loc. cit.*) is also described.

F. M. G. M.

Preparation of Esters of Hydrogenised Cinchona Alkaloids. VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 253357. Compare A., 1912, i, 1013, and preceding abstract).—The following esters are of therapeutic value.

Hydrocinchonine ethyl carbonate, colourless, tasteless needles, m. p. 134°, is obtained when cinchonine ethyl carbonate (30 parts) dissolved in 160 parts of alcohol is shaken with 1 part of colloidal palladium in 60 parts of water until the absorption of hydrogen ceases.

Benzoylhydrocupreine, colourless crystals, m. p. 172°, is prepared from hydrocupreine.

Dibenzoylhydrocupreine, needles, has m. p. 147°, whilst *ethylhydrocupreine ethyl carbonate* is obtained from ethylhydrocupreine and ethyl chloroformate in benzene solution; it is conveniently isolated in the form of its *salicylate*, colourless crystals, m. p. 138—142°.

F. M. G. M.

Physostigmine [Eserine]. FRANZ EISSLER (*Biochem. Zeitsch.*, 1912, **46**, 502).—Eserine gives with diazotised sulphanilic acid in alkaline solution a red colour, which indicates the presence of a pyrrole ring.

This result is in accordance with the recent investigations of Salway (T., 1912, **101**, 978). S. B. S.

d-**Lupanine.** AUGUST BECKEL (*Arch. Pharm.*, 1912, **250**, 691—710. Compare A., 1911, i, 743).—In continuation of previous work, the oxidation of *d*-lupanine by various agents has been investigated, and the products obtained are described.

Chromic acid in large excess oxidises lupanine to a substance containing two additional oxygen atoms, but this was produced in too small quantity to be isolated. Hydrogen peroxide gives rise to two products: the first of these gives an *aurichloride*, m. p. 214°, crystallising in needles, and the other an *aurichloride*, m. p. 188—189°, and *platinichloride*, m. p. 222—227°, crystallising in rosettes of needles. Analyses of these double salts indicate that both oxidation products have the formula $C_{15}H_{24}O_2N_2$. Potassium permanganate in presence of sodium carbonate oxidises lupanine to a *product*, $C_{15}H_{24}O_3N_2$, which was isolated as the *aurichloride*, m. p. 188—189°, and converted into the *platinichloride*, $B_2,H_2PtCl_6,2H_2O$, m. p. 219—221° (decomp.), crystallising in needles.

In the action of bromine on lupanine no fission occurs, as has been suggested by previous workers (Callsen, A., 1900, i, 186; Soldaini, A., 1905, i, 371). A perbromide of the alkaloid is first formed, and this on warming with alcohol may give rise to several different products, depending on the conditions observed. In the present series of experiments, three products melting at 228—236°, 190—210°, and 186—188° respectively were obtained. The first of these consists essentially of *ethoxylupanine dihydrobromide*, $C_{15}H_{23}ON_2{\cdot}OEt,2HBr$, m. p. 227—228°, $[\alpha]_D^{17-23}$ $-129{\cdot}4°$, which crystallises in colourless, slender needles from boiling alcohol, and is apparently the "substance, $C_8H_{15}ON,HBr$," described by previous workers. The specific rotation falls, slowly in the cold, more rapidly on warming, when this substance is dissolved in hydrobromic acid, but returns to its normal value when the solution is mixed with alcohol and evaporated to dryness. In presence of excess of alkali the alkaloid is dextrorotatory. The *dihydriodide*, m. p. 221—222°, forms colourless needles; the *dithiocyanate*, $C_{15}H_{23}ON_2{\cdot}OEt,2HSCN,H_2O$, m. p. 172—174°, crystallises from water in colourless needles, and becomes anhydrous at 100°. The *aurichloride*, $(C_{15}H_{23}ON_2{\cdot}OEt)_2,4HCl,3AuCl_3$, m. p. 145—150°, crystallises in small, yellow leaflets, and on warming in dilute hydrochloric acid gives *hydroxylupanine aurichloride*,

$$(C_{15}H_{23}ON_2{\cdot}OH)_2,4HCl,3AuCl_3,$$

which sinters at 122—123°, and crystallises badly in leaflets. Ethoxylupanine does not readily reduce permanganate. Hydriodic acid converts it into a substance which was isolated as the methiodide; the latter resembles lupanine methiodide in rotation, crystalline form, and melting point, but on treatment with silver chloride and gold chloride yields an *aurichloride*, $(C_{15}H_{24}ON_2,MeCl,AuCl_3)_2,HAuCl_4$, m. p. 210°, crystallising in leaflets, whilst the aurichloride obtained in like manner from lupanine methiodide has the composition

$$C_{15}H_{24}ON_2,MeCl,AuCl_3,$$

and melts at 200—205°. The *platinichloride*, m. p. 224—226°,

crystallises in slender, brown needles, and is also abnormal in composition.

The second oxidation product, m. p. 190—210°, contained some ethoxylupanine dihydrobromide, and after the removal of this formed a crystalline mass, m. p. 192—194°, which was probably a mixture of hydrobromides.

The third product, m. p. 186—188°, on recrystallisation from boiling alcohol gave what seems to be a mixture of ethoxylupanine dihydrobromide with either hydroxylupanine hydrobromide or lupanine dihydrobromide, whilst from the mother liquor d-*lupanine dihydrobromide*, $B,2HBr,H_2O$, m. p. 188—189°, $[\alpha]_D + 45·9°$, was isolated.

T. A. H.

Morphineglucoside. CARL MANNICH (*Annalen*, 1912, **394**, 223—228).—Morphine in $N/2$-sodium hydroxide is shaken for six hours with ethereal β-acetylbromoglucose. The ethereal solution is shaken with 1% hydrochloric acid. The acid extract, by treatment with ammonia, yields *morphinetetra-acetylglucoside*,

$$C_{17}H_{18}O_3N·C_6H_7O_5Ac_4,H_2O,$$

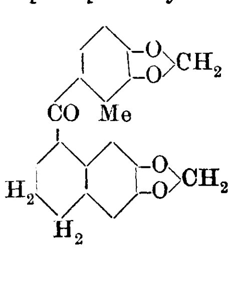
m. p. 154—156°, colourless needles (*hydrochloride*, m. p. about 220° [decomp.]). By hydrolysis with $N/2$-alcoholic potassium hydroxide, the substance yields *morphineglucoside*, $C_{17}H_{18}O_3N·C_6H_{11}O_5,H_2O$, m. p. 183—193°, fine needles. The glucoside, which is more conveniently obtained by the interaction of morphine, $N/2$-sodium hydroxide, and acetylbromoglucose in aqueous acetone and hydrolysis of the product, does not reduce boiling Fehling's solution, and yields dextrose and morphine by hydrolysis with $N/2$-hydrochloric acid on the water-bath.

C. S.

Alkaloids of Pareira Root. MAX SCHOLTZ (*Arch. Pharm.*, 1912, **250**, 684—691. Compare A., 1899, i, 92; 1907, i, 79; 1911, i, 913, and Faltis, A., 1912, i, 796).—A reply to Faltis (*loc. cit.*) criticising his results and suggesting, as the result of new analyses, that the bebeerines are better represented by the formula $C_{17}H_{19}O_3N$ than by those previously suggested by the author and by Faltis.

T. A. H.

Protopine and Cryptopine. PETER W. DANCKWORTT (*Arch Pharm.*, 1912, **250**, 590—646).—A résumé of previous papers relating to the distribution of protopine in the natural orders, *Papaveraceae* and *Fumariaceae*, and its characters and chemistry is first given. It is then shown by analogy with other papaveraceous alkaloids that protopine probably contains an *iso*quinoline group, and evidence is brought forward for the view that it contains two methylenedioxy-groups and a carbonyl group, and that the nitrogen atom has a $·CH_3$ group attached to it. On these and other grounds the annexed formula is assigned provisionally to the alkaloid.



Dicentra (*Diclytra*) *spectabilis* tubers yielded 0·65% of crude alkaloid, chiefly protopine. The latter has the formula $C_{20}H_{19}O_5N$, and crystallises from a mixture of chloroform and alcohol

in colourless prisms or from ether in nodular masses: both forms melt at 207°, but the first gives with sulphuric acid a yellow coloration changing to blue, reddish-violet, and green, and with Fröhde's reagent a yellowish-olive colour changing to dirty violet, green, blue, and finally green; the second form, on the contrary, with sulphuric acid gives a deep yellow, passing into green, dirty reddish-brown, and finally green, whilst with Fröhde's reagent it yields a yellowish-olive solution which becomes violet and finally green.

Protopine contains no hydroxyl groups or methoxyl groups, but gives Gaebel's test for dioxymethylene (A., 1910, i, 501), and the presence of the latter is confirmed by the fact that protopine, when heated under pressure with dilute sulphuric acid, yields a product giving the colour reactions of a catechol derivative. No direct evidence of the presence of a carbonyl group could be obtained. The occurrence of a $\colon NCH_3$ group was proved by Herzig and Meyer's method. The alkaloid is not reduced by aqueous colloidal platinum, but sodium amalgam in dilute acid converts it into *hydroprotopine*, $C_{20}H_{21}O_5N,\frac{1}{2}EtOH$, m. p. 120° (approx.) or 151—152° (dry), which crystallises from a mixture of ether and alcohol, becomes anhydrous at 100°, is easily soluble in chloroform or ethyl acetate, sparingly in alcohol and slightly in ether; the *hydrochloride* crystallises from alcohol in needles and from water in plates. On treatment with benzoyl chloride hydroprotopine is apparently first benzoylated and then partly converted by loss of H_2O into a *quaternary base*, $C_{20}H_{19}O_4N$, which has not been obtained free from the benzoylated product; it yields a *hydrochloride*, $C_{20}H_{19}O_4N,HCl,5H_2O$, m. p. 275° (approx. decomp.), which is crystalline and from which an *aurichloride*, $B,HAuCl_4$, crystallising in reddish-brown needles is obtainable; this hydrochloride on heating with sodium hydroxide in alcohol is converted into an isomeric *tertiary anhydro-base*, $C_{20}H_{19}O_4N$, m. p. 145°, crystallising in long needles. Both the quaternary and the tertiary anhydro-bases can be prepared in other ways from protopine and hydroprotopine; it is believed that this series of changes from protopine to the tertiary anhydro-base takes place in the following way:

$$\cdot NMe\cdot\dot{C}H\cdot CO\cdot \longrightarrow \cdot NMe\cdot\dot{C}H\cdot CH(OH)\cdot \longrightarrow \cdot(HCl)NMe\cdot CH\cdot CH(OBz)\cdot \longrightarrow$$
$$\cdot ClNMe\colon C\cdot CH_2\cdot \rightleftarrows \cdot(HO)NMe\colon CH\cdot CH_2\cdot \rightleftarrows \cdot NMe\cdot C\colon CH\cdot,$$

the compound represented by the fourth formula being the "hydrochloride" of the quaternary base, and that by the sixth formula being the tertiary anhydro-base.

Methyl iodide converts protopine into the methiodide, whilst methyl sulphate transforms it into *methylprotopine methosulphate*, $C_{20}H_{19}O_5NMe\cdot SO_4Me$, which crystallises from dilute alcohol: either of these substances on heating with alkalis yields *protopinemethine*, $C_{20}H_{18}O_5NMe$, m. p. 136—137°, crystallising in pearly leaflets, which in turn furnishes a crystalline *methiodide*; this on heating with alkali hydroxides in methyl alcohol yields trimethylamine and an amorphous product.

The tertiary anhydro-base also yields a crystalline *methiodide*, m. p. 230°, and a crystalline *methine* base, m. p. 112°, which fluoresces

in ether solutions and gives a bromine additive product. The *methine-methiodide*, rosettes of needles, is not decomposed on heating with alkalis in methyl alcohol, but on treating the methine base with methyl sulphate and heating the product with sodium hydroxide in methyl alcohol an amine is evolved and a resinous vinyl derivative is formed.

Oxidation experiments with protopine and its derivatives did not afford useful results, except in the case of protopinemethine, which on treatment with potassium permanganate in acetone solution yielded a basic substance and hydrastic acid (4 : 5-methylenedioxy-phthalic acid).

Cryptopine resembles protopine in its solubilities, and in physiological action, and like it contains no hydroxyl group and gives no oxime. Cryptopine contains a methylenedioxy-group, and two methoxyl groups. On reduction with sodium amalgam in dilute sulphuric acid it yields *hydrocryptopine*, m. p. 182—183°, which crystallises from ether and on treatment with benzoyl chloride gives the *hydrochloride* of a *quaternary base*. In view of this it seems likely that cryptopine differs from protopine only in containing two methoxyl groups in place of one methylenedioxy-group, but it is not clear which of the two methylenedioxy-groups of protopine is thus replaced (compare Pictet and Kramers, A., 1910, i, 502, and Brown and Perkin, P., 1891, **7**, 161). T. A. H.

Preparation of Acyl Derivatives of Theobromine KNOLL & Co. (D.R.-P. 252641).—*Acetyltheobromine*, colourless, odourless needles with a bitter taste and m. p. 165°, is obtained by the action of acetyl chloride on a solution of sodium theobromine in chloroform or xylene.

Benzoyltheobromine forms colourless, odourless, tasteless needles, m. p. 206° (about), and is most satisfactorily prepared from silver theobromine and benzoyl chloride in toluene solution.

These compounds are of therapeutic value, and analysis indicates that they are monoacyl derivatives. F. M. G. M.

The Chemical Constitution of Sparteine. CHARLES MOUREU and AMAND VALEUR (*Ann. Chim. Phys.*, 1912, [viii], **27**, 245—391).—A résumé of work already published (compare A., 1903, i, 717 ; 1904, i, 187 ; 1905, i, 608, 609, 659, 716 ; 1908, i, 43, 44, 103, 206, 563 ; 1911, i, 319, 562 ; 1912, i, 210, 296). W. G.

Some New Sparteine Salts. LOUIS CORRIEZ (*Chem. Zentr.*, 1912, ii, 1566 ; from *Bull. Sci. Pharmacol.*, **19**, 468—480).—The following salts are described : *Basic hydrobromide*, B,HBr [$B = C_{15}H_{26}N_2$], from the basic sulphate and barium bromide, prismatic crystals, m. p. 236°, $[\alpha]_D$ −16°6′ ; *di-iodide*, $B,2HI + H_2O$, m. p. (anhydrous) 225°, $[\alpha]_D$ −16°2′ ; *normal chlorate*, $B,2HClO_3$, colourless cubes, explodes at 147°, $[\alpha]_D$ −23°12′ ; *basic chlorate*, $B,HClO_3$, colourless prisms, explodes at 200—205°, $[\alpha]_D$ −16°3′ ; *normal perchlorate*,

$$B,2HClO_4 + 2H_2O,$$

prisms, m. p. 78°, anhydrous, 265°, explodes over 300°, $[\alpha]_D$ −17°30′ ;

basic perchlorate, $B,HClO_4$, m. p. 171°, $[\alpha]_D$ in methyl alcohol $-17°6'$, in acetone $-16°3'$; *dichromate*, $B,H_2Cr_2O_7$, orange-yellow prisms, decomposes at 128—129°; *normal salicylate*, $B,2C_7H_6O_3 + H_2O$, pale pink prisms, m. p. 78°, $[\alpha]_D$ $-8°42'$. J. C. W.

The Constitution of Sparteine Periodide and Sparteine Perbromide. LOUIS CORRIEZ (*Chem. Zentr.*, 1912, ii, 1826; from *Bull. Sci. Pharmacol.*, 1912, **19**, 533—540).—The formation of sparteine periodide by the action of 12% hydrogen peroxide on sparteine di-iodide may be expressed thus: $2C_{15}H_{26}N_2.2HI + O = 2C_{15}H_{26}N_2,HI + I_2 + H_2O$; $C_{15}H_{26}N_2,HI + I_2 = C_{15}H_{26}N_2,HI,I_2$. As it would follow from the latter equation, the periodide also results when sparteine mono- or di-iodide is treated with iodine. *Sparteine perbromide*,

$$C_{15}H_{26}N_2,2HBr,Br_2 + H_2O,$$

by the action of bromine on sparteine, both dissolved in fuming hydrobromic acid, forms yellow crystals, m. p. 193°. The formation of this perbromide will show the presence of sparteine in a dilution of 1 : 10,000. J. C. W.

New α-Methylsparteinium Salts. LOUIS CORRIEZ (*Chem. Zentr.*, 1912, ii, 1826; from *Bull. Sci. Pharmacol.*, 1912, **19**, 527—532).—Starting from α-methylsparteinium hydroxide, which is obtained in aqueous solution by the action of moist silver oxide on Moureu's α-sparteine methiodide (A., 1905, i, 608), the following salts have been prepared: *Hydrochloride* of *α-sparteine methochloride*,

$$C_{15}H_{26}N_2MeCl,HCl,3H_2O,$$

transparent, hygroscopic crystals, m. p. 194°, $[\alpha]_D$ $-23°9'$; *hydrobromide* of *α-sparteine methobromide*, $C_{15}H_{26}N_2MeBr,HBr,2H_2O$, m. p. 216°, $[\alpha]_D$ $-19°2'$; *α-methylsparteinium dichromate*,

$$C_{15}H_{26}N_2Me{\cdot}Cr_2O_7H,H_2O,$$

orange-yellow needles, decomposes at 120°; *α-methylsparteinium perchlorate*, $C_{15}H_{26}N_2Me{\cdot}ClO_4$, transparent needles, decomposes at 230°; *α-methylsparteinium picrate*, $C_{15}H_{26}N_2Me{\cdot}C_6H_2O_7N_3$, yellow needles, m. p. 218°. J. C. W.

Pyrrolidonecarboxylic Acid and Polypeptides Derived from It. EMIL ABDERHALDEN and ERICH WURM (*Zeitsch. physiol. Chem.*, 1912, **82**, 160—166).—Pyrrolidonecarboxyl chloride interacts with cholesterol in chloroform solution in the absence of moisture, forming *cholesteryl pyrrolidonecarboxylate*, $C_{26}H_{43}{\cdot}O{\cdot}CO{\cdot}CH{<}\begin{matrix}CH_2{\cdot}CH_2\\ NH{-}CO\end{matrix}$. This crystallises in colourless, matted needles, which sinter at 199—203°, m. p. 205°.

dl-*Pyrrolidonecarboxyl*-d-*alanine ester* crystallises in rosettes of needles, m. p. 125·5° (corr.), $[\alpha]_D^{20}$ $-46·42°$.

dl-*Pyrrolidonecarboxyl*-dl-*leucine ester* separates in prisms, m. p. 115—117° (corr.). E. F. A.

Chalkones and Hydrochalkones. III. GUIDO BARGELLINI and E. MARTEGIANI (*Gazzetta*, 1912, **42**, ii, 427—432. Compare this vol., i, 59).—The authors have applied the mode of reduction previously

described to compounds analogous to chalkones, but containing pyrrole and furan rings, instead of benzene rings. In all cases only two atoms of hydrogen were added, and the rings were not attacked; the experiments were conducted in alcoholic solution (compare Willstätter and Hatt, A., 1912, i, 545).

2-Cinnamoylpyrrole (compare Ciamician and Dennstedt, A., 1885, 378) is conveniently prepared by keeping a mixture of 2-acetylpyrrole and benzaldehyde in the presence of potassium hydroxide in aqueous-alcoholic solution. The *dihydro*-derivative, $C_{13}H_{13}ON$, forms colourless needles, m. p. 70—71°. It dissolves in concentrated sulphuric acid, giving a colourless solution.

2-mp-*Methylenedioxycinnamoylpyrrole*, $C_{14}H_{11}O_3N$, is obtained by keeping 2-acetylpyrrole and piperonaldehyde in the presence of potassium hydroxide in aqueous-alcoholic solution. It dissolves in concentrated sulphuric acid, giving an intense red coloration. On reduction it yields a *dihydro*-derivative, $C_{14}H_{13}O_3N$, which forms colourless needles, m. p. 84—85°, and dissolves in concentrated sulphuric acid, giving a colourless solution.

Furfurylidenepaenol (compare Courant and von Kostanecki, A., 1907, i, 75) gives a *dihydro*-derivative, $C_{14}H_{14}O_4$, which forms colourless needles, m. p. 72—73°.

2-*Furfurylideneacetylpyrrole*, $C_{11}H_9O_2N$, crystallises in yellow needles, m. p. 130—131°; it dissolves in concentrated sulphuric acid, giving an intense red coloration. Its *dihydro*-derivative, $C_{11}H_{11}O_2N$, crystallises in colourless needles, m. p. 70—71°. R. V. S.

Preparation of 2-Indolecarboxylic Acid and 2:3-Dihydroxyquinoline from Oxal-*o*-toluidic Acid. Indole Syntheses. II.

WALTER MADELUNG (*Ber.*, 1912, **45**, 3521—3527. Compare A., 1912, i, 499).—The synthesis of indole compounds recently described (*loc. cit.*) fails with the application of formyl derivatives, and so the direct synthesis of indole itself in this way fails. By the use of oxal-*o*-toluidic acid, however, the action proceeds in the normal manner with the formation of the expected indolecarboxylic acid, which by careful distillation can be converted into indole (Weissgerber, A., 1911, i, 155).

Oxal-*o*-toluidic acid is conveniently obtained by heating a mixture of equal quantities of *o*-toluidine and anhydrous oxalic acid for an hour at a temperature not exceeding 130°; the concentrated solution of the toluidine salt of the acid on treatment with the necessary quantity of dilute sulphuric acid gives a thick deposit of the free acid. On evaporating the solvent from an alcoholic solution of sodium ethoxide and potassium oxal-*o*-toluidate and raising the temperature of the resultant intimate mixture to 340—350°, reaction takes place with the formation of two products, one of which can be easily dissolved out with benzene. This substance by m. p. 199—202°, and by its yielding indole on heating was evidently indolecarboxylic acid.

The sparingly soluble constituent, prisms, m. p. 257—258°, gives a *diacetyl* derivative, needles, m. p. 211°, and produces with ferric chloride a bluish-green coloration; it is inappreciably attacked by phosphorus pentachloride even at 140°, the only result being a minute

quantity of a *substance*, m. p. 70—90°. It is highly probable that this second constituent of the mixture produced in the original synthesis is 2 : 3-*dihydroxyquinoline*. This decision is at variance with the published results of Friedländer and Weinberg (A., 1883, 351), who ascribe a considerably higher m. p. and no ferric chloride coloration. A repetition of Friedländer and Weinberg's method of preparation, namely, fusion of 3-chloro-2-hydroxyquinoline with potassium hydroxide, showed that under certain conditions the dihydroxyquinoline, m. p. above 300°, of these investigators becomes a subsidiary product, whilst a by-product mentioned by them becomes the main resultant substance, identical with the author's dihydroxyquinoline. The correctness of this view, that the earlier description of dihydroxyquinoline is a mistake, is confirmed by the action of phosphorus pentachloride, which converts the substance (m. p. above 300°) into a compound which sinters at 102°, decomposes at a higher temperature, and is quite distinct from 2 : 3-dichloroquinoline. D. F. T.

Preparation of Derivatives of 2-Phenylquinoline-4-carboxylic Acid and its Homologues. CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHERING (D.R.-P. 252643).—2-Phenylquinoline-4-carboxylic acid and its homologues, although of therapeutic value, have the disadvantage of a bitter taste; this drawback is absent in the amides which have now been prepared.

The *chloride* of 2-phenylquinoline-4-carboxylic acid is a yellow powder, m. p. 230°, and the *amide*, glistening, colourless, hair-like needles, m. p. 195°; whilst the *amide* of 2-phenyl-6-methylquinoline-4-carboxylic acid forms glistening needles, m. p. 257°.

F. M. G. M.

Salts of Acridine, Pyridine, and Quinoline. LEE H. CONE (*J. Amer. Chem. Soc.*, 1912, **34**, 1695—1706).—The object of this work was to study the analogy between the derivatives of the triphenylcarbinols and xanthenols, on the one hand, and those of the acridols on the other, and to show that this analogy extends to the salts of pyridine and quinoline. It has been found that the haloids of phenylacridol, pyridine, and quinoline react with silver to form silver haloids and unsaturated compounds, similar to triphenylmethyl, which readily absorb oxygen. The ammonium salts, such as phenylbenzyldimethylammonium chloride and tetramethylammonium iodide, do not react in this way. The conclusion is therefore drawn that the salts of acridine, pyridine, and quinoline are probably quinocarbonium salts and not ammonium salts, as has been generally assumed.

When diphenylacridol chloride (Gomberg and Cone, A., 1910, i, 59) is suspended in nitrobenzene and treated with molecular silver, a double *silver* salt, $C_{25}H_{18}NCl,AgCl$, is produced, together with an unsaturated compound which absorbs oxygen to form a peroxide, thus: (1) $C_{25}H_{18}NCl + Ag = C_{25}H_{18}N- + AgCl$; (2) $C_{25}H_{18}NCl + AgCl = C_{25}H_{18}NCl,AgCl$; (3) $2C_{25}H_{18}N- + O_2 = (C_{25}H_{18}N)_2O_2$.

When 5-*phenyl*-10-*methylacridol chloride hydrochloride*,

$$NMe{<}\begin{matrix}C_6H_4(Cl,HCl)\\C_6H_4\end{matrix}{>}CPh,$$

is heated at 90—100° and a current of air passed through it, it is converted into the *chloride*, $NMe<\genfrac{}{}{0pt}{}{C_6H_4Cl}{C_6H_4-}>CPh$, which, on being treated with molecular silver, yields a double *silver* salt,

$$C_{20}H_{16}NCl,AgCl,$$

and an unsaturated compound which absorbs oxygen.

If pyridine methyl iodide is shaken with nitrobenzene and excess of silver, a similar reaction occurs with formation of a double iodide and an unsaturated compound which absorbs oxygen. Quinoline methiodide behaves in the same way. E. G.

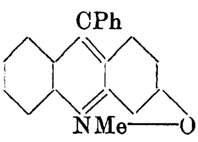
Acridine Derivatives. II. Analogue of *apo*Safranone in the Acridine Series. FRIEDRICH KEHRMANN and ZD. MATUSINSKY (*Ber.*, 1912, **45**, 3498—3505).—2-Hydroxy-5-phenylacridine is best obtained by heating, without stirring, an intimate mixture of *m*-hydroxydiphenylamine, benzoic acid, and zinc chloride at 180—200°, and finally at 210°, for half an hour at each temperature; a crystalline by-product is also obtained, the removal of which presents some difficulty. The hydroxyphenylacridine crystallises from hot saturated solutions in straw-yellow needles, m. p. 264°, and at the ordinary temperature in brick-red prisms, m. p. about 135°, changing to the yellow modification. On the contrary, the yellow form changes to the red by long keeping at the ordinary temperature. The suggestion is offered that the two modifications have an ortho- and a para-quinonoid constitution respectively:

$$C_6H_4<\genfrac{}{}{0pt}{}{CPh}{N}>C_6H_3\cdot OH \text{ and } C_6H_4<\genfrac{}{}{0pt}{}{CPh}{NH}>C_6H_3\colon O.$$

2-*Acetoxy*-5-*phenylacridine*, m. p. 151°, pale-yellow leaflets, reacts with methyl sulphate in nitrobenzene at 140—150° to form 2-*acetoxy*-5-*phenyl*-10-*methylacridinium methosulphate*,

$$CPh<\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_3(OAc)}>NMe\cdot SO_4Me,$$

citron-yellow needles, from which a *chloride*, *bromide*, *iodide*, and *platinichloride*, yellow to orange-red, crystalline salts, can be prepared.



By warming a dilute aqueous solution of one of these salts with sodium hydroxide on the water-bath, C-*phenyl*-N-*methyl*iso*acridone* (annexed formula), m. p. 231°, brownish-red or dark red needles, is obtained. This substance sublimes unchanged, does not react with alkalis, but forms with acids crystalline, red and yellow salts which are completely hydrolysed by water. It yields salts of the preceding acetoxyphenylmethylacridinium base by prolonged keeping with acetic anhydride and treatment of the resulting solution with metallic salts, and is converted by methyl sulphate in nitrobenzene at 150° into 2-*methoxy*-5-*phenyl*-10-*methylacridinium methosulphate*, citron-yellow needles, from which the corresponding *chloride*, *iodide*, *platinichloride*, and *dichromate* have been prepared. C. S.

Action of Phthalic Anhydride on Some Pyrrole Derivatives. HANS FISCHER and FR. KROLLPFEIFFER (*Zeitsch. physiol. Chem.*, 1912, **82**, 266—272).—The trisubstituted pyrroles are at

present characterised as picrates or as the azo-dyes formed with diazobenzenesulphonic acid. They also form characteristic crystalline phthalides when heated with phthalic anhydride and acetic acid in sealed tubes at 180—190°.

3-*Acetyl*-2 : 4-*dimethylpyrrolephthalide*,

$$C_6H_4<\begin{matrix}CO\cdot C:CMe \\ CO\cdot N\cdot CMe\end{matrix}>C\cdot COMe,$$

crystallises in faintly yellow-coloured needles, m. p. 183°. On heating with potassium hydroxide it is converted into the corresponding *acid*, which crystallises in slender, colourless needles, m. p. 176—178°.

Cryptopyrrolephthalide separates in brownish-yellow needles, m. p. 169°; the corresponding acid has m. p. 195° (decomp.).

Phonopyrrolecarboxylic acid phthalide forms faintly yellow-coloured needles, m. p. 225—226°; it can be prepared easily from syrupy phonopyrrolecarboxylic acid.

Haemopyrrolephthalide forms yellow prisms, m. p. 116°.

Tetramethylpyrrole and phthalic anhydride yield a *trimethylpyrrolephthalide*, crystallising in stunted, yellow prisms, m. p. 205°. The *acid* obtained on heating with potassium hydroxide has m. p. 204° (decomp.). E. F. A.

The Methylation of Gallocyanin, Pyrogallin, and Azurin.

FRIEDRICH KEHRMANN and A. BEYER (*Ber.*, 1912, 45, 3338—3345).—The preparation of oxonium salts analogous to those obtained from resorufin (Kehrmann and Vogt, A., 1910, i, 409) offers in the case of the above substances considerably more difficulty.

The starting substances, gallocyanin, its methyl ester, pyrogallin (m. p. 240—241°), and azurin were first carefully purified and their properties re-examined.

Gallocyanin, on methylation in sodium hydroxide solution with methyl sulphate, gave the phenolic *ether*, $O<\begin{matrix}C_6H(OMe)(CO_2H) \\ O\text{——}C_6H_3(NMe_2)\end{matrix}>N$, deep blue powder, m. p. 203—204°, which forms salts with acids and bases; the solution of this substance in fuming sulphuric acid when diluted changes colour from red to blue, and again to red, indicative of the existence of tri-, di-, and mono-acid salts. Simultaneously with the above ether there is obtained *dimethylgallocyanin*,

$$O<\begin{matrix}C_6H(OMe)(CO_2Me) \\ O\cdot C_6H_3(NMe_2)\text{——}\end{matrix}>N,$$

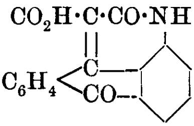
which is better obtained, however, by the action of methyl sulphate on the methyl ester of gallocyanin; it forms prisms with a bronze lustre, m. p. 197°, is insoluble in alkalis, but with acids gives crystalline salts; the solution in fuming sulphuric acid on dilution gives the same series of colour changes as the phenolic ether; *platinichloride*, crystalline.

Methyl sulphate acts on an alkaline solution of pyrogallin, giving a phenolic *ether*, $O<\begin{matrix}C_6H_2(OMe)\text{==} \\ O\cdot C_6H_3(NMe_2)\end{matrix}>N$, prisms with a green lustre, m. p. 199—200°. The solution in fuming sulphuric acid shows the usual colour changes on dilution.

Azurin can be methylated by heating with methyl alcohol containing a little hydrochloric acid, forming the *ester*, $O<\begin{matrix}C_6H_2(CO_2Me)= \\ O\cdot C_6H_3(NMe_2)\end{matrix}>N$, prisms with a metallic lustre, m. p. 190°; the solution in concentrated mineral acid changes from a blue to a red colour on dilution.

D. F. T.

Preparation of Anthrapyridonecarboxylic Acids. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 250885).—When the compound, $C_6H_4<\begin{matrix}CO \\ CO\end{matrix}>C_6H_3\cdot NH\cdot CO\cdot CH_2\cdot CO_2Et$ obtained by heating together molecular proportions of ethylmalonyl chloride and α-aminoanthraquinone at 200° is boiled with aqueous sodium hydroxide it yields *anthrapyridonecarboxylic acid*, $C_{17}H_9O_4N$ (annexed formula); this compound exhibits a yellow fluorescence when dissolved in concentrated sulphuric acid.



The analogous *compound*, $C_{17}H_{10}O_4N_2$, prepared from 1 : 4-diaminoanthraquinone is a red powder; and the *compound* from 4-chloro-1-aminoanthraquinone an orange-yellow powder. F. M. G. M.

Preparation of Anthraquinone Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 252839).—The condensation of aldehydes with *o*-diaminoanthraquinones has been recorded; this action is now found to take place with 1-amino-2-hydroxyanthraquinone or with 1-aminoanthraquinone-2-thiol, yielding compounds of the general formulæ:

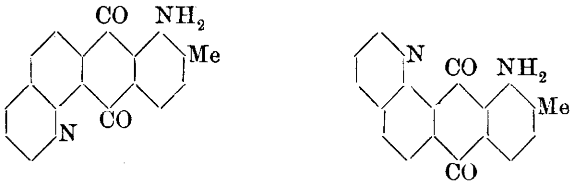
$$A<\begin{matrix}NH_2 \\ OH\end{matrix} \longrightarrow A<\begin{matrix}N \\ O\end{matrix}>CR. \qquad A<\begin{matrix}NH_2 \\ SH\end{matrix} \longrightarrow A<\begin{matrix}N \\ S\end{matrix}>CR.$$

The following *compounds* are described: from benzaldehyde with (1) 1-amino-2 : 4-dihydroxyanthraquinone, an orange, crystalline powder; (2) with 2 : 4-diamino-1-hydroxyanthraquinone, brown crystals; (3) with 3-amino-1 : 2-dihydroxyanthraquinone, orange needles; (4) with 1 : 5-diamino-2 : 4 : 6 : 8-tetrahydroxyanthraquinone; (5) with 1-aminoanthraquinone-2-thiol; from 1-amino-2 : 4-dihydroxyanthraquinone with paraformaldehyde, whilst the *anthra*-1 : 2-*oxazole* rom 1-amino-2-hydroxyanthraquinone forms yellow crystals.

F. M. G. M.

1-Amino-2-methylanthraquinone-α-quinolines. ALFRED SCHAARSCHMIDT and ALEX. STAHLSCHMIDT (*Ber.*, 1912, **45**, 3452—3456).—These substances have been prepared in order to ascertain what influence the presence of a quinoline nucleus has on the colour of the already intensely coloured 1-aminoanthraquinone. The dinitration of 2-methylanthraquinone by concentrated nitric and sulphuric acids yields a mixture of 1 : 5-*dinitro*-2-*methylanthraquinone*, m. p. 251—252°, and 1 : 8-*dinitro*-2-*methylanthraquinone*, m. p. 189—190°, which is separated by the sparing solubility of the former in boiling glacial acetic acid. The two substances, the orientation of the nitro-groups in which is assumed from analogy to the course of the nitration of anthraquinone,

are reduced by alkaline sodium sulphide to 1 : 5-*diamino*-2-*methylanthraquinone*, m. p. 201—202°, red needles, and 1 : 8-*diamino*-2-*methylanthraquinone*, m. p. 206—208°, brownish-red needles, from which the quinolines are obtained by the Skraup method. 1-*Amino*-2-*methylanthraquinone*-5-*quinoline* (formula I), m. p. 206—207, reddish-brown



(I.) (II.)

needles, dissolves in concentrated sulphuric acid with a brownish-yellow colour changing to blue by dilution with water. 1-*Amino*-2-*methylanthraquinone*-8-*quinoline* (formula II), m. p. 100°, reddish-brown crystals, forms violet solutions in dilute mineral acids. C. S.

The Purification and Separation of Anthraquinoneacridones from By-products. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 253090).—*Bromoanthraquinoneacridone*, a yellowish-red powder (prepared from anthraquinoneacridone), has m. p. above 300°, and is conveniently purified by isolation in the form of its *sulphate*, whilst the action of sulphuryl chloride on anthraquinoneacridone furnishes a mixture of two isomeric *chloroanthraquinoneacridones*. F. M. G. M.

[Preparation of 4 : 4′ - Diamino - 2 : 2′ - dimethyldiphenylmethane.] FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 252916).—4 : 4′-*Diaminodiphenylmethane* prepared from *m*-toluidine crystallises from hot water in colourless needles, m. p. 123° ; the solution of its hydrochloride gives a violet coloration with ferric chloride, and when fully diazotised and combined with α-naphthol-5-sulphonic acid (2 mols.) furnishes a brownish-red azo-colouring matter. F. M. G. M.

Preparation of Aminobenzoyl Derivatives of Aminobenzoyl-7-amino-1-naphthol-3-sulphonic Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 252159).—The tinctorial properties of the compounds obtained by the action of nitrobenzoyl haloids on aminobenzoyl-7-amino-1-naphthol-3-sulphonic acid and subsequent reduction have been recorded ; it is now found that these compounds can be obtained by the combination of an aminobenzoic acid with a nitrobenzoyl haloid, followed by condensation with 7-amino-1-naphthol-3-sulphonic acid and subsequent reduction. F. M. G. M.

Action of Hydroxylamine and of Phenylhydrazine on Urethanobenzylacetylacetone and on Ethyl Urethanobenzylacetoacetate. G. BIANCHI (*Gazzetta*, 1912, 42, ii, 496—512. Compare A., 1912, i, 542 ; Bianchi and Schiff, A., 1911, i, 977).—By the action of hydroxylamine on ethyl urethanobenzylacetoacetate, a stable

compound, $C_{16}H_{22}O_5N_2$, is obtained, which crystallises in colourless needles, m. p. 185° (sintering a few degrees previously). This compound is the normal *oxime*,

$$OH\cdot N{:}CMe\cdot CH(CO_2Et)\cdot CHPh\cdot NH\cdot CO_2Et.$$

The action of hydroxylamine on urethanobenzylacetylacetone yields two compounds. One, which forms heavy, prismatic crystals, m. p. 175° (decomp.), has the composition $C_{15}H_{20}O_4N_2$, and is the *monoxime*, $OH\cdot N{:}CMe\cdot CH(COMe)\cdot CHPh\cdot NH\cdot CO_2Et$; it is unstable and is obtained with difficulty. The other compound forms large, prismatic crystals, m. p. 94—95°; it is readily obtained and very stable; it has the composition $C_{15}H_{18}O_3N_2$ required by 4-*urethano-benzyl*-2 : 5-*dimethyl*isooxazole, $O\Big\langle\begin{matrix}CMe{:}C\cdot CHPh\cdot NH\cdot CO_2Et\\ N{=\!=}CMe\end{matrix}$. The oxime readily changes into the *iso*oxazole derivative.

[With Manlio Rocchi.]—The action of phenylhydrazine on urethanobenzylacetylacetone and on ethyl urethanobenzylacetoacetate yields in each case the normal monophenylhydrazone. *Urethano-benzylacetylacetonephenylhydrazone*, $C_{21}H_{25}O_3N_3$, crystallises in groups of needles, m. p. 149—150° (decomp.). *Ethyl urethanobenzylaceto-acetatephenylhydrazone*, $C_{22}H_{27}O_4N_3$, crystallises in groups of needles, m. p. 136—137°. R. V. S.

Benzoylation of Aminourazole. Robert Stollé and K. Krauch (*Ber.*, 1912, 45, 3307—3311).—By the action of benzoyl chloride on aminourazole in presence of pyridine there are obtained a dibenzoylaminourazole, $C_2H_2O_2N_4(COPh)_2$, a tribenzoylaminourazole, and what was considered to be a tetrabenzoyl derivative. The last did not give aminourazole on hydrolysis, yielding instead a dibenzoyl derivative which proved to be identical with the benzoylhydrazi-carbonyl, $COPh\cdot N\Big\langle\begin{matrix}NH\\ CO\end{matrix}$, obtained by Diels and Wagner (A., 1912, i, 511; compare Diels and Okada, *ibid.*, 918) by the action of alkali on chlorobenzoylcarbamide. The supposed tetrabenzoyl derivative is, therefore, *dibenzoylhydrazicarbonyl*, for which the symmetrical formula $CO\Big\langle\begin{matrix}N\cdot COPh\\ N\cdot COPh\end{matrix}$ is considered most probable.

Dibenzoylaminourazole crystallises in needles, m. p. 201°, and yields aminourazole on hydrolysis.

Tribenzoylaminourazole forms tiny needles, m. p. 234°.

Dibenzoylhydrazicarbonyl has m. p. 130°. With sodium ethoxide, ethyl dibenzhydrazidoformate, m. p. 130° (Stollé and Benrath, A., 1904, i, 935), is obtained. On heating the carbonyl at 280°, 2 : 5-di-phenyl-1 : 3 : 4-oxadiazole is formed. E. F. A.

Constitution of the Compound from Benzoyl Chloro-carbamide and Alkali. Peter J. Schestakov (*Ber.*, 1912, 45, 3273—3274. Compare Diels and Okada, A., 1912, i, 918; Diels and Wagner, A., 1912, i, 511).—A claim for priority. Schestakov, Kind,

and Lebedev (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 330) have prepared the compound described as benzoyl hydrazicarbonyl,

$$COPh\cdot N<\overset{NH}{\underset{CO}{|}},$$

by Diels and Okada, and ascribe to it the formula $COPh\cdot N<\overset{N}{\underset{C\cdot OH}{||}}$.

E. F. A.

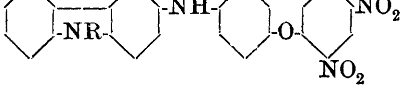
Preparation and Properties of 5-Aminoquinoline-6-carboxylic Acid and Certain Related Compounds. MARSTON T. BOGERT and HARRY LINN FISHER (*J. Amer. Chem. Soc.*, 1912, **34**, 1569—1576).—This investigation was undertaken with the object of preparing an aminocarboxylic acid of the anthranilic type from which substances belonging to new heterocyclic systems might be obtained.

A method is described for the preparation of 5-nitro-6-methylquinoline (Noelting and Trautmann, A., 1891, 325). 5-Amino-6-methylquinoline has m. p. 135° (corr.); attempts to oxidise this compound to 5-aminoquinoline-6-carboxylic acid were not successful.

5-*Aminoquinoline*-6-*carboxylic acid*, $NH_2\cdot C_9NH_5\cdot CO_2H$, m. p. 218·5° (decomp.), obtained in 30% yield by boiling 5-nitro-6-methylquinoline with alcoholic potassium hydroxide, crystallises in red nodules; it yields brown, amorphous precipitates with barium chloride, calcium chloride, cadmium iodide, copper sulphate, indium chloride, and mercuric chloride, and green precipitates with nickel chloride and silver nitrate. The *hydrochloride* has m. p. 264·7°. The *methyl* ester crystallises in bright red needles with $2H_2O$; the anhydrous form, m. p. 245° (corr.), is an amorphous, scarlet powder. 5-*Acetylamino*-6-*quinolinecarboxylic acid*, m. p. 237° (corr., decomp.), obtained by the action of acetic anhydride on the acid, forms slender, yellow needles; by prolonged heating with acetic anhydride it is converted into the *lactam*, $C_9H_5<\overset{CO}{\underset{NAc}{|}}$ or $C_9H_5<\overset{CO\cdot O}{\underset{N{=}CMe}{|}}$, m. p. 190° (uncorr.), which crystallises in nearly colourless needles, and reacts with primary amines to form naphtha*iso*triazines (this vol., i, 106). 5-*Benzylideneaminoquinoline*-6-*carboxylic acid*, $CHPh\!:\!N\cdot C_9NH_5\cdot CO_2H$, m. p. 221·4° (corr., decomp.), forms rosettes of needles. 5-*Hydroxyquinoline*-6-*carboxylic acid*, m. p. 211·7° (corr., decomp.), is obtained as a dark green precipitate by the action of nitrous acid on the hydrochloride of the amino-acid, and crystallises in rosettes of brown needles; it yields green, amorphous precipitates with barium chloride, zinc chloride, cadmium iodide, copper sulphate, mercuric chloride, and silver nitrate.

E. G.

Preparation of Condensation Products from 1-Chloro-2:4-dinitrobenzene with the Leucoindophenols derived from Carbazole. LEOPOLD CASSELLA & Co. (D.R.-P. 252642).—Compounds having the annexed general formula, where R is hydrogen or alkyl, are obtained by the action of 1-chloro-2:4-dinitrobenzene on the leucoindophenols prepared from *p*-nitrosophenol with carbazoles.

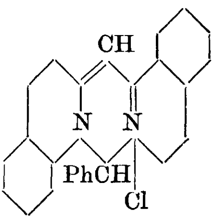


The *compounds* thus obtained

from the indophenols of carbazole with *p*-nitrosophenol (glistening, coppery leaflets, m. p. 190°) and from *N*-ethylcarbazole with *p*-nitrosophenol (small, reddish-brown needles, m. p. 223°) are described.

F. M. G.

Constitution of *iso*Quinoline Red. II. EDUARD VONGERICHTEN and W. HOMANN (*Ber.*, 1912, **45**, 3446—3452. Compare A., 1910, i, 201).—The basic substance, $C_{19}H_{12}ON_2$, obtained together with benzaldehyde or benzoic acid by the oxidation of *iso*quinoline red by potassium dichromate and dilute sulphuric acid, proves to be 2-*quinolyl-*2-iso*quinolyl ketone*, $C_9NH_6\cdot CO\cdot C_9NH_6$. It yields *iso*quinoline and quinaldic acid by heating with concentrated potassium hydroxide. It forms a *methiodide*, $C_{20}H_{15}ON_2I$, decomp. about 120°, and an *ethiodide*, decomp. about 160°. By treatment with aqueous silver sulphate, the methiodide yields a solution of the methosulphate, which is treated with sodium hydroxide and potassium ferricyanide, whereby quinaldic acid and *N*-methyl*iso*quinolone are produced. By reduction with alcoholic ammonium sulphide at 200°, *iso*quinoline red yields benzyl mercaptan and a *substance*, m. p. 231°, golden-yellow leaflets.



The preceding statements, together with the fact that the quinaldine cannot be replaced by lepidine or any other methylated quinoline in the preparation of *iso*quinoline red, lead to the annexed formula for this substance.

C. S.

Octachloroindigotin and Some Derivatives of Tetrachloroanthranilic and Tetrachlorophthalic Acids. WILLIAM R. ORNDORFF and E. H. NICHOLS (*Amer. Chem. J.*, 1912, **48**, 473—500).—By the action of dimethylaniline on the product of the diazotisation of tetrachloroanthranilic acid (Villiger and Blangey, A., 1909, i, 922), *dimethylaminobenzeneazotetrachlorobenzene*-o-*carboxylic acid*,

$$NMe_2\cdot C_6H_4\cdot N\colon N\cdot C_6Cl_4\cdot CO_2H,$$

is obtained as a brilliant red substance. The *acetyl* derivative of 5 : 6 : 7 : 8-tetrachloro-3 : 4-dihydro-2 : 4-benzoxaz-1-one (Villiger and Blangey, *loc. cit.*), m. p. 166·5° (corr.), crystallises in colourless, rectangular plates. When tetrachlorophenylglycine-*o*-carboxylic acid (A., 1910, i, 382) is boiled with acetic anhydride, *tetrachloroacetylindoxylic acid*, $C_6Cl_4{<}{}^{NAc}_{C(OH)}{>}C\cdot CO_2H$, m. p. 225° (corr.), is produced as a pale yellowish-green, crystalline powder; its *silver* salt forms light greyish-green needles containing $1H_2O$. If fused sodium acetate is used with the acetic anhydride, the reaction proceeds further, and mono- and di-acetyl derivatives of tetrachloroindoxyl are produced; the *acetyl* derivative, $C_6Cl_4{<}{}^{NAc}_{C(OH)}{>}CH$, m. p. 195° (uncorr.), crystallises in white, slender, microscopic prisms; the *diacetyl* derivative, $C_6Cl_4{<}{}^{NAc}_{C(OAc)}{>}CH$, m. p. 167° (uncorr.), forms very pale blue, rectangular prisms. On heating a solution of tetrachloroacetylindoxylic

acid in aqueous ammonia, *octachloroindigotin*,

$$C_6Cl_4<{NH \atop CO}>C:C<{CO \atop NH}>C_6Cl_4,$$

is produced as a purple, amorphous precipitate, which, when heated in a current of air at 360°, sublimes in small, rhombic plates.

Villiger's statement (A., 1909, i, 931) that dichlorophthalylhydroxylamine is converted into dichloroanthranilic acids by heating it with sodium carbonate solution, suggested that tetrachloroanthranilic acid might be similarly obtainable from the corresponding tetrachlorophthalylhydroxylamine (tetrachlorophthaloxime), and the following experiments were, therefore, carried out. When tetrachlorophthalic anhydride is heated with a solution of hydroxylamine in methyl alcoho *tetrachlorophthaloxime hydroxide methyl ether*,

$$CO<{-O- \atop C_6Cl_4}>C(OH)\cdot NH\cdot OMe,$$

m. p. 246—247° (corr., decomp.), is produced. If the tetrachlorophthalic anhydride is heated with an aqueous solution of hydroxylamine, *tetrachlorophthaloxime hydroxide*, $CO<{-O- \atop C_6Cl_4}>C(OH)\cdot NH\cdot OH$, m. p. 254° (corr.), is obtained, which crystallises in nearly white prisms. When this substance is heated at 50° or left in a vacuum desiccator with phosphoric oxide, it loses water and becomes converted into *tetrachlorophthaloxime*, $C_6Cl_4<{CO \atop C(:NOH)}>O$, which forms lemon-yellow prisms; the *sodium* salt is described; the *acetyl* derivative, m. p. 176° (corr.), crystallises in white needles. E. G.

[Preparation of Halogenated Derivatives of Indigoid Compounds.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 252387). —The bisulphite compounds of indigoid derivatives are readily halogenated, yielding *compounds* with a high halogen content. The bromination of the bisulphite compounds obtained from isatin chloride and carbazole, and of that from indoxyl-red,

$$C_6H_4<{NH \atop CO}>C:C<{-CH \atop C_6H_4}>N,$$

is described, and other compounds which can be similarly treated are mentioned. F. M. G. M.

Preparation of Condensation Products from Indigotin, its Homologues or Halogen-substitution Products. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 250744).—When indigotin, its homologues, or halogen-substitution products are heated at 150—200° in the presence of zinc chloride with benzoic anhydride (or substituted benzoic anhydrides), condensation products are formed which find employment in the preparation of dyes.

Indigotin (10 parts), zinc chloride (10 parts), and benzoic anhydride (40 parts) at 150—160° yield a yellow, crystalline *compound*, m. p. 357°.

The following analogous *compounds* are also described: from dibromoindigotin with benzoic anhydride, yellow crystals, m. p. 340° (about) from indigotin with *p*-toluic anhydride, pale yellow crystals,

m. p. 330°; from the same with dibromoindigotin, m. p. above 330°: from indigotin with *p*-methoxybenzoic anhydride, yellow crystals, m. p. 320°; and from indigotin with *o*-chlorobenzoic anhydride, m. p. above 340°. These compounds dissolve in concentrated sulphuric acid with red colorations, but are insoluble in alkaline hyposulphite; they can be prepared in the presence of an indifferent solvent or by the fusion of the constituents. F. M. G. M.

Buchner's Pyrazolinecarboxylic Acids. CARL BÜLOW (*Ber.*, 1912, 45, 3349—3355).—A reply to Darapsky's criticism (A., 1912, i, 391) of the author's view that the additive products of ethyl diazoacetate with olefinic esters are really open-chain compounds (A., 1912, i, 134, 316). D. F. T.

Condensation Product of Formaldehyde, Ammonia, and Antipyrine. CARL MANNICH and W. KRÖSCHE (*Arch. Pharm.*, 1912, 250, 647—667).—Antipyrine condenses with formaldehyde and ammonia, or with the hexamethylenetetramine formed from these two substances, to give triantipyryltrimethyleneamine,

$$N(CH_2{\cdot}O{\cdot}C_{11}H_{11}N_2)_3,$$

in the formation of which antipyrine is believed to react in the enolic form represented by the formula $NPh<\begin{matrix}C(OH){:}C \\ NMe—CMe\end{matrix}$. A similar condensation occurs with antipyrine derivatives so long as these are not substituted in position 4.

Triantipyryltrimethyleneamine hydrochloride, $C_{36}H_{40}O_3N_7Cl,6H_2O$, m. p. 178°, or 206° (dry), formed when the condensation is effected by hydrochloric acid, is crystalline. The free *base*, m. p. 259—260°, crystallises anhydrous from methyl alcohol. When boiled with hydrochloric acid, it yields formaldehyde, ammonia, and methylenebisantipyrine, which yields a trihydrated dihydrochloride (Schuftan, A., 1895, i, 482), and a *monohydrochloride*, $CH_2(C_{11}H_{11}ON_2)_2,HCl,3H_2O$, m. p. 94—95°, which on drying at atmospheric temperature over sulphuric acid becomes *anhydrous*, then melts at 100—110°, and on solution in acetone deposits some *anhydrous dihydrochloride*, m. p. 200—220°, leaving some free base in solution.

On treatment with sodium hydrogen sulphite and sulphurous acid, triantipyryltrimethyleneamine yields antipyrine, which appears to be formed direct from the parent substance, since sulphurous acid has no action on methylenebisantipyrine.

Tritolypyryltrimethyleneamine, $C_{39}H_{45}O_3N_7,7H_2O$, m. p. 214—215° (dry), formed by condensing hexamethylenetetramine with tolypyrine (*p*-tolyl-2 : 3-dimethyl-5-pyrazolone), crystallises from a mixture of methyl alcohol and water; the *hydrochloride*, $C_{39}H_{46}O_3N_7Cl,6H_2O$, m. p. 100—105°, or 191° (dry), forms short, stout needles. Sulphuroos acid in presence of sodium hydrogen sulphite hydrolyses it to tolypyrine, whilst hydrochloric acid converts it into ammonia, formaldehyde, and *methylenebistolypyrine*, m. p. 183—186°, or 190° (dry), which crystallises from 80% alcohol in slender needles, and can be prepared by condensing tolypyrine with formaldehyde.

Trihomoantipyryltrimethyleneamine, m. p. 280°, similarly obtained, crystallises from boiling methyl alcohol; the *hydrochloride*, m. p. 202°, crystallises from acetone. *Methylenebishomoantipyrine* crystallises from ethyl acetate in tablets with $1H_2O$, m. p. 120—130°, and after drying over sulphuric acid melts at 105—106°. The *dihydrochloride*,

$$C_{25}H_{30}O_2N_4Cl_2,3H_2O,$$

separates from 10% hydrochloric acid in stout crystals, m. p. 200—210°.

T. A. H.

Substituted α-Hydroxy- and α-Methyl-benziminazoles. OTTO KYM and L. RATNER (*Ber.*, 1912, **45**, 3238—3255. Compare A., 1904, i, 453; 1911, i, 1044).—*p*-Nitro-*o*-phenylenediamine reacts readily with carbamide, forming 5-nitro-2-hydroxybenziminazole,

$$NO_2\cdot C_6H_3<\substack{NH\\ N}>C\cdot OH$$

(compare Hager, A., 1885, 149). This reacts with phosphoryl chloride forming 2-chlorobenziminazole, from which the 2-hydroxy-compound is regenerated on boiling with concentrated hydrochloric acid. Ammonia or aniline converts it into corresponding 2-amino- or 2-anilino-derivatives. The property of the azo-dyes of all phenylated benziminazoles to dye cotton persists, although to a less degree, in the 2-hydroxy-compounds.

Both 2-hydroxyl- and 2-methyl-benziminazoles can be nitrated without difficulty, forming dinitro-derivatives. It was found impossible to open the iminazole ring in these by Bamberger's method—by means of benzoyl chloride and sodium hydroxide.

Dinitro-2-hydroxybenziminazole when heated with aniline yields nitro-2-hydroxyanilinobenziminazole,

$$NHPh\cdot C_6H_2(NO_2)<\substack{NH\\ N}>C\cdot OH,$$

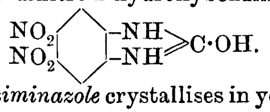
a red, crystalline compound, whereas the mononitro-2-hydroxybenziminazole does not react with aniline. This behaviour indicates that the second nitro-group has entered in the ortho-position to the first.

On reduction of the dinitro-compounds the diamino-compounds obtained behave as *o*-diamines, forming azimino-derivatives with nitrous acid and the corresponding dianhydro-derivatives when boiled with acetic acid. 2 : 7-Dimethylbenzdi-iminazole,

$$CMe<\substack{NH\\ N}>C_6H_2<\substack{NH\\ N}>CMe,$$

is shown to be identical with Nietzki's (A., 1887, 476, 477) diethenyl base obtained by nitration and reduction of diacetyl-*m*-phenylenediamine.

When 5 : 6-diamino-2-methylbenziminazole is fused with carbamide the dihydro-derivative already mentioned, 7-hydroxy-2-methylbenzdiiminazole, $CMe<\substack{NH\\ N}>C_6H_2<\substack{NH\\ N}>C\cdot OH$, is formed. These changes confirm the structure of dinitro-2-hydroxybenziminazole as



5-*Nitro-2-hydroxybenziminazole* crystallises in yellowish-white needles,

m. p. 308°; it is strongly acid, dissolving in alkali hydroxide with an intense orange-yellow coloration. It further has weak basic properties.

5 : 6-*Dinitro-2-hydroxybenziminazole* separates in centimetre-long, lustrous needles, m. p. above 300°; the solution in cold dilute alkali hydroxide is intense red, and it forms a deep red, crystalline sodium salt.

5 : 6-*Dinitro-2-methylbenziminazole* forms yellowish-white needles, m. p. 223°.

Nitro-2-hydroxyanilinobenziminazole crystallises in red platelets, m. p. 298°.

Nitroamino-2-hydroxybenziminazole, prepared by heating the dinitro-compound with ammonia at 180—210°, forms bright red, lustrous crystals, m. p. above 300°; it is soluble in concentrated hydrochloric acid, and also dissolves in dilute sodium hydroxide or ammonia with a deep red coloration.

5 : 6-*Diamino-2-hydroxybenziminazole* readily oxidises as free base; the *hydrochloride* forms a brown, microcrystalline powder; the *diacetyl* derivative crystallises in lustrous, silky needles, m. p. 293—294°; 2-*hydroxybenzdi-iminazole*, $\mathrm{N}{<}\genfrac{}{}{0pt}{}{\mathrm{NH}}{\mathrm{N}}{>}\mathrm{C_6H_2}{<}\genfrac{}{}{0pt}{}{\mathrm{NH}}{\mathrm{N}}{>}\mathrm{C\cdot OH}$, crystallises in yellow platelets, m. p. above 300°.

5 : 6-*Diamino-2-methylbenziminazole* crystallises in pale brown needles, m. p. above 300°; the *diacetyl* derivative separates in slightly pink-coloured, glistening needles, also m. p. above 300°. 2-*Methyi nzdi-iminazole* forms reddish-brown, stunted needles, m. p. above 300

2 : 7-Dimethylbenzdi-iminazole is obtained in lustrous, yehowish-white needles, m. p. outside the thermometer range.

7-*Hydroxy-2-methylbenzdi-iminazole* also forms lustrous, ehowish-white platelets, m. p. above 300°.

2-*Chloro-5-nitrobenziminazole* is a yellow, crystalline powder, m. p. 222—223°.

5-*Nitro-2-anilinobenziminazole* yields tiny, brown crystals, m. p. 278°.

5-*Nitro-2-aminobenziminazole* crystallises in a bulky mass of slender, yellow needles, m. p. 189—190°; the *acetyl* derivative is colourless.

E. F. A.

Constitution of Compounds from *o*-Diamines and α-Hydroxy-acids. Acetylation of Benziminazoles. AUGUSTIN BISTRZYCKI and GEORG PRZEWORSKI (*Ber.*, 1912, **45**, 3483—3495).—The product obtained by the interaction of 3 : 4-tolylenediamine and lactic acid is regarded as a tetrahydroquinoxaline by Georgescu, and as a benziminazole by Hinsberg. The authors now show that the latter view is correct and that the reaction is a general one; thus *o*-phenylenediamine and mandelic acid ($1\frac{1}{4}$ mol.) at 130—135° yield 2-α-hydroxybenzyl-benziminazole; *o*-phenylenediamine and lactic acid (3 mols.) at 105—110° yield 2-α-hydroxyethylbenziminazole; 3 : 4-tolylenediamine and mandelic acid ($1\frac{1}{4}$ mol.) at 130—135° yield 2-α-hydroxybenzyl-5-methylbenziminazole, and 3 : 4-tolylenediamine and lactic acid yield 5-methyl-2-α-hydroxyethylbenziminazole. These substances are identical with Georgescu's so-called tetrahydroquinoxalones.

o-Phenylenediamine and glycollic acid at 120° yield 2-*hydroxymethyl-*

benziminazole, $C_6H_4<\substack{NH\\N}>C\cdot CH_2\cdot OH$, m. p. 171—172°, colourless plates, which forms an *acetyl* derivative, m. p. 99—101°, by boiling with acetic anhydride and sodium acetate, and is oxidised by hot dilute alkaline potassium permanganate to *benziminazole-2-carboxylic acid*,

$$C_8H_6O_2N_2,2H_2O,$$

decomp. 169°, long prisms (*barium* salt, $C_{16}H_{10}O_4N_4Ba$), from which benziminazole is obtained by heating at 169°. The authors find that benziminazoles are readily acetylated by heating with acetic anhydride; thus benziminazole or benziminazole-2-carboxylic acid yields 1-*acetylbenziminazole*, m. p. 113—114°, long, prismatic needles, and 2-methylbenziminazole yields 1-*acetyl-2-methylbenziminazole*, m. p. 85—86°, colourless, microscopic needles or prisms.

3 : 4-Tolylenediamine and glycollic acid yield 5-*methyl-2-hydroxymethylbenziminazole*, m. p. 203°, plates or needles (*acetyl* derivative, m. p. 129—132°), from which Hinsberg's 5-methylbenziminazole-2-carboxylic acid, m. p. 156° (decomp.), is obtained by oxidation.

By oxidation with chromic and acetic acids, 2-α-hydroxybenzylbenziminazole yields 2-*benzoylbenziminazole*, $C_6H_4<\substack{NH\\N}>C\cdot COPh$, m. p. 209—210° (decomp.), microscopic needles (*phenylhydrazone*, m. p. 185—186°, yellow plates; *phenylmethylhydrazone*, m. p. 225°, yellow prisms), and 2-α-hydroxybenzyl-5-methylbenziminazole yields 2-*benzoyl-5-methylbenziminazole*, m. p. 140—141°, felted needles.

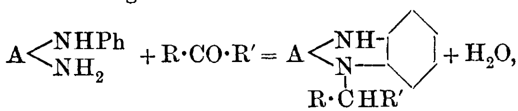
Equal molecular quantities of *o*-phenylenediamine and benzilic acid at 150—160°, or *o*-phenylenediamine (1·5 mol.) and chlorodiphenylacetic acid under the same conditions, yield a *substance*, $C_{20}H_{16}ON_2$, m. p. 221—223°, microscopic plates, which is probably 2-*hydroxydiphenylmethylbenziminazole*, $C_6H_4<\substack{NH\\N}>C\cdot CPh_2\cdot OH$. The 5-methyl *homologue*, m. p. about 255°, is obtained from 3 : 4-tolylenediamine and chlorodiphenylacetic acid, whilst diphenylacetic acid and *o*-phenylenediamine yield 2-*benzhydrylbenziminazole*, $C_6H_4<\substack{NH\\N}>C\cdot CHPh_2$, m. p. 218—220°, colourless, prismatic needles. C. S.

The Constitution of Acetyl-β-anthraquinonylmethylpyrazolone. RICHARD MÖHLAU (*Ber.*, 1912, 45, 3596).—The pyrazolone described recently (Möhlau, A., 1912, i, 704) is 4-acetyl-1-β-anthraquinonyl-3-methylpyrazolone. D. F. T.

Preparation of Nitrogenous Condensation Products of the Anthraquinone Series. ALFRED SCHAARSCHMIDT (D.R.-P. 251480).—When *o*-diaminoanthraquinones are condensed with benzanthrone or anthraquinone, ω-di- or ω-tri-halogenmethyl derivatives, aldehydes, carboxylic acids, or their chlorides, they furnish iminazole condensation derivatives.

Compounds from the condensation of 1 : 2-diaminoanthraquinone with anthraquinone-2-carboxylic acid and with *benzanthronecarboxylic acid* (a yellow powder obtained from *p*-tolyl-*o*-benzoic acid, glycerol, and sulphuric acid), and from 2 : 3-diaminoanthraquinone with ω-dichloro-β-methylanthraquinone are described. F. M. G. M.

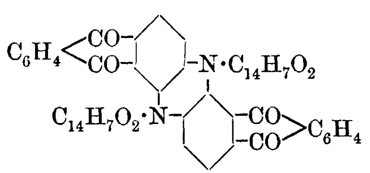
Preparation of Anthraquinone Derivatives containing Nitrogen. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 252529).—The action of aldehydes on aryl-*o*-aminoanthraquinones has previously been described (A., 1907, i, 1085); when these are replaced by ketones the following action occurs:



where A = anthraquinone, and R′ and R aryl or alkyl.

3-Bromo-2-amino-1-*p*-toluidinoanthraquinone (10 parts) when boiled with acetone (10 parts), zinc chloride (5 parts), and acetic acid (100 parts) yields a *compound*, bluish-red needles with metallic lustre; whilst *compounds* from the same base with acetophenone, and with isatin (blue needles), and from 3 : 7-dibromo-2 : 6-diamino-1 : 5-dianilinoanthraquinone with acetone are described in the original. These compounds all furnish soluble *sulphonic acids*, which dye wool in blue shades. F. M. G. M.

[Preparation of Anthracene Derivatives.] FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 251021).—When the dyes obtained from di- and tri-anthrimides by the action of aluminium chloride are treated (in a paste) with sodium hypochlorite at 80° new compounds are formed.



Dianthraquinonylindanthren, $C_{56}H_{26}O_8N_2$ (annexed formula), orange-yellow needles, which decomposes at high temperatures with partial sublimation, is thus obtained from the product furnished by αα-dianthrimide; whilst the dye from 1 : 5-di-α : α-anthriminoanthraquinone and aluminium chloride yields under similar conditions a *compound* consisting of a reddish-brown powder. F. M. G. M.

Indamines. FRITZ ULLMANN and JOHANN GNAEDINGER (*Ber.*, 1912, **45**, 3437—3446).—Indamines are readily obtained by passing air through a cold dilute aqueous solution of equal molecular quantities of a meta-diamine and *p*-aminophenol hydrochloride after the addition of dilute sodium hydroxide (2 mols.); thus *m*-tolylenediamine and *p*-aminophenol yield *2-amino-4′-hydroxy-5-methylindamine*,

$$NH{:}C_6H_2Me(NH_2){:}N{\cdot}C_6H_4{\cdot}OH,$$

decomp. about 165°, green metallic needles containing $3H_2O$. It is readily soluble in aqueous sodium hydroxide, and by reduction with alkaline sodium hyposulphite yields *2 : 4-diamino-4′-hydroxy-5-methyldiphenylamine*, $C_6H_2Me(NH_2)_2{\cdot}NH{\cdot}C_6H_4{\cdot}OH$, m. p. 215°, colourless crystals (*sulphate*, $C_{13}H_{15}ON_3,H_2SO_4$, m. p. 202°). By the prolonged passing of air through its suspension in hot water, the indamine is converted into the *phenazine*, $NH_2{\cdot}C_6H_2Me{<}\overset{N}{\underset{N}{|}}{>}C_6H_3{\cdot}OH$, m. p.

above 360°, red needles with green reflex (*hydrochloride*, m. p. above 360°, red needles with green reflex; *diacetyl* derivative, m. p. 291°, darkening at 282°, yellow crystals).

m-Phenylenediamine and *p*-aminophenol yield Nietzki's so-called aminoindophenol, which, however, on account of its solubility in sodium hydroxide, is more suitably regarded as the hydroxyindamine, $NH{:}C_6H_3(NH_2){:}N{\cdot}C_6H_4{\cdot}OH$. The phenazine obtained by its further oxidation has m. p. above 360°, not 268° as given by Nietzki; also the diacetyl derivative has m. p. 275°, not 258°.

3′-*Chloro-2-amino-4′-hydroxy-5-methylindamine*,

$$NH{:}C_6H_2Me(NH_2){:}N{\cdot}C_6H_3Cl{\cdot}OH,$$

m. p. 185°, metallic violet needles containing H_2O, obtained from *m*-tolylenediamine and 2-chloro-*p*-aminophenol, yields 3′-*chloro-2 : 4-diamino-4′-hydroxy-5-methyldiphenylamine*, m. p. 212°, colourless needles, by reduction, and the *phenazine*, $C_{13}H_{10}ON_3Cl$, m. p. above 360° (*diacetyl* derivative, m. p. 274°), by oxidation.

6-Chloro-*m*-phenylenediamine and *p*-aminophenol yield the *indamine*, $NH{:}C_6H_2Cl(NH_2){:}N{\cdot}C_6H_4{\cdot}OH$, decomp. 108°, metallic violet crystals containing H_2O (the corresponding *phenazine* and its *diacetyl* derivative have m. p. above 360° and 307° respectively), whilst 6-chloro-*m*-phenylenediamine and 2-chloro-*p*-aminophenol yield the *indamine*,

$$NH{:}C_6H_2Cl(NH_2){:}N{\cdot}C_6H_3Cl{\cdot}OH,$$

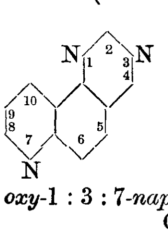
decomp. 128°, metallic violet needles containing H_2O.

By a similar process of oxidation, α-naphthol and *p*-aminophenol yield the *dihydroxyindonaphthol*, $OH{\cdot}C_6H_4{\cdot}N{:}C{<}\begin{matrix}C_6H_4\text{———}\\ CH{:}C(OH)\end{matrix}{>}CO$, m. p. 298°, glistening, green leaflets changing to a red powder at 120°. This substance, the constitution of which is proved by its formation from potassium β-naphthaquinone-4-sulphonate and *p*-aminophenol hydrochloride in cold aqueous solution, condenses with *o*-phenylenediamine in alcoholic solution to form the *hydroxyanilinonaphthazine*,

$$OH{\cdot}C_6H_4{\cdot}NH{\cdot}C_{10}H_5{<}\begin{matrix}N\\ |\\ N\end{matrix}{>}C_6H_4,$$

m. p. 291°, orange crystals. C. S.

Synthesis of 1 : 3 : 7-Naphtha*iso*triazines: Derivatives of a New Heterocyclic System. MARSTON T. BOGERT and HARRY LINN FISHER (*J. Amer. Chem. Soc.*, 1912, **34**, 1576—1580).—In another paper (this vol., i, 98) the authors have described 5-aminoquinoline-6-carboxylic acid, its acetyl derivative, and the lactam of the latter. From these substances, compounds have been prepared containing the new nucleus (annexed formula), which is designated the 1 : 3 : 7-naphtha*iso*triazine nucleus.



2 : 3-*Dihydro-1 : 3 : 7-naphtha*iso*triazine-4-one* (4-*hydroxy-1 : 3 : 7-naphtha*iso*triazine*),

$$\begin{matrix}CH{=}N\\ |\\ NH{\cdot}CO\end{matrix}{>}C_9NH_5 \rightleftarrows \begin{matrix}CH{=}N\\ |\\ N{:}C(OH)\end{matrix}{>}C_9NH_5,$$

m. p. 298·7° (corr.), obtained in 10% yield by heating 5-aminoquinoline-6-carboxylic acid with excess of formamide at 140° in

a sealed tube, crystallises in lustrous, pink prisms. The *2-methyl* derivative, m. p. above 300° (decomp.), prepared by boiling the lactam of 5-acetylaminoquinoline-6-carboxylic acid with solution of ammonia, forms slender, yellow needles, and, when heated with benzaldehyde and a few drops of acetic anhydride, yields the *2-styryl* derivative, $CHPh{:}CH{\cdot}C_{11}H_6ON_3$, m. p. above 300° (decomp.), as a yellow, crystalline powder. The 2 : 3-*dimethyl* derivative,

$$\begin{matrix} CMe{=}N \\ | \\ NMe{\cdot}CO \end{matrix}{>}C_9NH_5,$$

m. p. 178° (uncorr.), prepared by the action of methylamine on the lactam, crystallises in long, yellow needles. The *2-methyl-3-ethyl*, *2-methyl-3*-n-*propyl*, *3-phenyl-2-methyl*, and *3*-p-*anisyl-2-methyl* derivatives have m. p. 152·5° (uncorr.), 121—122° (uncorr.), 263—263·5° (corr.), and 246·9—247·9° (corr.) respectively. The *3-amino-2-methyl* derivative, m. p. 256·7° (corr.), obtained by the action of hydrazine on the lactam, is colourless; the *3-acetylamino-2-methyl* derivative has m. p. 268·5—269·5° (corr.), and the *3-benzylideneamino-2-methyl* derivative, m. p. 222·6° (corr.). The *3-anilino-2-methyl* derivative, $\begin{matrix} CMe{=\!=\!=}N \\ | \\ N(NHPh){\cdot}CO \end{matrix}{>}C_9NH_5$, m. p. 249·5—250·5° (corr.), crystallises in pale brown needles.

1 : 2 : 3 : 4-*Tetrahydro*-1 : 3 : 7-*naphtha*iso*triazine*-2 : 4-*dione* (2 : 4-*dihydroxy*-1 : 3 : 7-*naphtha*iso*triazine*),

$$\begin{matrix} CO{\cdot}NH \\ | \\ NH{\cdot}CO \end{matrix}{>}C_9NH_5 \rightleftharpoons \begin{matrix} C(OH){:}N \\ | \\ N{:}C(OH) \end{matrix}{>}C_9NH_5,$$

m. p. above 300°, is obtained as a yellow or brown powder by fusing a mixture of 5-aminoquinoline-6-carboxylic acid and carbamide.

E. G.

[Preparation of Anthracene Derivatives.] CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 253088).—It is found that the previously described ψ-azimino-compounds (A., 1912, i, 1035) obtained by oxidising the azo-compound formed by coupling 2-aminoanthracene with diazotised 2-aminoanthraquinone can be nitrated, and the so-obtained *nitro-* or *dinitro*-compounds reduced with sodium sulphide or alkaline sodium hyposulphite to the corresponding *amino-* or *diamino*-compounds. The nitrated products are greenish-yellow, and the amino-derivatives, brownish-black, powders.

F. M. G. M.

Methyliminothiotriazine. ADRIANO OSTROGOVICH (*Chem. Zentr.*, 1912, ii, 607; from *Bull. Soc. Şti. Bucureşti*, 1912, 21, 27—31).—The 2-imino-6-thiol-4-methyl-1 : 3 : 5-triazine, already described (A., 1912, i, 320), on oxidation with nitric acid (D 1·4) yields cyanuric acid, and with alkaline permanganate gives iminoketomethyltriazine (A., 1904, i, 832), the picrate of which melts at 221—221·5°, not 121—121·5° as stated previously. Iminothiolmethyltriazine does not give up its sulphur to mercuric oxide, but yields a stable mercury salt when mercuric chloride is added to its solutions in aqueous sodium hydroxide.

T. A. H.

Quadriurates. WILLEM E. RINGER and J. I. J. M. SCHMUTZER (*Zeitsch. physiol. Chem.*, 1912, 82, 209—220. Compare Kohler, A., 1911, i, 243, 690).—The hypothesis that the so-called quadriurates are mixed crystals has been tested experimentally, a series of quadriurates of varying composition having been examined chemically and crystallographically. This hypothesis is satisfactory when it is assumed that the urates represent solid solutions of uric acid in ordinary mono-metal urates, which are formed at high temperatures, but are unstable at lower temperatures, and tend to part with the excess of uric acid.

E. F. A.

Preparation of Aminobenzoylamino-compounds FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 252376).—When sodium diaminobenzoyldiaminostilbenedisulphonate is fused during half an hour with *p*-nitrobenzoyl chloride and the *di*-p-*nitrobenzoyl* derivative subsequently reduced with iron and acetic acid, it furnishes the *compound*, $C_2H_2[C_6H_3(SO_3Na)\cdot NH\cdot CO\cdot C_6H_4\cdot NH\cdot CO\cdot C_6H_4\cdot NH_2]_2$.

Other analogous compounds with valuable tinctorial properties can be obtained in the benzidine, tolidine, or dianisidine series.

F. M. G. M.

Separation of Proteoses by Ultra-filtration. EDGARD ZUNZ (*Bull. Acad. roy. Belg.*, 1912, 656—674. Compare A., 1911, i, 1050). —The composition of the filtrate obtained from identical solutions of Witte's peptone, submitted under the same conditions to Bechhold's method of ultra-filtration, varies appreciably from filter to filter, although the latter are made as alike as possible. Further, the filtrate varies during the course of the same experiment, at one time the ultrafilter allowing certain proteoses to pass and at another time retaining a portion of them. The four groups of proteoses established by Pick cannot be satisfactorily separated by successively employing ultrafilters with smaller and smaller pores. The ultra-filtration causes a dissociation of each of these groups of proteoses into several fractions. In these groups the proteoses, the aliphatic amino-nitrogen of which can be detected by van Slyke's method, pass completely through an ultra-filter made by means of a 6% collodion solution. W. G.

Changes in the Physical Conditions of Colloids. XIV. The Hydration of Various Protein Compounds, with Special Reference to the Action of Caffeine. WOLFGANG PAULI and OSKAR FALEK (*Biochem. Zeitsch.*, 1912, 47, 270—299).—The general theory of Pauli's as to the high degree of hydration of the protein ion is confirmed by a series of measurements of the changes of viscosity of well dialysed gelatin solutions on addition of acids and alkalis, in both of which cases well-marked maxima are observed. According to the theory, salts combine with the protein, and when these are present, the number of free proteins ions is diminished. The addition of salts diminishes the viscosity, and this effect was quantitatively measured in the case of several salts.

Caffeine has, however, a peculiar action on the ox- and horse-serum proteins, in that it increases the viscosity of the acid-protein mixtures

(and according to Pauli the state of hydration in solution). This effect has been measured in a large number of cases. The magnitude of the effect is also influenced by the nature of the acid employed. A similar effect was produced by theophylline, but not by diethylglycinamine caffeine or caffeine ethylenediamine, both of which produce a depression of viscosity. Caffeine does not effect the hydration of gelatin or fibrin, as it does not cause these substances to take up more water. The reason of the peculiar action of caffeine on certain proteins may be due to formation of complex double compounds. It does not appear to be due to direct salt formation, as determined by the effect of addition of caffeine to protein solutions on the electrolytic conductivities, the osmotic pressures, or the hydrogen-ion concentrations as measured by the electrometric method. S. B. S.

The Oxidation Relations of Certain Heavy Metals in Combination with Protein, and Some Physico-chemical Properties of the Same. II. CARLO CERVELLO and CORRADO VARVARO (*Arch. expt. Path. Pharm.*, 1912, **70**, 369—374).—The coagulation rate of zinc albuminate and mercury albuminate is greater than that of the simple protein, but less than that of the albuminates of manganese and copper. Iron albuminate is not altered by boiling. Complete coagulation with precipitation of denaturated protein is only obtained with zinc albuminate. In weakly acid or neutral solutions, the other metallic albuminates give only a cloudy fluid on heating: this is most marked with mercury, and least with manganese albuminate. In reference to their oxidative powers, as measured by the effect on indigotin and similar substances, the albuminates of iron and copper are most energetic; those of mercury, zinc, and manganese follow in the order named. The albuminates therefore behave like simple metallic salts. W. D. H.

The Kyrine Fraction obtained on Partial Hydrolysis of Proteins. I. PHŒBUS A. LEVENE and F. J. BIRCHARD (*J. Biol. Chem.*, 1912, **13**, 277—289).—Siegfried's hypothesis regarding kyrine is that it is a fragment of the protein molecule which resembles natural protamines. The kyrine fraction obtained in the present research by Siegfried's method of partial hydrolysis of gelatin yielded on hydrolysis arginine, lysine, glutamic acid, glycine, and proline in peptide linking. Probably two peptides were present, one containing lysine and three monoamino-acids, and the other, arginine and one monoamino-acid. Further investigations are being prosecuted. W. D. H.

The Isoelectric Point of Casein. LEONOR MICHAELIS and H. PECHSTEIN (*Biochem. Zeitsch.*, 1912, **47**, 260—268).—The isoelectric point was determined by ascertaining the optimal mixture for precipitation of sodium acetate and acetic acid solutions, and also by the method of electrocataphoresis. In the former case the salt concentrations in the various series of experiments were kept constant, and in the latter case, the salt content was kept very low. By these methods the isoelectric point was found to be $2{\cdot}5 \times 10^{-5}$ and $2{\cdot}4 \times 10^{-5}$.

respectively. In the presence of salts a certain asymmetry of behaviour was observed, in that after twenty-four hours excess of acid above the isoelectric point allowed greater precipitation than deficit of acid.

S. B. S.

Blood Pigment. LÉON MARCHLEWSKI (*Zeitsch. physiol. Chem.*, 1912, 82, 413—414. Compare Grabowski and Marchlewski, A., 1912, i, 1015).—The conclusion that hæmopyrrole whether derived from blood pigment or chlorophyll contains 3-methyl-4-ethylpyrrole is confirmed by Piloty and Stock (A., 1912, i, 923), who obtain the same substance from hæmin. The synthesis of chlorophyll in plants begins probably with that of 3-methyl-4-ethylpyrrole. E. F. A.

Nomenclature of Derivatives of the Blood Pigment. KARL BÜRKER (*Zeitsch. physiol. Chem.*, 1912, 82, 346).—Instead of Abderhalden's (A., 1912, i, 521) nomenclature of hæmatin for hæmochromogen and oxyhæmatin for hæmatin, it is suggested to use the terms reduced hæmatin and oxyhæmatin. E. F. A.

Methylation of Hæmin. IV. WILLIAM KÜSTER (*Zeitsch. physiol. Chem.*, 1912, 82, 113—159).—In the preparation of hæmin by Mörner's method using methyl alcohol, a crude product is obtained in satisfactory amount containing very little protein, which usually consists mostly of methylhæmin mixed with a little dimethylhæmin. There is evidence that there are two methylhæmins, one or the other being formed from ox-blood according to the conditions. One isomeride is insoluble in 5% sodium carbonate; the other is soluble in sodium carbonate, and also in 0·7% potassium carbonate. The dissolved dye contains chlorine.

The first isomeride loses chlorine without dissolving, and forms a methylhæmatin; a similar compound is formed by the action of methyl-alcoholic sodium hydroxide.

The dehydrochloride products prepared from the methylhæmins are of different composition, the one being normal, the other having taken up a molecule of water.

Methylhæmatin and hæmatin when dissolved in methyl alcohol containing sulphuric acid and the boiling solution precipitated by hydrochloric acid yield dimethylated products which do not contain the calculated proportion of chlorine for hæmin derivatives and are soluble in acidified methyl alcohol. Dehydrochloromethylhæmin under similar treatment does not show a complete addition of hydrogen chloride.

Dehydrochlorohæmin is converted into dimethylhæmin. Dimethylhæmin forms a dimethylated dehydrochloro-product.

Methylhæmin is hydrolysed by more than three molecules of 1% sodium hydroxide in the cold; dimethylhæmin requires warming to effect hydrolysis. Dimethylhæmin is readily converted into dimethylhæmatin by the action of methyl alcoholic sodium hydroxide.

E. F. A.

Preparation of Hæmatoporphyrin from Carbon Monoxide Blood. VINZENZ ARNOLD (*Zeitsch. physiol. Chem.*, 1912, 82, 273—275).—Pure hæmatoporphyrin, particularly suited for spectroscopic work and free from brown-coloured impurities, is obtained by completely replacing the oxygen in blood by carbon monoxide before acting on it with sulphuric acid. E. F. A.

Formation of Porphyrin. HANS FISCHER and FRIEDRICH MEYER-BETZ (*Zeitsch. physiol. Chem.*, 1912, 82, 96—108).—The exact conditions for the preparation of mesoporphyrin are described. On oxidation with lead peroxide in acid solution, methylethylmaleinimide,

$$NH<\begin{matrix}CO\cdot CEt \\ \Vert \\ CO\cdot CMe\end{matrix},$$

and hæmatic acid, $NH<\begin{matrix}CO\cdot CMe \\ \Vert \\ CO\cdot C\cdot CH_2\cdot CH_2\cdot CO_2H\end{matrix}$, are obtained. On reduction by means of hydrogen iodide in acetic acid and phosphonium iodide, the same products were obtained as are given by hæmin, including hæmopyrrole and phonopyrrolecarboxylic acid. Mesoporphyrin is considered to be a simple reduction product of hæmin minus its iron. Possibly the porphyrin spectrum is due to the elimination of the complex iron grouping from hæmin; in fact, the complex iron salt of porphyrin shows the hæmin spectrum. It is probable that two alcoholic hydroxyl groups are reduced in the formation of mesoporphyrin.

Pure mesoporphyrin has no poisonous photobiological action, whereas hæmatoporphyrin when injected subcutaneously into mice which are exposed to light causes death. E. F. A.

[Guanylic Acid.] IVAR BANG (*Biochem. Zeitsch.*, 1912, 46, 500—501).—The author believes that the guanylic acid recently isolated in the form of a crystalline brucine salt by Levene and Jacobs (A., 1912, i, 926) is not guanylic acid itself, but a scission product. S. B. S.

The Pentose of Guanylic Acid. KG. O. AF KLERCKER (*Biochem. Zeitsch.*, 1912, 47, 331—342).—The author gives a general view of the literature concerning the sugar derived from the pancreatic nucleic acid, guanylic acid, and allied substances. He prepared the osazone from guanylic acid, and obtained rotations of $-0{\cdot}59$ to $-0{\cdot}64°$ for 0·2 gram in 10 c.c. for various preparations recrystallised from alcohol. For *l*-arabinose preparations obtained in the same way he obtained numbers from $+0{\cdot}62$ to 0·69°, and for *l*-xylose preparations $-0{\cdot}67$ and 0·70°. The sugar from which the guanylic acid pentosazone was prepared was lævorotatory, and as xyloses yield osazones which rotate in the opposite direction to the sugars themselves, the conclusion is drawn that the guanylic acid pentose is not *l*-xylose, but probably belongs to the *d*-arabinose group. The conclusion is also supported by the general character of the osazones as regards behaviour on crystallisation and appearance. Nevertheless, the author states that the optical properties of the phenylpentosazones do not

form a satisfactory criterion for distinguishing between the various sugars. S. B. S.

The Optimal Hydrogen-ion Concentration for the Liquefaction of Gelatin by Trypsin. SVEN PALITZSCH and L. E. WALBUM (*Biochem. Zeitsch.*, 1912, **47**, 1—35).—Fermi's method was employed, but was modified in two particulars, in that, firstly, boracic acid was added to the gelatin to avoid change of hydrogen-ion concentration during the digestion, and, secondly, the digestion mixture was neutralised after completion of the action of trypsin, so that the actual cooling process took place at the same hydrogen-ion concentration, for it was found that solutions of undigested gelatin solidified more slowly in alkaline than in neutral solutions in the absence of boric acid, although there was not much difference when this acid was present. By means of this method it was found that the optimal conditions for liquefaction were at the following hydrogen-ion concentrations: at 30°, $10^{-9\cdot9}$; at 37°, $10^{-9\cdot7}$; at 45°, $10^{-9\cdot1}$; at 55°, $10^{-8\cdot0}$; that is to say, the higher the temperature, the nearer to the neutral point is the hydrogen-ion concentration for tryptic activity when measured by the Fermi process. S. B. S.

The Mechanism of Pepsin Digestion. JOHANNE CHRISTIANSEN (*Biochem. Zeitsch.*, 1912, **47**, 226—249).—The viscometric method was adopted, and in the preliminary experiments on the action of acid on genuine proteins (dialysed serum proteins, etc.), it was found that the addition of acid increased the viscosity of the solutions up to a certain maximum point, after which further additions caused a diminution. The Günzburg reaction for hydrochloric acid becomes positive at the point of maximal viscosity, thus bearing out Pauli's theory that at this point the solution contains essentially chlorine ions and heavily hydrated protein ions. The viscosity is diminished by filtration through paper, more especially when only just sufficient acid is present to produce the maximum readings. With larger excess of acid, the effect of filtration becomes less marked. Similar results were obtained on filtration of mixtures of protein and alkali, and the results indicate that the protein ion is adsorbed by the paper. In investigating the action of pepsin, viscosity changes of mixtures having the same initial viscosity but different amounts of acid (that is, amounts of acid less and more than necessary to produce a mixture with the maximum viscosity) were chosen. It was found that such corresponding mixtures, under the influence of pepsin, changed their viscosities at the same rate, which fact seems to indicate that in the neighbourhood of maximal viscosity the rate of pepsin action is independent of the hydrogen-ion concentration. This result is not in accordance with results obtained with coagulated egg-white, which requires a certain excess of acid for maximal digestion rate. The difference is ascribed to the change in the character of the protein. Preliminary experiments carried out with dialysed sheep serum-albumin, in which the rate of formation of acid albumin was ascertained (this is only formed in this case when pepsin is present as well as acid), also indicated that the maximum rate of formation of this product takes place at the

point of maximum viscosity (that is, when there are the maximum number of protein ions present). S. B. S.

The Enzymes of the Pancreas. I. The Generation of Trypsin from Trypsinogen by Enterokinase. JOHN MELLANBY and V. J. WOOLLEY (*J. Physiol.*, 1912, **45**, 370—388).—The time occupied in activating trypsinogen by enterokinase is a function of the amount of the latter enzyme added. As the action proceeds, trypsin is produced at a constantly increasing rate. The reaction is accelerated by rise of temperature; it occurs best in a neutral medium, is delayed by alkali, and stopped by acid. There is no evidence that trypsin can activate trypsinogen, or that trypsin acts as a co-enzyme to enterokinase. Proteins apparently delay activation, because the trypsin first formed is adsorbed by the protein; the delay varies in different proteins. The following theory is advanced: Enterokinase is a proteolytic enzyme acting best in a neutral medium; trypsinogen contains a protein moiety with which trypsin is combined, and in this combination the proteolytic properties of trypsin are masked. The generation of trypsin from trypsinogen by enterokinase depends on the adsorption of the enterokinase by the protein moiety of the trypsinogen; digestion of the protein moiety follows, and trypsin is thus liberated. W. D. H.

Action of Hydrogen Chloride on Invertase. II. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1912, **82**, 377—390. Compare following abstract).—Purified invertase takes up considerable quantities of hydrogen chloride, losing its specific activity. The greater part of the hydrogen chloride is removed on keeping in a vacuum, but the hydrolytic activity is not regained.

The invertase preparation contained 5·57% of nitrogen, 2·3% being amide nitrogen and 3·17% titratable in presence of formaldehyde. The ash amounted to 22·2%; the acidity was five to six times as large as in the case of purified diastase.

The destruction of the enzymic activity is not due to the formation of salts with the basic or other atomic groups of the enzyme, but the action of the acid reduces the amount of nitrogen which can be titrated in presence of formaldehyde, pointing to the formation of condensation products between the carboxyl and amino-groups.

The active component of invertase accordingly possesses a different constitution from that of diastase. E. F. A.

Action of Hydrogen Chloride on Diastase. I. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1912, **82**, 276—325).—When dry hydrogen chloride is passed over purified diastase the enzyme takes up a good deal of the gas, forming with it a loose chemical compound; the enzyme loses its specific activity. On exposure in a vacuum the hydrogen chloride is removed and the activity of the enzyme restored. It is shown that the hydrogen chloride is not fixed to the amide or secondary nitrogen atoms of the enzyme complex, and that only part is attached to the basic groups. The action of the acid does not cause any particular hydrolysis of the enzyme molecule. The specific

enzyme action of diastase is due to the atomic groups which can fix hydrogen chloride. E. F. A.

Malt Diastase, and the Action of Potassium Phosphates on It. RUTGER C:SON HEYL (*J. pr. Chem.*, 1912, [ii], **86**, 433—457).—The author has studied the diastatic hydrolysis of starch under various conditions by determining the amount of maltose produced, according to Bertrand's method (A., 1907, ii, 136).

In the first part of its course, the diastatic actions follow the logarithmic curve, and in such a manner as if only a part of the starch were capable of hydrolysis.

The magnitude of this part depends on the concentration of the starch and of the enzyme, and also on the presence of electrolytes and proteins. In the last part of its course, the reaction proceeds with extreme slowness.

Potassium dihydrogen phosphate exercises an activating influence on the enzyme, and the same is true with respect to the action of dipotassium hydrogen phosphate on old solutions of the enzyme; in freshly prepared solutions the latter salt exerts a retarding influence.

The activating action of the phosphates is considerably influenced by the presence of proteins in the enzyme solutions. F. B.

Reaction between Enzymes and Other Substances. SVEN G. HEDIN (*Zeitsch. physiol. Chem.*, 1912, **82**, 175—178).—Introductory to following paper. W. D. H.

The Action of Certain Colloids on the Inhibition of Enzyme-actions. G. JAHNSON-BLOHM (*Zeitsch. physiol. Chem.*, 1912, **82**, 178—208).—Saponin completely hinders the inhibitory effect of charcoal on rennet, and partly that of normal serum. The saponin appears to liberate the enzyme which is adsorbed by the charcoal, and the reaction is a rapid one. It is accelerated by elevation of temperature, and by increase in the amount of saponin. Saponin increases the inhibitory effect of immune serum on rennet. Saponin partly activates a solution of rennet-zymogen. It acts similarly on trypsin adsorbed by charcoal, but has no effect on the antitryptic action of serum-albumin. Cholesterol acts like saponin on charcoal and rennet, but increases the inhibitory effect of normal serum. It has no influence on the antitryptic action of charcoal and serum-albumin. Egg-white if treated with hydrochloric acid and neutralised, partly inhibits the anti-rennetic power of normal serum. W. D. H.

The Coagulation of Milk by Rennet. JOHN MELLANBY (*J. Physiol.*, 1912, **45**, 345—362).—The clotting of milk by pancreatic rennet follows the same general laws as that by gastric rennet, but the two enzymes are distinct, because they differ in the effect of alkali on them; their anti-enzymes in serum are specific, and pancreatic rennet requires a greater amount of calcium than gastric rennet does. In the case of both enzymes, calcium salts may be replaced by salts of barium, strontium, or magnesium. There is no indication from electrical conductivity determinations that calcium enters into chemical com-

bination during the curdling process. The hypothesis is advanced that all proteolytic enzymes curdle milk, provided suitable conditions are provided; those, like pepsin, which act best in an acid medium requiring less calcium than those which, like trypsin, act in a alkaline medium. The coagulation of milk is due to the adsorption of the enzyme by the caseinogen, and the enzyme-caseinogen complex is precipitated by the bivalent calcium ions of the milk; the quantity of ionised calcium salt required to effect precipitation is intimately related to the quantity of enzyme adsorbed. A method based on this hypothesis is described for the detection and estimation of proteolytic enzymes. W. D. H.

The Biochemical Rôle of Peroxydases in the Transformation of Orcinol into Orcein. JULES WOLFF (*Compt. rend.*, 1912, 155, 1031—1032. Compare A., 1912, i, 928).—The action of ammonia and atmospheric oxygen on orcinol in dilute solutions is a very slow oxidation, this being the first condition for the formation of orcein. The introduction of a peroxydase influences far more the formation of the colouring matter than the amount of oxygen absorbed. W. G.

The Nomenclature of the Polyphenoloxydases. FR. BATELLI and (Mlle.) LINA STERN (*Biochem. Zeitsch.*, 1912, 46, 395—396).—The authors recommend the term *polyphenoloxydase* to indicate an enzyme which accelerates the oxidation of polyphenols and the corresponding amino-derivatives. Such ferments are to be distinguished from those of the character of tyrosinase, which acts similarly on monophenols, and which are designated simply *phenoloxydases*. The expression phenolase is to be avoided in this sense, as it indicates a ferment which accelerates the hydrolysis of an aromatic ester. S. B. S.

Preparation of Organic Arsenic Compounds. HEINRICH BART (D.R.-P. 250264. Compare La Costa and Michaelis, A., 1880, 396; Schraube and Schmitt, A., 1894, i, 237).—The following organic arsenic compounds have been obtained by treating diazotised solutions of the following bases with sodium arsenite and subsequently heating in the presence of sodium hydroxide until the evolution of nitrogen ceases. p-*Bromophenylarsinic acid* (colourless needles) from *p*-bromoaniline; o-*benzoarsinic acid* (colourless needles) from *o*-amino-benzoic acid; p-*acetylaminophenylarsinic acid* from monoacetyl-*p*-phenylenediamine; *p*-tolylarsinic acid (Abstr., 1880, 396) from *p*-toluidine: and *compounds* from potassium *iso*diazobenzene and *o*-nitro*iso*diazobenzene; from 4-nitro-2-aminophenol; from *p*-nitro-aniline (which is best decomposed in tartaric or oxalic acid solutions), and from the same base decomposed in the presence of sodium *p*-nitro-phenylarsenite; whilst *p*-aminophenylarsinic acid furnishes *benzene*-p-*diarsinic acid*.

The *sodium* salts of these compounds are colourless or grey needles, and the original contains numerous formulæ illustrating possible phases in their formation. F. M. G. M.

Preparation of Derivatives of 3 : 3′-Diamino-4 : 4′-dihydroxyarsenobenzene. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 250745).—When 3 : 3′-diamino-4 : 4′-hydroxyarsenobenzene is treated with halogenated acetic acid (or its homologues) in aqueous alkaline solution it yields neutral, soluble compounds of therapeutic value.

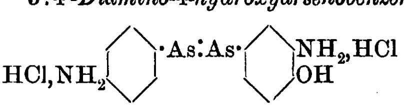
The *compound*, $NH_2 \cdot C_6H_3(OH) \cdot As \colon As \cdot C_6H_3(OH) \cdot NH \cdot CH_2 \cdot CO_2H$, is obtained when 3 : 3′-diamino-4 : 4′-dihydroxyarsenobenzene (100 parts), dissolved in a mixture of methyl alcohol (300 parts), and water (300 parts) containing sodium hydroxide (4 mols.), is treated with chloroacetic acid (50 parts) and potassium iodide (36 parts) and heated at 60—65° during two to three hours in an indifferent gas with exclusion of air; the product is isolated by the limited addition of acid. The brownish-yellow *sodium* salt is precipitable with alcohol; the *potassium* and *ammonium* salts forms similar powders.

The *compound*, $NH_2 \cdot C_6H_3(OH) \cdot As \colon As \cdot C_6H_3(OH) \cdot NH \cdot CHMe \cdot CO_2H$, a yellow powder, is prepared in a similar manner with α-bromopropionic acid, and furnishes *alkali* salts, whilst *diaminodihydroxyarsenobenzenediacetic acid*, $As_2[C_6H_4(OH) \cdot NH \cdot CH_2 \cdot CO_2H]_2$, is obtained with bromoacetic acid.

F. M. G. M.

Preparation of Unsymmetrical Aromatic Arseno-compounds. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 251104).—When an equimolecular mixture of two arylarsinic acids (or oxides) is reduced it yields an unsymmetrical aromatic arseno-compound.

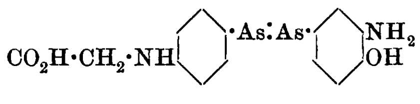
3 : 4′-*Diamino-4-hydroxyarsenobenzene hydrochloride* (annexed formula),



a yellow, microcrystalline powder, is obtained as follows: *p*-Aminophenylarsinic acid (21·7 parts) or its equivalent of *p*-aminophenylarsenious oxide (A., 1909, i, 347) and 23·3 parts of 3-amino-4-hydroxyphenyl-1-arsinic acid (A., 1910, i, 803) in methyl alcohol (100 parts) and concentrated hydrochloric acid (39 parts) is slowly stirred into a mixture of stannous chloride (100 parts) dissolved in alcohol (300 parts) to which has been added 500 parts of alcohol saturated with hydrogen chloride and 17 parts of hydriodic acid (D 1·7), the temperature meanwhile being maintained at −5° to −10°; the product is slowly precipitated in crystalline form. The *sulphate* forms a flocculent, yellow insoluble precipitate.

Phenylglycylarsenious chloride, $AsCl_2 \cdot C_6H_4 \cdot NH \cdot CH_2 \cdot CO_2H,HCl$, a crystalline paste which can be washed with acetic acid and ether, is prepared by reducing a concentrated hydrochloric acid solution of phenylglycylarsinic acid (to which a trace of hydriodic acid has been added) with sulphurous acid at −10°; it is decomposed readily by alkalis to the corresponding hydroxide.

3-*Amino-4-hydroxy-4′-glycylarsenobenzene* (annexed formula) is ob-



tained as a viscous, yellow paste when molecular proportions of the foregoing chloride and 3-amino-4-hydroxyphenyl-

arsenious oxide (A., 1911, i, 1055) in methyl-alcoholic solution are reduced with sodium hyposulphite at the ordinary temperature.

3′: 5′-*Dichloro-3-amino-4 : 4′-dihydroxyarsenobenzene*, a yellow powder, is prepared from 3-amino-4-hydroxyarsenious oxide and 3 : 5-*dichloro-4-hydroxyphenylarsenious oxide*, $AsO\cdot C_6H_2Cl_2\cdot OH$, which latter compound is obtained by the reduction of dichloro-*p*-hydroxyphenylarsinic acid (*loc. cit.*); 3-*amino-4-hydroxyarsenobenzene*, $C_6H_5\cdot As_2\cdot C_6H_3(NH_2)\cdot OH$, a fawn-yellow powder, is prepared from phenylarsenious oxide and 3-amino-4-hydroxyphenylarsenious oxide. F. M. G. M.

Preparation of Products Reduced Beyond the Arseno-stage from Substituted Aromatic Arsinic Acids. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 251571).—It is found that when powerful reducing agents (such as tin, zinc, or iron) in concentrated acid solution act on arylarsinic acids that they can be reduced beyond the arseno-condition (compare Palmer and Dehn, A., 1902, i, 86).

The following *compounds* are described:

(1) From *p*-hydroxyphenylarsinic acid as a colourless precipitate, soluble in alkalis, and isolated by means of carbon dioxide; it darkens at 75° and decomposes violently at 155°.

(2) From *p*-aminophenylarsinic acid, a colourless oil, b. p. 132°/10 mm., which exposed to air is rapidly converted into diaminoarsenobenzene.

(3) From phenylglycylarsinic acid, a colourless precipitate which rapidly darkens, and is isolated in the form of its *zinc* salt.

(4) From 3-nitro-4-hydroxyphenylarsinic acid (A., 1910, i, 803), isolated as its *zinc* salt; the free *arsine* is a colourless powder darkening at 100° and decomposing violently at 135°.

F. M. G. M.

Formation of Organo-metallic Compounds during Electrolytic Reductions. JULIUS TAFEL (*Ber.*, 1912, **45**, 3321).—Polemical against Law (T., 1912, **101**, 1016, 1544). A claim for priority. Law's statement that the formation of organo-metallic compounds at mercury cathodes has never been observed is incorrect (compare A., 1906, i, 941; 1911, i, 764). T. S. P.

Chemico-therapeutical Researches on Mercury Compounds. Mercuridi-*p*-aminophenol. ERNEST FOURNEAU and A. VILA (*J. Pharm. Chim.*, 1912, [vii], **6**, 433—441).—p-*Nitrophenylmercuric acetate*, $C_8H_7O_5NHg$, obtained by the action of mercuric acetate on sodium *p*-nitrophenol dissolved in boiling water, crystallises in flattened, colourless needles, and on treatment with carbon dioxide furnishes the corresponding *oxide* (compare A., 1911, i, 1056). The latter by a complex series of reactions, which are discussed in detail in the original, gives with sodium sulphide, *sodium di*-p-*nitromercuridiphenol*, $C_{12}H_{10}O_6N_2HgNa_2$, crystallising in garnet-red needles, from which the corresponding *mercuridi*-p-*nitrophenol* is liberated by the action of acids. This on reduction in alkaline solution by sodium hyposulphite yields *di*-p-*aminomercuridiphenol*, $Hg[C_6H_3(OH)NH_2]_2$, crystallising in heavy needles, insoluble in water, but readily soluble in alcohol; the *hydrochloride* forms brilliant needles soluble in water. The free base oxidises rapidly in alkaline solution on exposure to air.

This substance is toxic, producing the ordinary symptoms of mercurial poisoning, due no doubt to the liberation of simple mercury derivatives by oxidation in the organism. The *acetyl* derivative crystallises in slender needles, is soluble in alkalis, forming stable solutions, and is much less toxic than the parent base. T. A. H.

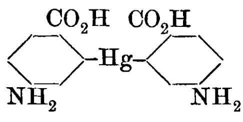
Preparation of Nuclear-substituted Mercury Derivatives of Polysubstituted Phenols. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 250746. Compare A., 1911, i, 1056; 1912, i, 754).—Organic mercury compounds have previously been prepared (compare Dimroth, A., 1902, i, 656, and *loc. cit.*), and the following more complex derivatives are now described.

The crystalline *compound*, $OH\cdot C_6H_2Me_2\cdot Hg\cdot OAc$, is obtained when 12 parts of *p*-xylenol (A., 1878, ii, 410) dissolved in methyl alcohol are treated with mercuric acetate (30 parts) in water (100 parts) and gently warmed until the addition of an alkaline hydroxide ceases to precipitate mercuric oxide.

Similar *compounds* from creosol, pyrogallol 1 : 3-diethyl ether (A., 1878, ii, 869), and from bromo-*p*-xylenol (A., 1878, ii, 410) are described in the original. F. M. G. M.

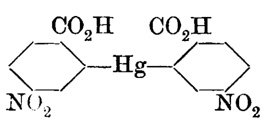
Preparation of Derivatives of Aminobenzoic Acid and its Salts Containing Mercury in the Ring. VEREINIGTE CHEMISCHE WERKE AKTIENGESELLSCHAFT (D.R.-P. 249725).—When the mercury salts of *o*-, *m*- or *p*-nitrobenzoic acid are heated during some hours at about 225°, the mercury becomes attached to a ring carbon atom; these *nitro*-compounds can then be reduced to the corresponding amines.

pp-*Diamino*-oo′-*mercuridibenzoic acid* (annexed formula), a colourless (to yellow) crystalline powder, is obtained by reducing the nitro-compound with ferrous sulphate in alkaline solution; the crystalline *hydrochloride* can be isolated by means of alcohol. The *barium*, *calcium*, *silver*, and *lead* salts are precipitable; the nickel salt gives a greenish-blue, and the iron salt a brown, solution; the green solution of the copper salt becomes brown when boiled, a characteristic which distinguishes it from the solution of the copper salt of the nitro-compound, which is blue and unaffected by boiling.



The ortho- and meta-compounds have similar reactions, and are obtained by the same method; or the mercury salt can be replaced by other salts of aminobenzoic acids, which are then heated with a salt of mercury. F. M. G. M.

Preparation of Dinitrodiphenylmercuridicarboxylic Acids. VEREINIGTE CHEMISCHE WERKE AKTIEN GESELLSCHAFT (D.R.-P. 251332. Compare preceding abstract).—A further account of the preparation of *pp*-dinitro-*oo*′-mercuridibenzoic acid, in which a catalyst, such as stannous chloride or ferrous hydroxide, is employed to assist the condensation; together with the preparation and properties of the *sodium*, *silver*, *barium*, *nickel*, and *cobalt* salts.



mm'-Dinitro-*oo'*-mercuridibenzoic acid and its *sodium*, *silver*, *barium*, *nickel*, and *iron* salts are also described; the salts of these compounds are extremely poisonous, and possess a powerful therapeutic action. F. M. G. M.

Preparation of Esters of Aromatic Carboxylic Acids containing Mercury and their Products of Hydrolysis. WALTER SCHOELLER and WALTHER SCHRAUTH (D.R.-P. 248291. Compare A., 1912, i, 754).—When glycyl salicylate (182 parts) and mercuric acetate (318 parts) are boiled together during several hours in methyl-alcoholic solution, a crystalline *ester*, m. p. 165—170° and containing 45·5% Hg, is obtained, which, on hydrolysis, furnishes a compound identical with "hydrargyrum salicylicum." Methyl anthranilate (165 parts) under similar conditions furnishes a *product*, m. p. 191°, containing 47·28% Hg, and on hydrolysis an inner *anhydride* containing 57·3% mercury; whilst *iso*butyl *p*-aminobenzoate yields a *compound*, m. p. 208° (decomp.), with mercury content 44·24%, and an *anhydride* containing 59·51% Hg.

The *phenyl glycyl* ester has m. p. 128—131°, contains 45·9% Hg, and the corresponding *anhydride* has 57·3% Hg. F. M. G. M.

Physiological Chemistry

The Regulation of Neutrality by the Respiratory Centre, and its Stimulability in Maintaining the Carbon Dioxide Tension of the Blood. KARL A. HASSELBALCH (*Biochem. Zeitsch.*, 1912, **46**, 403—439).—The conception underlying these investigations is the following: The magnitude of the lung ventilation is regulated by the magnitude of the stimulus and the stimulability of the breathing centre. The stimulus is the excess of the hydrogen-ion concentration above normal of the blood. A given magnitude of stimulus will cause a greater ventilation of the lungs the greater the stimulability of the centre, and vice versa. The C_H of the blood will alter therefore in the inverse ratio to the stimulability of the centre. This theory was tested in the following way: Considerable changes in the C_H of the urine were brought about on normal individuals by changes in the diet. The magnitude of the changes thus caused were greater than deviations from the normal found in pathological urine. The effect of such a change was to cause a change in the tension of the alveolar carbon dioxide in an opposite direction. It was experimentally shown, furthermore, that the changes in diet did not affect the stimulability of the centre. This fact was ascertained by measuring the effect on the respiration of breathing increased quantities of carbon dioxide. It was further found that the C_H of the blood (measured under a constant carbon dioxide tension) altered under varying conditions of diet, in the

same direction as the C_H of the urine. The alveolar carbon dioxide tension appears to alter in such a way that the actual C_H of arterial blood (measured under the same carbon dioxide tension as exists in the arteries) remains a constant under the varying conditions. The theory is supported by experiments in which the stimulability of the centre was artifically diminished (as, for example, by morphine) or increased. S. B. S.

Absence of Apnœa After Forced Breathing. WALTER M. BOOTHBY (*J. Physiol.*, 1912, **45**, 328—337).—In some persons, forced breathing is not followed by apnœa; the loss of carbon dioxide consequent on forced breathing is made up within a few minutes, but not so rapidly as when apnœa occurs. This exceptional condition is probably due to a compensating diminution of the circulation through the respiratory centre, in consequence of which the gas tensions in the centre are still capable of exciting it. W. D. H.

The Differences in Composition between Arterial and Venous Blood. HUGO WIENER (*Zeitsch. physiol. Chem.*, 1912, **82**, 243—265).—The total protein in the blood of the renal vein is less than in that of the carotid artery and femoral vein (dog). Venous blood is relatively rich in globulin, but this is not so marked in the blood of the renal vein. In nephritis, the reverse obtains.
W. D. H.

Distribution of Sodium and Potassium in the Animal Organism. P. J. GÉRARD (*Chem. Zentr.*, 1912, ii, 846—847; from *Bull. Sci. pharm.*, 1912, **19**, 265—283).—In three successive venesections, the ratio K : Na in rabbit's blood varied between 0·68 and 0·61. The sodium in contrast to the potassium remained constant, deficiences of the former being replaced by sodium withdrawn from the tissues. The ratio was also determined in various marine and land animals, and in various secretions. The author, when working with mice and frogs, was unable to confirm the antagonistic action of sodium salts on the toxic action of potassium salts, as demonstrated by Loeb in the case of *Fundulus*. The toxic action of potassium depends to a large extent on the concentration of the solution employed. S. B. S.

The Influence of Nitrogenous Metabolism Products which Occur Naturally in Blood and Urine on the Blood Pressure. E. LOUIS BACKMAN (*Chem. Zentr.*, 1912, ii, 624; from *Zentr. Physiol.*, 1912, **26**, 166—169).—Urea in from 2—10% solutions in saline caused a rise of blood-pressure (maximum 26 mm. mercury) when injected into rabbits. Ammonium carbamate in 0·5% solution caused a lasting rise, whereas in 0·1% solution it exerted no action. Ammonium carbonate in 0·6% solution caused a lowering of blood-pressure (maximum 38 mm.), but in 0·1% solution a lasting rise. Six % ammonium hippurate caused a transient rise (9 mm.), followed by a lowering. Three % solutions caused a slight rise. Creatine, hypoxanthine, and sodium urate caused lasting rises. Allantoin in

2% solution caused a lasting rise (maximum 5 mm.), and in 1% also a rise after a considerable latent period. Urea also exerts an influence on the heart beats. A mixture of 2% urea, 0·05% ammonium carbamate, 1% sodium hippurate, 1% creatine, 0·2% hypoxanthine, 0·01% xanthine, 0·03% sodium urate causes a large (maximum 46 mm.) and long lasting rise, but has small influence on the frequency of the heart beat. The investigations indicate that nitrogenous metabolism products exert an autoregulatory function in the organism, and their action explains certain pathological conditions in gout and nephritis.

S. B. S.

The Part Played by the Suprarenals in the Normal Vascular Reactions of the Body. G. von Anrep (*J. Physiol.*, 1912, **45**, 307—317).—Stimulation of the splanchnic nerves causes a rise of blood-pressure, which occurs in two phases. The second phase is accompanied by constriction of peripheral blood-vessels (even after denervation) and by increased cardiac activity (also after denervation). This second rise is due to discharge of adrenaline into the circulation, and is absent after extirpation of the two suprarenal glands.

W. D. H.

Local Vascular Reactions and their Interpretation. G. von Anrep (*J. Physiol.*, 1912, **45**, 318—327).—The contraction of blood-vessels, described by Bayliss as a local reaction of the vessel wall to increased internal pressure, is due to the action of adrenaline, the secretion of which is increased under the conditions of his experiments. The dilatation of blood-vessels, ascribed by Bayliss to lowering of internal pressure, is due to the direct action on the vessel walls of asphyxial products. W. D. H.

Glycolysis. III. The Influence of Glycine and Boric Acid Anions on the Oxidative Destruction of Dextrose in the Presence of Phosphates. Walther Löb and S. Gutmann (*Biochem. Zeitsch.*, 1912, **46**, 288—295. Compare A., 1911, ii, 504).—It has been already shown that phosphate mixture accelerates the destruction of dextrose by hydrogen peroxide. This is not due to the neutrality of the medium, but is specific for phosphates, as no acceleration takes place when neutral borate or other mixtures of the same hydrogen-ion concentration are employed. The authors now show that the addition of such a borate mixture to the phosphate mixture exerts no very marked action, whereas a similar glycine mixture (prepared according to Sörensen) exerts a marked inhibitory action on the glycolysis.

S. B. S.

The Significance of Proteolysis in Specific Hæmolysis. Kohshi Ohta (*Biochem. Zeitsch.*, 1912, **46**, 247—252).—An immune serum (sheep's blood into rabbit) hæmolyses the specific blood (of sheep) without any proteolysis. S. B. S.

The Influence of the Hydrogen-ion Concentration on Specific Precipitin Reactions. Leonor Michaelis and Heinrich Davidsohn (*Biochem. Zeitsch.*, 1912, **47**, 59—72).—The forma-

tion of specific precipitins and agglutins is, within wide limits, independent of the hydrogen-ion concentration. This factor only comes into play, to any extent, when the reacting substances are in very dilute solutions. In this respect, the precipitin reaction differs from the non-specific precipitation of colloids, as no optimal conditions for precipitin reaction, analogous to the isoelectric point, could be discovered. These results indicate that there is some specific chemical affinity coming into play, and the electric charge of the particles plays only a subordinate part. S. B. S.

The Coagulation of Blood. ERNST FULD and ERICH SCHLESINGER (*Chem. Zentr.*, 1912, ii, 1569; from *Berlin klin. Woch.*, 1912, **49**, 1323—1327).—Dialysis of the blood against an isosmotic salt solution deprives the plasma of its power of coagulating, the crystalloid which is removed being the calcium salt of fibrin. The absence of this salt also hinders the formation of another necessary element in coagulation, namely, the fibrin ferment, for the development of which, cytothrombin from the cells and plasmothrombin from the plasma are also necessary. The injection of cytothrombin into a vein at once causes coagulation, owing to the formation of this ferment, *neothrombin*. The smallest amounts of enzymes would soon set up fermentation processes, which would hinder the circulation, were there not also present substances which prevent coagulation.

Fibrin may be redissolved by fibrinolysis, which is partly due to salt action and also to an enzymatic agent, *thrombase*. J. C. W.

The Dissociation of Oxyhæmoglobin in Human Blood During Partial Carbon Monoxide Poisoning. J. B. S. HALDANE (*Proc. physiol. Soc.*, 1912, xxii–xxiv; *J. Physiol.*, **45**).—The presence of carboxyhæmoglobin in the blood delays the dissociation of the oxyhæmoglobin present, so that even though the amount of oxyhæmoglobin may be half the normal (as it may also be in a man with anæmia without grave results), the combination of the remaining half of the hæmoglobin with carbon monoxide produces a serious state of affairs. W. D. H.

Blood-relationships of Animals as Displayed in the Composition of the Serum-proteins. I. A Comparison of the Serum of the Horse, Rabbit, Rat, and Ox in the Normal and Fasting Condition. T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1912, **13**, 325—340).—The amounts of insoluble globulin, total globulin, and total albumin in serum were determined by the author's refractometric method. In the rabbit the results agree with those arrived at by others in other ways. Horse serum yields not more than 40% of the total albumin in crystalline form. In fully fed animals the three groups of proteins vary greatly; but the average values are characteristic of the species. In fasting, the total protein is also highly variable; in starvation it rises. In rabbit, ox, and horse, inanition increases the relative amount of albumin, whereas in rat and dog the reverse obtains. W. D. H.

The Diastatic Action of Human Saliva. GOICHI HIRATA (*Biochem. Zeitsch.*, 1912, **47**, 167—183).—The diastatic value of saliva (as determined by Wohlgemuth's method) remains practically constant throughout the day, and is not influenced by the time of meals or the diet. The value is also independent of the amount of saliva secreted, and of the age or sex of the individual. It has the same value in certain pathological cases investigated as in normal cases, and appears to be uninfluenced by the hæmoglobin content of the blood. In the case of the Japanese, it varies between $D^{38°}_{30'}$ 160 and 640 in different individuals. S. B. S.

Formation of Hydrochloric Acid in the Stomach. J. LÓPEZ-SUÁREZ (*Biochem. Zeitsch.*, 1912, **46**, 490—499).—The author discusses the evidence as to the acid-secreting function of the oxyntic cells of the stomach, and considers that this has not been demonstrated. By direct chemical analysis he shows that the mucous membrane of the fundus contains more chlorine than that of the pylorus. He shows, furthermore, by Macallum's histological method that the ordinary cells contain more chlorine than the oxyntic cells. S. B. S.

The Fat-hydrolysing Ferment in Gastric Juice, and its Estimation. HEINRICH DAVIDSOHN (*Chem. Zentr.*, 1912, ii, 1378—1379; from *Berl. klin. Woch.*, 1912, **49**, 1132—1134).—Rona and Michaelis's drop method for following the course of butyrin hydrolysis (A., 1911, ii, 302) has been applied to a large number of gastric juices, and a widely varying enzyme action has been observed. Directions are given whereby the method may be applied to the estimation of this hydrolytic enzyme. J. C. W.

Tryptic Digestion of Cynoscion regalis. GEORGE F. WHITE and ADRIAN THOMAS (*J. Biol. Chem.*, 1912, **13**, 111—116).—The flesh of *Cynoscion regalis*, an American fish known commonly as the weak-fish or squeteague, was subjected to tryptic digestion in vitro, and the amino-acids in the digest were determined by Sörensen's formaldehyde method. The results were regular and in accord with those obtained by van Slyke's nitrous acid method for estimating amino-nitrogen. The relatively low rate at which the protein becomes soluble agrees with the results of metabolism experiments. Very low cleavage products are formed as soon as the protein passes into solution, the average size of the peptides being 2·02 after half an hour's digestion; but there is a very stable nitrogen complex which is not attacked by trypsin. W. D. H.

Animal Calorimetry. V. The Influence of the Ingestion of Amino-acids on Metabolism. GRAHAM LUSK and J. A. RICHE (*J. Biol. Chem.*, 1912, **13**, 155—184. Compare A., 1912, ii, 1189).—After giving meat, the metabolism of the dog during the second hour rose almost to a maximum, and the respiratory quotient was 0·9; it therefore appears that carbohydrate and not additional protein is oxidised during this period. After the ingestion of amino-acids and especially of glycine, there is a similar increase in the metabolism;

this can have nothing to do with deamidation or urea-formation, but is attributed to a direct stimulating action of the amino-acids on the cells of the body. A mixture of five amino-acids produced a more rapid metabolism than when given singly, and more than meat containing the same amount of nitrogen. W. D. H.

Animal Calorimetry. VI. The Influence of Mixtures of Food-stuffs on Metabolism. GRAHAM LUSK and J. A. RICHE (*J. Biol. Chem.*, 1912, **13**, 185—208).—Further details are given of the effect of diet on metabolism, and the conception of the process put forward is that to a basal metabolism (at rest) there may be added metabolism due to plethora, that is, an increased supply of fats and carbohydrates, or the superadded metabolism may be due to the stimulus of amino-acids. When these two are added to each other there is no summation of effects. W. D. H.

Fatty Acid Metabolism in the Liver. II. The Relation of the Fatty Acids in the Food of the Plaice to those in their Livers and Myotomes. V. H. MOTTRAM (*J. Physiol.*, 1912, **45**, 363—369).—The fatty acids of the mussel have a high iodine value, which falls between that of the fatty acids of the liver and those of the myotomes of the plaice. Such fatty acids are therefore not characteristic of the vertebrates, and they occur before the appearance of a true liver. Their formation is not exclusively a liver function. The experiments on the feeding of plaice on mussels cannot, however, be considered a refutation of Leathes' theory of the desaturating influence of the liver in fatty acid metabolism. W. D. H.

The Biochemical Synthesis of Fatty Acids from Carbohydrates. IDA SMEDLEY (*Proc. physiol. Soc.*, 1912, xxv—xxvii; *J. Physiol.*, **45**).—Various hypotheses to explain the conversion of carbohydrate into fat are discussed. Although pyruvic and other α-keto-acids have not yet been detected in the tissues, the theory is favoured that pyruvic acid is an intermediate product. W. D. H.

Maintenance Experiments with Isolated Proteins. THOMAS B. OSBORNE, LAFAYETTE B. MENDEL, and EDNA L. FERRY (*J. Biol. Chem.*, 1912, **13**, 233—276).—Details are given and general questions discussed on the nutrition of white rats for long periods on foods containing a single purified protein. With the precautions described this is possible, and they can be so maintained for periods equal to their adult lives. This is true for gliadin, edestin, and casein, which are proteins of very different composition. As glycine is absent from casein, lysine and glycine from gliadin, and phosphoproteins from gliadin and edestin, and purines throughout are practically absent, the synthetic activities of the animal body are clearly brought to mind. The possibilities of transmutation of amino-acids must be considered, and the view that proteins as near as possible in constitution to those in an animal's body are most nutritious must be regarded with caution. Long-continued experiments are necessary in all such work. Changes in the nitrogen balance over short periods may be entirely deceptive. W. D. H.

The Influence of Lecithin on the Nitrogen and Phosphorus Balance. ALDO PATTA (*Chem. Zentr.*, 1912, ii, 939—940; from *Arch. Farm. sperim.*, 1912, **13**, 515—528).—Small quantities of lecithin (0·05 to 0·10 gram) administered subcutaneously to a dog scarcely altered the nitrogen and phosphorus metabolism when there was a small deficit in these substances. Larger doses (0·5 to 0·75 gram) caused a sparing action, which was small when the nitrogen and phosphorus ingested were insufficient, but was marked when these elements were in excess of the body needs. The sparing action of the phosphorus was larger than the amount injected as lecithin, and the fact that the injection caused an increase of the nitrogen in the urine, at the expense of the fœcal nitrogen, indicates that the lecithin stimulates the degradation of the injested proteins. S. B. S.

Retention of Nitrogen after Feeding on Ammonium Salts. E. GRAFE (*Zeitsch. physiol. Chem.*, 1912, **82**, 347—376).—The present experiments on pigs confirm those previously recorded on dogs (A., 1912, ii, 659). Administration of ammonium salts mixed with abundance of carbohydrate leads to nitrogenous equilibrium, or even a retention of nitrogen. W. D. H.

The Creatine Metabolism of the Growing Pig. ELMER V. McCOLLUM and H. STEENBOCK (*J. Biol. Chem.*, 1912, **13**, 209—218).—In some animals (for instance, the rabbit) fasting causes the appearance of creatine in the urine. In dogs, depletion of the liver of glycogen leads to the same result, and Mendel and Rose (A., 1911, ii, 1002, 1007) consider that there is a definite relationship between creatine and carbohydrate metabolism; they further think that creatine is not a result of exogenous protein metabolism, but only of endogenous metabolism. The present experiments on pigs were planned to investigate this question, but it was found that in this animal fasting does not lead to the appearance of creatine in the urine; this is explained in differences of metabolic habit. When a rabbit fasts the total nitrogen excreted rises, indicating an increase of protein katabolism. This does not happen in the dog, or only slightly, and not at all in the pig. The pig is an efficient fat-storer, so he might be expected to use it readily for energy production. On an uniform diet considerable irregularities in the excretion of creatine occur, and the idea that creatine is destroyed by enzymes is supported. Data are also given which leave but little doubt that creatine may arise from exogenous as well as from endogenous protein metabolism, and that its source, or one of its sources, is arginine, is regarded as probable. W. D. H.

The Behaviour of Some Hydantoin Derivatives in Metabolism. I. Hydantoin and Ethyl Hydantoate. HOWARD B. LEWIS (*J. Biol. Chem.*, 1912, **13**, 347—356).—After hydantoin is given, an insoluble benzylidenehydantoin can be recovered from the urine, which accounts for only part of the hydantoin administered. No toxic effects follow, which is against Lusini's theory of the toxicity of $\begin{matrix}-HN\\-HN\end{matrix}\!\!>C{:}O$ groups.

Hydantoic acid, of which hydantoin is the cyclic anhydride, is not destroyed in metabolism when given as the ethyl ester. The hydantoin nucleus is not destroyed in the body of cat, rabbit or dog.
W. D. H.

Purine Metabolism. X. The Property of the Organism to Destroy, or Form by Oxidative Processes, Uric Acid in Animals Capable of Producing this Acid Synthetically. VITTORIO SCAFFIDI (*Biochem. Zeitsch.*, 1912, **47**, 215—225).—In experiments carried out with ducks, it was found that animals which normally synthesise uric acid can also destroy this acid after ingestion when added to a normal diet, to the extent of 33—59% of the total. They can also degrade guanine to xanthine, and into still simpler complexes which no longer contain a purine group. From the xanthine thus formed, a certain amount of uric acid can be formed by an oxidative process. Ingestion of nucleic acid also causes a slight increase in the amount of purine bases execreted and a considerable increase in the uric acid, the origin of which is ascribed to the protein groups.
S. B. S.

The Metabolism of Endogenous and Exogenous Purines in the Monkey. ANDREW HUNTER and MAURICE H. GIVENS (*J. Biol. Chem.*, 1912, **13**, 371—388).—In the urine of the guenon monkey (*Cercopithecus*), allantoin accounts for 75% of the nitrogen arising from the katabolism of endogenous purines. The rest appears principally as purine bases, uric acid being practically absent on a purine-free diet. Allantoin is a true end-product. When purines are given, allantoin is increased, and uric acid appears as an intermediate product. Only 12—54% of total purine intake is accounted for. The deficit is probably due to decomposition prior to absorption. There is no approach in this monkey to the human type of nuclein metabolism.
W. D. H.

Absorption from the Stomach. OTTO FOLIN and HARRY LYMAN (*J. Biol. Chem.*, 1912, **13**, 389—391).—A reply to London's recent criticisms (A., 1912, ii, 1189).
W. D. H.

Behaviour of Intestinal Wall After a Prolonged Period of Functional Inactivity. PAOLO MARICONDA (*Zeitsch. physiol. Chem.*, 1912, **82**, 406—412).—After making a Vella fistula, a dog was kept for several months so that no local stimulus had reached the intestine. The amount of fluid secreted by the intestinal wall was now very small, and the amount of the various enzymes was also reduced, although not to the same extent. The results are opposed to the theory that the secretory function of the intestine is due to chemical stimuli carried to it by the blood. Sucrose introduced into the fistula passes the wall without being changed; the selective absorptive power of the intestinal wall has been destroyed.
E. F. A.

Absorption of Cholic Acid in the Dog's Intestine. BAREND C. P. JANSEN (*Zeitsch. physiol. Chem.*, 1912, **82**, 342—345).—Experiments with intestinal loops showed that in all probability cholic acid is absorbed unchanged by the intestinal wall.
W. D. H.

The Fate of Deeply-degraded Proteins in the Intestine. PETER RONA (*Biochem. Zeitsch.*, 1912, 46, 307—316).—Experiments were carried out with the object of ascertaining whether any protein synthesis takes place in the small intestine. Pieces of surviving intestine were placed in Tyrode's solution and various digestion products or mixtures of amino-acids were placed either in the solution in which the intestine was kept or introduced directly into the lumen. The experiments were carried out at 38°, and during this time the intestine maintained its peristaltic movements. The amino-nitrogen was estimated both before and after the experiment. There was generally an increase in this nitrogen at the end, due probably to amino-substances given up by the intestine itself. The amount of increase was of the same order as that in which the experiments were carried out in Tyrode's solution without any addition. No evidence was obtained therefore of any synthetical process affecting amino-derivatives in the intestine. S. B. S.

The Investigation of the Permeability and Antagonistic Action of Electrolytes by means of a New Method. JACQUES LOEB (*Biochem. Zeitsch.*, 1912, 47, 127—166).—It has been already repeatedly shown by the author, in experiments on *Fundulus* eggs, that treatment with a solution of one salt alone (for example, sodium chloride) alters the permeability of the membrane, and that this alteration can be inhibited by the addition of certain quantities of another salt (calcium chloride). Salt solutions, of such composition that the antagonistic action of the salts is at its maximum, are designated equilibrated solutions. If fertilised eggs of *Fundulus* be brought into a solution of 50 c.c. $3M$-sodium chloride + 2 c.c. $10/8M$-calcium chloride, they will remain on the surface for three days, after which the membrane will be rendered permeable by the hypertonic solution; the eggs will then begin to shrink, and owing to the passage outwards of water, the specific gravity will increase and they will then sink in the solution. If brought into a solution of $3M$-sodium chloride alone, without presence of calcium chloride, they will sink within three to four hours, and the membrane rapidly becomes permeable. Similar phenomena are observed when the eggs are brought into other corresponding solutions containing only salts. By the method of experiment the various earlier investigations of the author have been confirmed. The changes in the permeability appear to be due chiefly to the proteins, and there is an antagonism between the action of acids and the corresponding salts, which is characteristic of proteins, as Pauli and his pupils have shown. Furthermore, the antagonism in the system H_2SO_4–Na_2SO_4 is more complete than in the system HCl–NaCl. The antagonistic action of these acids and salts on the *Fundulus* egg, as studied by the method described above, confirms the theory as to the alterations of the proteins by salts. The quantitative study of the action of alcohols, however, indicates that these alter the permeability by the action on the fatty constituents of the membrane. Provided that the action has not gone too far, the change of permeability produced by salts is a reversible one, and eggs, which have been a short time in a toxic

solution, will recover their normal properties when brought into an equilibrated solution. Eggs will also remain alive in distilled water, and fish will develop, but they will not recover their impermeability. If such eggs are brought into a solution of 50 c.c. $3M$-calcium chloride + 2 c.c. $10/8M$-calcium chloride, they sink in a few hours.

S. B. S.

The Influence of Neutral Salts on Ferment Action. II. EMIL STARKENSTEIN (*Biochem. Zeitsch.*, 1912, **47**, 300—319. Compare A., 1910, i, 449).—The number of salt molecules necessary to activate to the maximum extent an inactive diastase preparation is proportional to the amount of ferment. This fact suggests a process for the determination of the quantity of ferment in a given organ. For this purpose the organ is dried, a 5% suspension of the dried powder is made up, and dialysed. The amount of salt which produces the maximum diastatic effect with this fluid can then be ascertained. By this means the diastase content in various animal organs was investigated. Organs of warm-blooded animals contain more ferment than those of the cold-blooded. The ferments obtained from both kinds of animals work more rapidly at higher temperatures.

S. B. S.

Lipoids. XVI. The Cholesterol Content of Different Parts of the Brain. SIEGMUND FRÄNKEL, P. KIRSCHBAUM, and KURT LINNERT (*Biochem. Zeitsch.*, 1912, **46**, 253—256).—The cholesterol was estimated as its digitonin derivative. In a human brain 4·03% was found in the pons and medulla oblongata, 2·47% in the white matter of the cerebrum, and 1·31% in the cerebellum.

S. B. S.

The Colloidal Structure of Nerve Cells and the Changes which they Undergo. G. MARINESCO (*Zeitsch. Chem. Ind. Kolloide*, 1912, **11**, 209—225).—The ultra-microscopic structure of nerve cells is described and interpreted on the assumption that the cell constituents are of colloidal character. The structural changes which are observed when the nerve cells are subjected to the action of acids, alkali, salts, and various other substances, such as ethyl alcohol, carbamide, glycerol, sucrose, chloral hydrate, and antipyrine, are also described in detail.

The results of these ultra-microscopic observations seem to show that the particular structures which are presented by the nerve cells after treatment by the usual fixing and colouring methods are essentially determined by the nature of the histological processes employed. The fixing reagents have, in general, a coagulating effect on the colloidal cell constituents, and the observed facts agree with the view that the protoplasm is a negative colloid.

H. M. D.

Chemical and Biochemical Investigations on the Nervous System under Normal and Pathological Conditions. IV. The Chemical Composition of the Brain in Progressive Paralysis. DOMENICO CARBONE and GIACOMO PIGHINI (*Biochem. Zeitsch.*, 1912, **46**, 450—469).—The analyses of brains taken from

individuals who have suffered from progressive paralysis and Dementia præcox paraxoica were compared with those obtained from mentally normal individuals. Whereas normal brains contain about 23% of dry substance, those from mentally afflicted (five cases) varied between 17 and 21%. Against a normal value of 20%, the acetone extracts of the abnormal brains varied between 22·87% and 31·32%. The light petroleum extracts varied between 11·23% and 23·14%, as compared with the amount from normal brains of 27·84%. The cholesterol varied between 13·9 and 24·2%, and the other extractives between 4·5 and 11·84% as compared with the normal values of 10·96 and 9·64%. Full details as to analytical methods are described by the authors. S. B. S.

Broncho-dilator Nerves. WALTER E. DIXON and FRED RANSOM (*J. Physiol.*, 1912, **45**, 413—428).—The broncho-dilator nerves are of sympathetic origin. Adrenaline given to an animal showing bronchial tonus causes active temporary dilatation; atropine causes passive permanent dilatation. W. D. H.

The Influence of Inorganic Salts on the Perfused Heart. W. BURRIDGE (*Quart. J. expt. Physiol.*, 1912, **5**, 347—372).—Potassium salts give rise to two types of contraction in cardiac muscle (frog), which are termed "tonic contraction" and "contraction effect." Some salts produce one, others the other effect, but all temporarily abolish rhythmical activity, and may produce "heart block" if perfused at high pressure. The effects are mainly explained by considering that these salts displace calcium salts, and the various calcium salts are displaced at varying rates. Seasonal variations noted are explained as due to changes in the balance between calcium and potassium salts in the heart muscle; temperature may also be a factor. W. D. H.

Physiology and Pharmacology of the Cardiac Vagus. I. The Influence of Chloral Hydrate on the Result of Vagus Stimulation. OTTO LOEWI (*Arch. expt. Path. Pharm.*, 1912, **70**, 323—342).—Intravenous injection of chloral hydrate in small doses has no effect on blood pressure and heart rate, but almost completely annuls the return of the heart-beat during vagus stimulation. Large doses abolish vagus excitability. Camphor has also no effect on blood-pressure or pulse rate, but influences vagus stimulation in a similar way. The action of pilocarpine and muscarine is similarly weakened. W. D. H.

Physiology and Pathology of the Cardiac Vagus. II. The Importance of Calcium for Vagus Action. OTTO LOEWI (*Arch. expt. Path. Pharm.*, 1912, **70**, 343—350).—Partial removal of calcium by small amounts of oxalate increases the excitability towards electrical stimuli of various nerves; the least affected is the pelvic nerve, but the chorda tympani and especially the vagus are profoundly affected. This is not inhibited by calcium. The action of muscarine on the frog's heart occurs after it is rendered poor in calcium,

or free from calcium. The paralysis of the vagus by pilocarpine or muscarine in mammals and frogs is not influenced by calcium.

W. D. H.

Physiology and Pharmacology of the Cardiac Vagus. III. Vagus Excitability and Vagus Poisons. OTTO LOEWI (*Arch. expt. Path. Pharm.*, 1912, **70**, 351—368).—In very small doses muscarine (and pilocarpine) increases vagus excitability in the frog. In vagus paralysis produced by these drugs there exists neither in frog nor rabbit any automatic ventricular action. The effect of prolonged electrical stimulation of the nerve is either increased by muscarine or unaffected by it, according to the duration of the stimulation or the dose of the poison. Similarly, the pilocarpine effect can be superposed on the muscarine effect, or vice versa. Physostigmine does not sensibilise the muscarine or pilocarpine action. The action of pilocarpine and muscarine is considered to be on the myoneural junction.

W. D. H.

The Behaviour of Acetic Acid in the Artificial Perfusion of the Liver. ADAM LOEB (*Biochem. Zeitsch.*, 1912, **47**, 118—126). —Various results obtained by Embden and his school are recapitulated, and reasons are given as to why acetic acid might be expected as a normal degradation product of fats, carbohydrates, and proteins, especially through the intermediation of pyruvic acid. As no evidence could be obtained of the formation of acetic acid when pyruvic acid was added to blood in a perfusion experiment, the effect of adding the former acid itself to the blood was investigated. It was found that, during perfusion, a very marked disappearance of this acid took place. It was also found, without exception in ten experiments, that the addition of acetic acid to the perfusion of blood caused a marked increase in the formation of acetoacetic acid. The mechanism of this reaction is discussed, and it is provisionally suggested that the degradation of acetoacetic into acetic acid is a reversible process:

$$CH_3\cdot CO\cdot CH_2\cdot CO_2H \rightleftharpoons 2CH_3\cdot CO_2H,$$

and for this reason the acetic acid may inhibit the degradation of the acetoacetic acid normally formed to simpler products.

S. B. S.

The Fate of Glyoxylic Acid in the Animal Body. GEORG HAAS (*Biochem. Zeitsch.*, 1912, **46**, 296—306).—On incubation of minced liver of various animals with glyoxylic acid, this substance partly disappeared, but no definite degradation products were isolated. Its perfusion through rabbit's liver gave rise to formic acid, and this acid could also be isolated in the urine of a dog which had received glyoxylic acid *per os*.

S. B. S.

The Destruction of Alkaloids by the Body Tissues. A. J. CLARK (*Quart. J. expt. Physiol.*, 1912, **5**, 385—398).—The liver of frog and rabbit possesses the power of destroying atropine; this persists after the cells are destroyed, and is due to a soluble substance resembling an enzyme in its action. The heart and kidneys of the frog and the

blood of the rabbit have the same power in a less degree, but all the other tissues are destitute of the power. None of the tissues in cat, rat, and dog has the power, and the minimal lethal dose of atropine is highest in those animals the livers of which can destroy it.

W. D. H.

The Distribution of Nitrogen in Autolysis, with Special Reference to Deaminisations. GERTRUDE D. BOSTOCK (*Bio-Chem. J.*, 1912, **6**, 388—415).—The following nitrogen fractions in the autolysis products of liver were determined: ammonia, amide nitrogen, and amino-acid nitrogen. It was necessary to ascertain these factors in order to determine the fate of ammonium salts and amino-acids when digested with liver tissue. In fresh liver the soluble nitrogen fraction is characterised by its low ammonia and amino-nitrogen content. The latter, however, increases after forty-eight hours' incubation at the expense of the undetermined nitrogen fraction. The rate of autolysis reaches its maximum within this period. Acids stimulate and alkalis depress the autolysis rate, and the distribution of nitrogen differs under these two conditions. Acids cause a lower and alkalis a higher percentage of ammonia and undetermined nitrogen fractions than in the control autolyses without addition of either acid or alkali. The reverse is the case with regard to the amide or amino-acid nitrogen. Putrefactive organisms cause a higher percentage of ammonia and undetermined nitrogen. No evidence could be obtained of the formation of amide nitrogen from ammonium sulphate or lactate when digested with liver pulp. There is also no evidence of liberation of ammonia from glycine. In view of the formation of ammonia by putrefactive organisms, any statements as to the liberation of this substance from amino-acids when digested with tissues must be received with caution.

S. B. S.

The Permeability of the Kidneys to Sugar after Repeated Injections of Adrenaline. ARTUR VON KONSCHEGG (*Arch. expt. Path. Pharm.*, 1912, **70**, 311—322).—Diuresis which follows the injection of adrenaline is independent of glycosuria. After salt diuresis is produced, it is not possible to produce glycosuria by such injections; the blood contains no excess of sugar, but the kidneys themselves contain more than normal. Inhibition of glycosuria is not brought about by the kidneys being unable to take up sugar from the blood.

W. D. H.

The Amount of Silicic Acid in Human Thyroid Glands. HUGO SCHULZ (*Biochem. Zeitsch.*, 1912, **46**, 376—392).—The mean content of the normal glands from the neighbourhood of Greifswald was 0·0084%, and that of pathological glands from the same district, 0·0175%. The pathological glands from Zürich, on the other hand, contained as much as 0·0434%. The author, nevertheless, gives reasons for not believing that goitre is due to water containing silicic acid, and he failed to produce the disease experimentally in animals which had received over long periods water containing relatively large quantities of the acid.

S. B. S.

The Creatine-splitting Enzyme of the Parathyroids and the Suprarenals. ALBERT HOLMES ROWE (*Amer. J. Physiol.*, 1912, **31**, 169).—A creatine-splitting enzyme is present in the thyroparathyroid tissue; this confirms the results of Gottlieb and Staugassinger. A similar enzyme is found in suprarenal extract. There is no evidence that either the parathyroids or the suprarenals contain a creatine-splitting enzyme which can be activated by the other.

W. D. H.

The Chemistry of Normal and Eclamptic Placenta. L. MOHR and W. HEIMANN (*Biochem. Zeitsch.*, 1912, **46**, 367—373).—Estimations were made of the water content, total phosphoric acid and nitrogen, ether soluble substances, cholesterol, neutral fat, and diastearyllecithin. The last-named was appreciably larger in normal placenta than in cases of eclampsia. There was no marked difference in the other factors. S. B. S.

The Physico-chemical Basis of a Theory of Muscular Contraction (Zuntz's Theory). WILLIAM N. BERG (*Pflüger's Archiv.* 1912, **149**, 195—220. Compare A., 1912, ii, 1077).—A critical and antagonistic discussion of Zuntz's theory; the main point is that lymph contains practically no carbon dioxide in the simple gaseous condition, and that when gases are dissolved in water they behave differently from substances in true solution, and, with the exception of hydrogen chloride and ammonia, exert no osmotic pressure. The carbon dioxide which is formed by muscular activity has therefore no osmotic pressure. W. D. H.

The Anaphylactic Reaction of Plain Muscle in the Guinea Pig. HENRY H. DALE (*Proc. physiol. Soc.*, 1912, xxvii—xxix; *J. Physiol.*, **45**).—Experiments on the plain muscle (uterus) of the guinea pig sensitised to horse-serum and other proteins; it reacts in response to minute doses (one in a million) of the specific antigen; after response it is completely desensitised; it can be re-sensitised by soaking in the serum of sensitised guinea pigs. The time relations of the reaction exclude the production of a poison by parenteral digestion. The antigen acts on the sensitised muscle like a stimulant drug, the peculiar feature being that the "receptive or anti-substance" is detachable. There is much evidence in favour of the view that the anaphylactic anti-substance is identical with precipitin. W. D. H.

Synthesis of Lecithin in the Hen and the Character of the Lecithins Produced. ELMER V. MCCOLLUM, J. G. HALPIN, and A. H. DRESCHER (*J. Biol. Chem.*, 1912, **13**, 219—224. Compare A., 1912, ii, 368).—Further experiments are given to show that hens fed on a diet free from lipoids produce eggs which contain lecithin or lecithins. These differ in the nature of their fatty acid radicles, and variation may be produced by the nature of the lipoids of the diet.

W. D. H.

Red Colouring Matter of Boiled Crabs. EUGÈNE GRANDMOUGIN (*Chem. Zeit.*, 1912, **36**, 1377—1378).—The change of colour observed

when crab-shells are boiled has been attributed by Kornfeld to the formation of alizarin-red, which depends on the presence of alizarin and aluminium oxide in the unboiled shell.

The author points out that the presence of anthraquinone in the normal organism has not previously been observed. He also finds that the colouring-matter of crab- and lobster-shell, unlike alizarin-red, is soluble in alcohol or ether, and is very sensitive to light. When dissolved in alcohol, it shows characteristic absorption bands in the green portion of the spectrum which differ completely from the bands given by alizarin. It possesses no dyeing power. Finally, the presence of compounds of aluminium in the shell could not be detected with certainty.

The exact nature of the colouring matter has not been determined, but the presence of anthraquinone derivatives is extremely improbable.

H. W.

The Bio-chemistry of Termites. The Chemical Composition of the Fæcal Stalactites of Entermes monoceros. KONRAD SCHÜBEL (*Arch. expt. Path. Pharm.*, 1912, **70**, 303—310).—The tree ant of Ceylon protects its nest by so-called stalactites, and it has been surmised that these contain cantharidin or some similar poison. The present work shows that the material consists of an organic non-toxic substance with a small amount of inorganic salts. The ash has the following percentage composition: SiO_2, 45·2; P_2O_5, 1·09; $Fe_2O_3 + Al_2O_3$, 23·5; Mn_3O_4, 1·05; CaO, 14·25; MgO, 1·5, and $K_2O + Na_2O$, 13·3. By distillation in a vacuum it was proved that the fæcal matter contains preformed an olefine, probably $C_{35}H_{70}$, m. p. 75°. These animals live almost exclusively on flies and algæ. W. D. H.

Metabolism Studies on the Cold-blooded Animals. I. The Urine of the Fish. W. DENIS (*J. Biol. Chem.*, 1912, **13**, 225—232). —The urine of the dog-fish is clear, odourless, and almost colourless; it is acid to litmus. It darkens and becomes cloudy when kept. It gives the murexide reaction, and contains creatinine, but not creatine. The following is the average composition, expressed in grams per litre: total nitrogen, 4·2; urea nitrogen, 3·4; ammonia nitrogen, 0·3; chlorides (as NaCl), 12·8; phosphates (as P_2O_5), 4·5; total sulphur (as SO_3), 7·1, and total sulphates (as SO_3), 3·4. The goose fish (*Lophius piscatorius*) is the only teleost so far investigated; in general appearance and reaction, the urine resembles that of the dog-fish; uric acid, creatine, and creatinine were absent. The one specimen examined contained, in milligrams per litre, total nitrogen, 400; urea nitrogen, 248, and ammonia nitrogen, 2. W. D. H.

Behaviour of Alicyclic Compounds in Coupling with Glycuronic Acid in the Organism. JUHO HÄMÄLÄINEN (*Chem. Zentr.*, 1912, ii, 854—856; from *Skand. Arch. Physiol.*, 1912, **27**, 141—226). —A number of terpenes and allied compounds dissolved in olive oil were fed to rabbits. The urine produced was collected, and the coupled glycuronic acids formed were either isolated or the products of their hydrolysis by acids were examined.

Menthene in this way gave rise to a product which on hydrolysis yielded a *hydrocarbon*, $C_{10}H_{16}$, b. p. 178—180°, that on hydration gave a dihydric *alcohol*, $C_{10}H_{20}O_2$, m. p. 55—59°, which may be *p*-menthan-2 : 4-diol. Dihydrocarveol in the same way yielded a menthadiene, $C_{10}H_{16}$, b. p. 179—181°, which on oxidation gave dihydrocarvone, and on hydration furnished *p*-menthan-2 : 8-diol. Terpin yielded a menthadiene, b. p. 178—181°, which gave terpin hydrate and terpineol on hydration, and terpenylic acid on oxidation with chromic acid. Menthone, before coupling with glycuronic acid, appears to be oxidised to Δ^4-menthen-3-one, since the latter is produced on hydrolysis of the coupled product.

Thujone is apparently first converted in the organism into *p*-menthan-2-one-4-ol by addition of 1 mol. of water. On hydrolysis the coupled product yields carvenone, whilst oxidation with sodium hypobromite gives ω-dimethyllævulic acid. Thujyl alcohol, under like conditions, seems to be converted into *p*-menthan-2 : 4-diol, since the latter is formed on hydrolysis of the coupled glycuronic acid produced in the organism.

Sabinol yields *sabinolglycuronic acid*, $C_{16}H_{24}O_7$, m. p. 82—83°, as a colourless, glassy mass, giving crystalline *sodium* and *strychnine* salts. The latter has m. p. 196—197°, $[\alpha]_D^{20}$ − 39·66° in alcohol, and crystallises with $2H_2O$ in needles from hot water. Sabinene yields a coupled product, which on hydrolysis with 5% sulphuric acid gives a gelatinous substance that on hydrolysis with stronger acid yields Δ^1-menthenone (?).

Pinene and nopinene appear to undergo oxidation before coupling, since the coupled product yields *p*-cymene on hydrolysis. Camphane is also oxidised in the organism, and yields a mixture of d- and l-*borneolglycuronic acids*, $C_{16}H_{26}O_7$, m. p. 163—165°, $[\alpha]_D^{20}$ − 56·91°, as a colourless, crystalline mass.

l-Fenchyl alcohol furnishes *fenchylglycuronic acid*, $C_{16}H_{26}O_7,H_2O$, m. p. 124—126°, $[\alpha]_D^{20}$ − 63·07°, crystallising from acetone and yielding well crystallised salts. l-iso-*Fenchylglycuronic acid*, m. p. 140—150°, $[\alpha]_D^{20}$ − 81·02°, is amorphous.

Camphenilolglycuronic acid, $C_{15}H_{24}O_7$, m. p. 150—153°, is a colourless mass, obtained by the use of either camphenilol or camphenilone, the latter apparently undergoing initial reduction in the organism.

α-Santenol gives rise to *α-santenolglycuronic acid*, $C_{15}H_{24}O_7,H_2O$, m. p. 160—161°, $[\alpha]_D^{20}$ − 56·6°, a colourless mass, which yields crystalline salts. *β-Santenol* also couples unchanged, furnishing β-santenolglycuronic acid, which was not isolated, but was found to yield santene on acid hydrolysis. Santenone is first oxidised to *santenonol*, $C_9H_{14}O_2$, m. p. 92—93°, crystallising in colourless leaflets, giving a crystalline *semicarbazone*, m. p. 222—223°, and yielding santenic acid on oxidation. *Santenonolglycuronic acid*, $C_{15}H_{22}O_8$, yields a crystalline *strychnine* salt, $C_{36}H_{44}O_{10}N_2,2H_2O$, m. p. 171—172°, and gives santenonol on hydrolysis.

Camphene hydrate couples unchanged with glycuronic acid in the organism, and the product on hydrolysis gives camphene, by loss of water from the regenerated camphene hydrate. T. A. H.

The Relationships between Tumour Cells and Blood-serum. ERNST FREUND and GISA KAMINER (*Biochem. Zeitsch.*, 1912, 46, 470—482).—The property possessed by normal sera of destroying carcinoma cells is due to an ether-soluble, nitrogen-free fatty acid. The property of carcinomatous serum of protecting carcinomatous cells from destruction, and of giving specific turbidity with saline extracts of carcinomas, is due to the euglobulin (nucleoglobulin) fraction of the serum which is soluble in sodium carbonate, and is distinguished from normal nucleoglobulin by its high content of carbohydrate group. The property of carcinoma extracts of giving turbidities with carcinomatous sera is due to a nitrogen-free carbohydrate compound. The specific precipitates of carcinomatous and sarcomatous extracts with their respective sera are characterised in the former case by carbohydrate-rich substances, and in the latter case by groups yielding the biuret reaction. The carcinomatous precipitates carry down from solution added carbohydrates, whereas the sarcomatous precipitates carry down added peptone. The tumour cells themselves show a similar adsorptive capacity, the carcinomatous cells binding sugar, lecithin or nuclein, whereas the sarcomatous cells bind peptones and nuclein. S. B. S.

The Interstitial Granules (Liposomes) in Fatty Metamorphosis of Striated Muscle. E. T. BELL (*J. Path. Bact.*, 1912, 17, 147—159).—Fatty metamorphosis may be produced in the leg muscles of a rat by applying a ligature round the thigh; in the fibres of these muscles the liposomes stain with greater intensity, and are much larger than normal; this is especially the case in well nourished animals, or if the rat is fed on fat. Pathological fatty metamorphosis is an exaggeration of a normal process, and consists in an increase in the size, staining capacity, and often the number of liposomes. Part of the fat is already present when the process begins. The increase of size is probably due to the accumulation of triolein. W. D. H.

Nature of the So-called Klausner Serum Reaction. G. KLAUSNER (*Biochem. Zeitsch.*, 1912, 47, 36—58).—The author has already shown that sera from certain cases of syphilis yield a precipitate when diluted with three times the volume of water. This property is lost if the serum is previously extracted with ether, and is restored by the addition to the serum of the lecithin–cuorin–cephalin fraction of brain lipoids. A serum can also be rendered non-precipitable by water if heated, but in this case the precipitability (activation) is not restored by lipoids. A serum activated by brain lipoids can also be inactivated by heating. The property of restoring activity by lipoids is not destroyed by heating. An artificially activated serum (by lipoids) if inactivated by heat is not rendered active again by the addition of fresh serum; hence, the activating property of lipoids is best if they are heated in the presence of serum. In all cases both of artificial and natural precipitin reactions, the optimal condition for precipitation is dilution with three times the volume of water. The natural precipitin reaction, when destroyed by heat, is not restored on the addition of fresh serum. A positive serum. inactivated by extraction with ether, can be reactivated

by the addition of the ethereal extract, which can also activate a normal inactive serum. Strong concentrations of the ethereal extracts of normal serum, dissolved in water, can also activate a normal serum. These results indicate that the precipitation is not due to globulins, and that in syphilitic sera the abnormalities are due to excess of lipoids. S. B. S.

Bence-Jones Proteinuria. E. PROVAN CATHCART and J. HENDERSON (*J. Path. Bact.*, 1912, **17**, 238—248).—A detailed account of the examination of the urine in a case of this disease. The general result of an examination of the protein present is that the findings of Hopkins and Savory (A., 1911, ii, 417) are confirmed. W. D. H.

The Action of Carbon Dioxide on the Vascular System. S. ITAMI (*J. Physiol.*, 1912, **45**, 338—344).—Small percentages of carbon dioxide produce a rise of arterial pressure mainly by increasing the force of the heart. Higher percentages (over 8%) produce increased constriction of the arterioles by stimulating the vaso-motor centre, and probably from an increased activity of the suprarenal glands. W. D. H.

Diuretic Action of Mercury Preparations. D. FERRON (*Chem. Zentr.*, 1912, ii, 370; from *Arch. Farm. sperim.*, 1912, **13**, 283—288).—Intravenous injection of doses of 0·000010 to 0·000025 gram-equivalents of mercuric chloride per kilo. of body-weight causes in rabbits an appreciable diuresis, but in larger doses the effect is less than that of the saline injection alone, owing to the toxic properties. A simultaneous injection of sodium chloride decreases the toxic effects, and, vice versa, mercuric chloride diminishes the toxic effects of hypertonic sodium chloride solution. S. B. S.

Action of Mercury Preparations on Spirochaete Diseases. I. Chemical-therapeutic Action of Mercury Compounds, Especially of a New Mercury Preparation which Strongly Attacks Spirochaete, but is only very Slightly Poisonous. WILHELM KOLLE, M. ROTHERMUND, and S. PESCHIĖ (*Chem. Zentr.*, 1912, ii, 1574—1575; from *Deut. med. Woch.*, 1912, **38**, 1582—1585).—The therapeutic action of many mercury preparations, such as colloidal mercury, mercury peptonate, dinitromercuridibenzoic acid, sulphaminophenyldimethylpyrazolonemercury, etc., has been examined. The aliphatic compounds do not differ very much in their action, but the benzene and pyrazolone compounds show many differences in toxicity and in the relation of the curative to the toxic dose. Sulphamino-compounds show a great lowering of the poisonous nature of mercury preparations without a diminution in their spirillocidal properties, and sulphaminophenyldimethylpyrazolonemercury is especially to be recommended. J. C. W.

Action of Mercury Preparations on Spirochaete Diseases. II. The Toxicology and Pharmacology of Some Mercury Compounds. J. ABELIN (*Chem. Zentr.*, 1912, ii, 1575; from *Deut. med. Woch.*, 1912, **38**, 1822—1825. Compare preceding abstract).—The poisonous nature of mercury compounds is influenced by their

chemical constitution; the introduction of sulpho- or amino-groups or of doubly-linked carbon atoms diminishes their toxicity. The most poisonous compounds are those in which the mercury is easily ionised, such as mercuric chloride. After injection of mercury preparations, the metal is always found in the liver. J. C. W.

The Sugar of the Blood and Urine under the Influence of Continuous Adrenaline Infusion. M. J. GRAMENITZKI (*Biochem. Zeitsch.*, 1912, **46**, 186—209).—Adrenaline was continuously administered to rabbits by Straub's infusion apparatus, and the effect on the sugar content in the blood and urine with varying dilutions of the drug was ascertained. It was found that there is in general a proportionality between the strength of the adrenaline stimulus, and both the resulting hyperglycæmia and glycosuria. Under urethane narcosis, the amount of adrenaline necessary to produce glycosuria is below the normal. Under these conditions, the strength of the adrenaline stimulus necessary to produce glycosuria is less than that required to raise the blood-pressure. The adrenaline administration increases the diuresis within a few minutes, and this effect is often, but not always, accompanied by glycosuria. The diuretic effect of urethane is to be ascribed to its urea components, whereas its glycosuric effects can only be partly ascribed to these.

Under urethane narcosis, artificially introduced sugar disappears more slowly than in normal animals; it also disappears more slowly from bound animals than from animals which are free. Venesection causes a distinct but slight hyperglycæmia, which is sometimes accompanied by glycosuria. The effects of the narcotic, etc., were investigated in some detail in view of criticisms on Ritzmann's work, which was also carried out in Straub's laboratory. In experiments on non-narcotised animals, it was found that the proportionality between the adrenaline stimulus and the effects was more marked than in the narcotised animals. The primary effect is hyperglycæmia, which can be quite marked (up to 0·2%) even when there is no glycosuria. The smallest stimulus necessary to produce glycosuria is higher in non-narcotised than in narcotised animals. The diuretic action of adrenaline follows definite laws, and is independent of the glycosuric effect. The general theory of the drug action is discussed. S. B. S.

Effect of Adrenaline on the Pulmonary Circulation. E. M. TRIBE (*Proc. physiol. Soc.*, 1912, xx—xxii; *J. Physiol.*, 45).—The conflicting results of previous workers on this question are probably due to the use of different preparations. Adrenaline preparations free from preservative cause constrictions at body temperatures. Preparations of adrenaline chloride preserved with 0·5% chloretone cause distinct dilatation of the pulmonary vessels. The constriction obtained with pure adrenaline is, however, hardly comparable with that seen in organs supplied by vaso-motor nerves, and the question of the existence of such nerves in the lung-vessels is left undecided.

W. D. H.

The Vascularity of the Liver. VIII. The Influence of Adrenaline on the Arterial Inflow. RUSSELL BURTON-OPITZ (*Quart. J. expt. Physiol.*, 1912, **5**, 309—324).—The complex nature of the blood supply of the liver renders the interpretation of records a matter of difficulty, and much of this and the following papers is devoted to a discussion of this question. There appears, however, no doubt that adrenaline constricts the arterioles of the liver, and leads then to a rise of pressure in the hepatic artery and an increase in the arterial inflow, the general blood-pressure being also raised. This is followed by a period of lessened inflow, although the hepatic pressure is still high, but the general pressure is only slightly elevated. Exceptions to this rule are explained by the fact that an injection of adrenaline does not necessarily imply that it enters the hepatic artery; it might be swept past the orifice of the artery; a similar accident in the case of arteries supplying other organs might explain unexpected results there. W. D. H.

The Vascularity of the Liver. IX. Influence of Amyl Nitrite on the Arterial Inflow. RUSSELL BURTON-OPITZ (*Quart. J. expt. Physiol.*, 1912, **5**, 325—328).—Inhalation of amyl nitrite causes a fall of general arterial pressure, but also causes a local change in the liver circulation. The fall of pressure in the hepatic artery is proportional to the general fall. On discontinuing the inhalation the pressure returns very slowly to normal. The arterial inflow is directly proportional to the systemic pressure, and the local changes are attributed wholly to the general effect. W. D. H.

The Vascularity of the Liver. X. The Influence of Adrenaline on the Venous Inflow. RUSSELL BURTON-OPITZ (*Quart. J. expt. Physiol.*, 1912, **5**, 329—342).—Evidence is adduced that the liver possesses two separate motor mechanisms, one in the terminals of the hepatic artery, and the other in the radicles of the portal vein, both of which are stimulated by adrenaline. W. D. H.

Metabolism Experiments in the Administration of Atophan. WITOLD SKÓRCZEWSKI and J. SOHN (*Chem. Zentr.*, 1912, ii, 1381; from *Zeitsch. expt. Path. Ther.*, 1912, **11**, 254—263).—Experiments on normal persons and on sufferers from gout show that the administration of atophan causes an increase in the output of uric acid, which, however, falls off with subsequent doses, more purine bases being discharged. An alteration in the functions of the kidneys is presumed, for a retention of chlorides immediately follows the administration. The atophan urine always gives the diazo-reaction, which becomes weaker after several doses; it also gives the phenol reaction with bromine water, a dirty rose-coloured precipitate with Millon's reagent, a yellow precipitate with phosphotungstic acid, and a green colour with a mixture of ammonium sulphate and ammonia.
J. C. W.

Why Does Atophan Increase the Excretion of Uric Acid? WITOLD SKÓRCZEWSKI (*Chem. Zentr.*, 1912, ii, 1679; from *Zeitsch. expt. Path. Ther.*, 1912, **11**, 501—507. Compare preceding abstract).—

The action of atophan is presumed to be an oxidation disturbance, of which the interference in the degradation of uric acid is a special case. This affords an explanation of the variations in uric acid values, the increase in neutral sulphur, and the appearance of the diazo-reaction in atophan urine. J. C. W.

The Formation of Phenol from *p*-Cresol in the Organism of the Dog. MAX SIEGFRIED and R. ZIMMERMANN (*Biochem. Zeitsch.*, 1912, **46**, 210—224).—In view of Baumann's conceptions as to the degradation of tyrosine in the organism through *p*-cresol and *p*-hydroxybenzoic acid to phenol, the effect of the administration of *p*-cresol was investigated, and it was found to yield phenol; 32—48% of the phenolic substances administered were recovered in the urine, of which 23—46% was in the form of phenol. Various modifications in the technique of phenol and cresol estimation are given, chiefly with regard to the method of bromination, and the addition of sufficient alkali before evaporating the urine to prevent loss of phenol.

S. B. S.

Formation of Glycine in the Body. II. ALBERT A. EPSTEIN and SAMUEL BOOKMAN (*J. Biol. Chem.*, 1912, **13**, 117—132).—Free leucine does not yield glycine, although it undergoes decomposition in the body. When benzoyl-leucine is given with benzoic acid, the output of hippuric acid is much greater than the leucine alone allows. Phosphorus poisoning causes no increased production of glycine or hippuric acid. Phosphorus plus benzoic acid has also no such effect unless the animal is fasting; then the increase must be due to massive disintegration of protein. Much of the glycine liberated on feeding with benzoic acid must be the result of a synthesis in the body. W. D. H.

Tolerance to Nicotine. WALTER E. DIXON and W. E. LEE (*Quart. J. expt. Physiol.*, 1912, **5**, 373—382).—A person tolerant to nicotine may be so because nicotine is not absorbed, but this is unlikely. A second explanation may be that it is more readily destroyed by the tissues. The present experiments were made on rabbits, and in thirteen out of sixteen experiments, tolerance was established, the drug being injected under the skin, or into the blood-stream. The analyses of the tissues show that the second explanation given above is correct, but that all the cells of the body do not possess the power of destroying nicotine in equal measure: the liver is the most effective. Evidence is adduced that the destruction is probably oxidative and due to the action of an enzyme. W. D. H.

The Oxidation of *p*-Phenylenediamine by Animal Tissues. FR. BATTELLI and (Mlle.) LINA STERN (*Biochem. Zeitsch.*, 1912, **46**, 317—342).—It is shown in investigations of the oxidative functions of tissues that the *p*-phenylenediamine reaction is better than the indophenol reaction. All tissues can oxidise this substance. The amount of oxygen consumed was in most cases measured, and it was found that in the accessory respiration of the tissues the amount consumed

was the sum of that used up by the tissues, when without the reagent plus the amount necessary to oxidise the reagent. In the primary respiration, on the other hand, the *p*-phenylenediamine oxidation partly replaced the tissue respiration. The oxidation is most intensive in the heart, red muscles, liver and kidney, and much less in the pancreas, spleen, and lungs. With the exception of the pancreas, the tissues maintain their oxidative capacity for a long time after death. Under similar conditions of experiment, most tissues use up the same amount of oxygen for oxidising *p*-phenylenediamine as they do for succinic acid; the brain, however, uses up more. In muscles and liver, no more oxygen is used up if both substances are present than if they are present alone. The blood is an energetic oxidiser, but not the serum, and the action appears to be due mostly to the hæmoglobin, as in the blood of some animals, the oxidative capacity remains after heating to 60°, or treatment with pancreatin. This is not even lost after heating the blood with mineral acids. An aqueous extract of liver inhibits the oxidative capacity of the blood, and the inhibitory action is not destroyed by warming to 60°. Blood has no appreciable oxidative action on succinic acid. S. B. S.

The Influence of Various Factors on the Oxidation of *p*-Phenylenediamine by Animal Tissues. FR. BATTELLI and (Mlle.) LINA STERN (*Biochem. Zeitsch.*, 1912, **46**, 343—366).—Small amounts of acid or alkali inhibit oxidation. There is no marked optimal temperature of reaction between 30° and 50°, but the action is lost by heating tissues to 60° for ten minutes. In medium concentrations, salts accelerate the reaction, exerting an inhibitory action at higher concentrations. Up to a certain limit the rate of oxidation increases with an increase of the concentration of the *p*-phenylenediamine. The oxydase is not washed out from the tissues by water, and the washed tissues still contain the oxydase. In oxygen, the reaction is more energetic than in air. The oxydase is destroyed by treating the tissues with alcohol or acetone, or with weak solutions of mineral acids. Aqueous extracts of tissues oxidise in presence of hydrogen peroxide, and this function is not lost on heating. The washed residue of muscular tissue will not oxidise in the presence of the peroxide after heating to 60°. Treatment of tissue with pancreatin diminishes the oxidative capacity. Both fresh and heated pancreatin increase the oxidative capacity of the vegetable polyphenoloxydases. Catalysts accelerating the oxidation of *p*-phenylenediamine and succinic acid are distinguishable from other oxydases by the facts that they are not dissolved out by water, and are destroyed by alcohol, acetone, or trypsin. With the exception of those of the brain, the catalysts appear to be identical. S. B. S.

Pharmacology of Picrotoxin, Picrotin, and Picrotoxinin. ALFREDO CHISTONI (*Chem. Zentr.*, 1912, ii, 371—372; from *Arch. Farmacol. sperim.*, 1912, **13**, 220—240).—Picrotoxin and picrotoxinin, in concentration 1 in 2000, reduce the tone and the amplitude of the contractions of smooth muscle, but in concentration 1 in 10,000 they increase the amplitude and diminish the number of contractions,

and either do not influence or slightly increase the tone of smooth muscle; picrotin is inactive.

All three substances, in a concentration of 1 in 2000, slightly increase the tone of striped muscle.

The frequency and contraction of the amphibian heart are affected by picrotoxin and picrotoxinin, due to their action on the muscle; picrotin is inactive.

Picrotoxin and picrotoxinin intravenously injected in dogs reduce the pulse and increase the blood pressure, due to stimulation of the pneumogastric and the vasomotor centres.

All three substances (1 in 2000—4000) still the isolated hearts of cats and rabbits, but this effect ceases when the poisons are removed. In a concentration of 1 in 80,000, picrotoxin at first quickens and then slows the heart's action, and these effects are not inhibited by the previous application of atropine. Picrotoxinin (1 in 80,000) at first strengthens and quickens the heart's action by its effect on the vagus, but finally stills the heart by direct action on the muscle fibres. Picrotin (1 in 40,000) accelerates the heart-beats and reduces the strength of the pulse. T. A. H.

The Poisonous Nature of Methyl and Ethyl Alcohols. ALEXANDER LANGGAARD (*Chem. Zentr.*, 1912, ii, 1382—1383; from *Berl. klin. Woch.*, 1912, **49**, 1704).—Methyl alcohol is more poisonous than ethyl alcohol when taken in repeated small quantities, but ethyl alcohol is much more dangerous when taken in a single large dose.

J. C. W.

Hæmolytic Substances obtained from Serum, and the Vitellus of Egg, Submitted to the Action of Venoms. C. DELEZENNE and (Mlle.) S. LEDEBT (*Compt. rend.*, 1912, **155**, 1101—1103. Compare *ibid.*, 1911, **152**, 790; **153**, 81).—Cobra venom acts on the serum of horse blood or the vitellus of egg, giving rise, by diastatic action of the venom on the lecithin, to *haemolysin*, which differs from lecithin in that it is soluble in water and insoluble in ether, and its molecule does not contain any unsaturated fatty acids (oleic acids). It resembles lecithin in its solubility in alcohol.

In the case of the serum the venom-serum mixture attains a maximum hæmolytic power, which then decreases until the mixture is inactive. At the same time a very fine precipitate of calcium soaps (palmitate and stearate) is produced. This diminution in activity, which is peculiar to serum, corresponds with further decomposition of the hæmolysin, and if the serum is dialysed prior to addition of the venom, the second stage in the action does not occur, and it behaves in the same manner as the vitellus of egg. The liquid resulting from the dialysis of the serum produces this secondary effect on addition to a venom-vitellus mixture. W. G.

Chemistry of Vegetable Physiology and Agriculture.

A Hygienic Pipette for Bacteriological and Chemical Work. SERGEI TSCHACHOTIN (*Centr. Bakt. Par.*, 1912, i, **67**, 319—320).—The pipette is intended to facilitate the removal of liquid cultures of pathogenic organisms, volatile poisonous compounds, or liquids above flocculent precipitates. A double-bored rubber cork is cut transversely, and between the two parts an ordinary rubber cap, such as is used for closing bacterial tube-cultures, is interposed and the three cemented together. Holes are made through the rubber cap with a hot needle, and two tubes are introduced: (*a*) a short straight one projecting slightly above and below the cork; (*b*) a siphon tube having the longer arm through the cork. A test-tube, having a diameter slightly larger than that of the rubber cork, is used as receiver, and closed by means of the flange of the rubber cap. The short arm may then be placed in the liquid to be pipetted off, and the cork of the pipette depressed slightly into the tube; the short glass tube is then closed by the fore-finger and the cork raised slightly. By this means a sufficient vacuum is created in the tube to cause the liquid to siphon over, and the flow is stopped by raising the short arm out of the liquid.

H. B. H.

Detection of Chitin in Bacteria. A. VIEHOEVER (*Ber. Deut. botan. Ges.*, 1912, **30**, 443—452).—Chitin was found to be present in a number of bacteria, and the occurrence of glucosamine in bacterial material is attributed chiefly to the abundant presence of chitin rather than to glucoproteins.

The results are of interest in removing a supposed difference between fungi and bacteria. That fungi contains chitin has been known for a long time.

N. H. J. M.

Gas Metabolism of Bacteria. I. Fermentation of Dextrose by Bacillus coli, B. typhosus, and Bacterium welchii. FREDERICK G. KEYES and LOUIS J. GILLESPIE (*J. Biol. Chem.*, 1912, **13**, 291—304).—The evolution of gas accompanying bacterial growth on media containing dextrose was studied by an exact method. Dextrose peptone media yield with *B. coli* more carbon dioxide than hydrogen on anaërobic fermentation; on a medium of ammonium lactate, disodium phosphate, and dextrose, nearly equal volumes of the two gases are obtained, the mean value of $CO_2:H_2$ being 1·06. This ratio is raised by the presence of oxygen, and by increase of phosphate. With *B. typhosus* the ratio is never below 19; with *Bacterium welchii* it is 1·48.

W. D. H.

Gas Metabolism of Bacteria. II. The Absorption of Oxygen by Growing Cultures of Bacillus coli and Bacterium welchii. FREDERICK G. KEYES and LOUIS J. GILLESPIE (*J. Biol. Chem.*, 1912, **13**, 305—310).—For both micro-organisms the absorption of oxygen

simulates a unimolecular reaction, but the respiratory quotients are widely different. With varying oxygen pressures the ratio $CO_2 : H_2$, varies enormously for *B. coli*, but only slightly for *Bact. welchii*.

W. D. H.

Activation of Certain Processes of Microbic Oxidation by Uranium Salts. HENRI AGULHON and R. SAZERAC (*Compt. rend.*, 1912, **155**, 1186—1188).—A further study of the influence of uranyl acetate on *Mycoderma aceti* (compare A., 1912, ii, 973) and a comparative trial of the influence of uranyl nitrate and uranyl acetate on the sorbose bacteria. In the case of the acetic acid ferment, 1 part of uranyl acetate per 1000 gives an increase of 57% in the acid production, and even at a dilution of 1 in 100,000 an increase is shown at the end of seven days. With the sorbose bacteria, uranyl nitrate increases the rate of oxidation up to concentrations of 1 in 5000, but stops all fermentation at 1 in 1000. At all concentrations the acetate has a more favourable influence than the nitrate, and 1 part of the acetate in 10,000 produces an increase yield of 76%. W. G.

Action of Infinitesimal Doses of Different Alkaline Substances, Fixed or Volatile, on the Vitality of Microbes. AUGUSTE TRILLAT and M. FOUASSIER (*Compt. rend.*, 1912, **155**, 1184—1186).—A study of the effect of adding minute quantities of various alkalis and organic bases to distilled water, to which is then added a drop of dilute, microbic, aqueous emulsion, containing no nutrient medium. The results, expressed in numbers of colonies formed, are given for the organism *M. prodigiosus*. With pure water there is slight growth for twenty-four hours and then the organism dies. Death is immediate with sodium hydroxide until a dilution of 1 in 50,000 is reached, and it is only in the case of ammonia, at dilutions of 1 in 50,000 and higher, that there is any marked increase in the number of colonies. With organic bases at higher orders of dilution (1 in 250,000) the number of colonies formed is greater with fatty amines than ammonia, and still greater with aromatic amines, although even here death ensues after fifteen days. The addition of traces of putrefactive gases to the distilled water allows cultivation to proceed even after three months. W. G.

Putrefaction with Special Reference to the Proteus Group. LEO F. RETTGER and CLYDE R. NEWELL (*J. Biol. Chem.*, 1912, **13**, 341—346).—Putrefaction is taken to mean decomposition of protein with the production of malodorous substances. The power to bring this about has been attributed to various members of the *Proteus* group acting anaërobically. The present experiments do not confirm this.

W. D. H.

The Influence of Organic Acids on the Fermentation by Yeast. FRITZ JOHANESSOHN (*Biochem. Zeitsch.*, 1912, **47**, 97—117).—Formic acid and its higher homologues accelerate, in sufficiently dilute solutions, the rate of fermentation by yeast. The optimal action for each acid lies at the same molecular concentration. The smallest

quantities of the acids which stop fermentation do not kill the yeast. The stoppage of fermentation depends on the concentration of the acid and not on the absolute quantity present. The relationship between this concentration and the quantity of yeast is not a simple proportional one, but can be represented by the equation of a parabola. No appreciable adsorption of acids by yeast takes place. The essential action of acids is to be ascribed, not to the ions, but to the whole undissociated molecule. S. B. S.

The Mechanism of Alcoholic Fermentation. ALEXANDER VON LEBEDEV (*Biochem. Zeitsch.*, 1912, **46**, 483—489).—A reply to the criticisms of Harden and Young (A., 1912, ii, 670). S. B. S.

The Mechanism of Alcoholic Fermentation. II. ALEXANDER VON LEBEDEV and N. GRIAZNOV (*Ber.*, 1912, **45**, 3256—3272. Compare A., 1911, ii, 816, 1122).—Pure glyceraldehyde is fermented by extract of dried yeast directly to carbon dioxide and alcohol. Hexosephosphoric ester is not formed as intermediate compound as in the case of the fermentation of dihydroxyacetone.

It is further shown that during the fermentation of sugar by yeast extract, acetaldehyde is not reduced to alcohol; on the other hand, in the absence of sugar, yeast extract is able to reduce acetaldehyde to alcohol. This reduction is effected by an enzymatic process.

It is considered that during fermentation hexose is hydrolysed to two trioses, one of which, glyceraldehyde, loses hydrogen, forming pyruvic acid, which undergoes rearrangement immediately and breaks down into acetaldehyde and carbon dioxide (compare Neuberg, A., 1911, ii, 976, 1019, 1020). Methylglyoxal hydrate is possibly an intermediate product (Neuberg and Kerb, A., 1912, ii, 973); preliminary experiments indicate that methylglyoxal is fermentable by yeast juice.

The decomposition of hexose into two molecules of triose is regarded as a reversible reaction; it will proceed when part of the triose is withdrawn as hexosephosphate, so that this last compound acts as a regulating factor. The following complete scheme is suggested for fermentation:

$$4C_6H_{12}O_6 = 8C_3H_6O_3.$$

Glyceraldehyde.	Dihydroxyacetone.
$4C_3H_6O_3 - 4H_2 = 4C_3H_4O_3$	$4C_3H_6O_3 + 4RHPO_4 =$
$4C_3H_4O_3 = 4C_2H_4O + 4CO_2$	$4C_3H_5O_2RPO_4 + 4H_2O$
$4C_2H_4O + 4H_2 = 4C_2H_5{\cdot}OH$	$= 2C_6H_{10}O_4(RPO_4)_2 + 4H_2O$
	$= 2C_6H_{12}O_6 + 4RHPO_4$

$$2C_6H_{12}O_6 = 4C_3H_6O_3, \text{ etc.}$$

E. F. A.

Influence of Pressure on Alcoholic Fermentation. LÉON LINDET and L. AMMANN (*Bull. Soc. chim.*, 1912, [iv], **11**, 953—956).—Regnard has shown already that under a pressure of 600 atmospheres yeast still ferments sugar solutions. In the present paper it is demonstrated that under such pressures as may occur in practice in fermenting liquids with yeast in closed vessels, the reproduction of

yeast and the fermentation go on at the same rate as under atmospheric pressure, although when the experiments are conducted under such conditions that the air is not renewed, fermentation and the multiplication of the yeast-cells take place more slowly, although the same production of carbon dioxide and alcohol is eventually reached.

T. A. H.

Is Ethyl Alcohol Produced by Yeast Fermentation in Absence of Sugar? CARL NEUBERG and JOHANNES KERB (*Chem. Zentr.*, 1912, ii, 1299—1300; from *Zeitsch. Gärungsphysiol. Mykologie*, 1912, 1, 114—120).—Since pyruvic acid is easily attacked by yeast with the formation of acetaldehyde (A., 1911, ii, 1019) it was expected that the ferment alone might be able to carry the reduction further. No alcohol could be found, however, but in the presence of sugar, much less aldehyde was formed than the amount of pyruvic acid destroyed would warrant. It seemed, therefore, that in normal alcoholic fermentation, a substance is produced which can reduce pyruvic acid or acetaldehyde to alcohol. Formic acid suggested itself, but was found to be without influence. Glycerol, however, had the effect of largely diminishing the output of acetaldehyde. J. C. W.

The Primary Transformation of Hexoses by Alcoholic Fermentation. HANS VON EULER and TH. BERGGREN (*Chem. Zentr.*, 1912, ii, 1383—1384; from *Zeitsch. Gärungsphysiol. Mykologie*, 1912, 1, 203—218).—The addition of yeast extract to living yeast expedites fermentation by 100%, and the difference, ΔC, between the change in optical rotatory power and the carbon dioxide developed (compare A., 1912, ii, 377) is increased by 20%. Assuming that fermentation proceeds in two stages, hexose $\longrightarrow$ intermediate product and intermediate product $\longrightarrow$ alcohol and carbon dioxide, it follows that, if the extract contains only one co-enzyme the first stage will be accelerated, but if there is a co-enzyme in the extract appropriate to each stage, then the two reactions will be unequally accelerated according to the relative amounts of the co-enzymes. Sodium nucleate also increases the activity of living yeast. J. C. W.

The Effect of Phosphates on the Work of the Proteolytic Enzymes in Yeast. NICOLAUS IWANOV (*Chem. Zentr.*, 1912, ii, 1384—1385; from *Zeitsch. Garüngsphysiol. Mykologie*, 1912, 1, 230—252).—The action of antiproteolytic by-products in yeast fermentation may be overcome by the addition of acid phosphates. Experiments with dead yeast cells (hefanol) show that the decomposition of albumin increases with the concentration of potassium dihydrogen phosphate, and that this increase is independent of temperature. By decreasing the volume of liquid, or by the addition of autolysis products, the action is still further increased, whereas leucine and tyrosine do not influence the process, but dipotassium hydrogen phosphate hinders it.

The proteolytic enzyme may be partly extracted from hefanol by means of water. When heated to 80°, it becomes inactive, but the addition of potassium dihydrogen phosphate revives its activity. It

seems that this salt is able to regenerate the peptase and to promote its action. J. C. W.

Comparative Influence of Potassium, Rubidium, and Cæsium on the Development and Sporulation of Aspergillus niger. BENJAMIN SAUTON (*Compt. rend.*, 1912, **155**, 1181—1183).—*Aspergillus niger* was cultivated on Raulin's liquid in the presence of equivalent amounts of potassium, rubidium, and cæsium as chlorides, and the crops weighed after four days at 37°. Potassium causes an enormous increase in the crop, which is diminished by 50% on replacing the potassium by rubidium, whilst cæsium is not a nutrient substance for the organism. In a mixture of the chlorides, *Aspergillus niger* fixes the potassium before the rubidium and cæsium, thus forming a means of freeing the two latter from the last traces of the former metal. Potassium plays an important part in the sporulation, although in the absence of zinc this could not be conclusively demonstrated. On substituting rubidium or cæsium for potassium no spores are formed. W. G.

The Scission of α- and β-Methylglucoside by Aspergillus niger. ARTHUR W. DOX and RAY E. NEIDIG (*Biochem. Zeitsch.*, 1912, **46**, 397—402).—*Aspergillus niger* acts on the two glucosides in exactly the opposite way to that in which yeast acts, for it readily hydrolyses the β-form (100% within six days), whereas it acts only slowly on the α-form, hydrolysing only 8% in twenty days. No capacity of adaptation of the ferment to the α-form could be demonstrated. S. B. S.

The Behaviour of Moulds (Aspergillus niger and Penicillium crustaceum) towards Phytin. M. A. JEGOROV (*Zeitsch. physiol. Chem.*, 1912, **82**, 231—242).—The moulds mentioned grow well in a solution of phytin, and assimilate its phosphorus, especially in the presence of sucrose and peptone or glycerol. They split off phosphoric acid in high measure from the phytin. W. D. H.

Decomposition of Carbamide, Uric Acid, Hippuric Acid, and Glycine by Moulds. ALEXANDER KOSSOWICZ (*Bied. Zentr.*, 1912, **41**, 791—792; from *Zeitsch. Garüngsphysiol. Mykologie*, 1912, **1**, 60—60). —Pure cultures of the following moulds were found to assimilate urea, uric acid, hippuric acid, and glycine under sterilised conditions: *Botrytis bassiani*, *Aspergillus niger*, *Isaria farinosa*, a *Fusisporium*, *Mucor Boidin*, and *Phytophthora infestans*. *Penicillium brevicaule* and *P. crustaceum* utilise urea, uric acid, and glycine, whilst *Cladosporium herbarum* and *Aspergillus glaucus* only utilised urea and uric acid as sources of nitrogen. N. H. J. M.

The Apparent Respiration of Dead Cells in the Reduction of Pigments. OTTO MEYERHOF (*Pflüger's Archiv*, 1912, **149**, 250—274).—Neutral and weakly alkaline acetone yeast possesses a measurable power of taking up oxygen, and this is increased in the presence of methylene-blue. In the presence of dead cells, reduction

of methylene-blue occurs also, but it occurs also if the dead cells are absent. It is, therefore, not due to anything of the nature of vitality. In one living animal cell, the egg of the sea-urchin, dissolved oxygen is present. W. D. H.

The Action of Uranium on the Plant Cell. C. ACQUA (*Chem. Zentr.*, 1912, ii, 1471; from *Arch. Farmacol. sperim.*, 1912, **14**, 81—84).—Dilute solutions of uranium salts (1 : 20,000 to 1 : 40,000) are absorbed by the cells of the roots of higher plants, where they hinder the division of the nuclei, and, consequently, the growth. The cells of the green parts are less permeable to uranium salts, and are therefore scarcely injured. Thorium and manganese salts have a similar but much smaller effect. J. C. W.

Absorption of Aniline Dyes in Living Plant Cells. E. KÜSTER (*Bied. Zentr.*, 1912, **41**, 763—764; from *Jahrb. wiss. Bot.*, 1911, **50**, 261).—It is shown that a considerable number of dyes, insoluble in fats, are abundantly taken up by plant cells. Overton's lipoid hypothesis regarding the nature of the outer layer of protoplasm is, therefore, insufficient, whilst Ruhland's opinion that there is no relation between the diffusibility of dyes and their penetration into plant cells is incorrect. N. H. J. M.

The Physical Character of Bio-electrical Differences of Potential. REINHARD BEUTNER (*Biochem. Zeitsch.*, 1912, **47**, 73—93).—The difference of potential at the contact surfaces—part of plant/aqueous solution of an electrolyte—can be altered in the sense that increasing dilution of the electrolyte makes the solution more positive. The change can be expressed by the following equation.

$$\text{Pot. diff. } 1 - \text{Pot. diff. } 2 = 58 \log \frac{c_1}{c_2} - 58 \log \frac{1 + \sqrt{1 + 10^6 m^2 c_1^2}}{1 + \sqrt{1 + 10^6 m^2 c_2^2}}$$

where

$$\log \frac{1}{m} = \frac{\text{Limiting value of potential difference} - \text{Pot. diff. for } c = n/500}{58}.$$

The method of arriving at these equations is given, and also an experimental verification of the same. The biological significance is also discussed. S. B. S.

Sterile Cultures of a Higher Plant. Assimilation of Nitrogen as Ammonia and as Nitrates. IVAN SCHULOV (*J. exper. Landw.*, 1912, **13**, 200—205 (in Russian), 205—206 (German Abstr.). Compare Hutchinson and Miller, A., 1909, ii, 923).—The results of sand culture experiments, under sterilised conditions, showed that nitrogen in the form of ammonium sulphate is assimilated by maize plants. It is also shown that the availability of phosphorite is considerably increased by the employment of ammonium nitrate, and that ammonium nitrate overcomes the injurious action of ammonium sulphate.

N. H. J. M.

Localisation and Function of Potassium in Plants. TH. WEEVERS (*Bied. Zentr.*, 1912, **41**, 764—765; from *Rec. trav. bot. Néerland.*, 1911, **8**, 289—332).—By means of Macallum's reagent

(sodium cobaltinitrate with ammonium sulphide and glycerol) it was found that potassium is present in all parts of *Thallophytes*, whilst negative results were obtained with the pollen grains of crocus and tulips. The greatest amount of potassium in *Phanerogams* was found in the young, embryonal tissues rich in plasma, and in the parenchyma of leaves, seeds, roots, and stems.

The conclusion is drawn that potassium takes part in the production of proteins. Its absence in the chlorophyll is opposed to the theory of Grafe and Stoklasa, that it takes part in the process of assimilation. N. H. J. M.

Chlorogenic and Saccharic Acids in Latex. K. GORTER (*Rec. trav. chim.*, 1912, 31, 281—286).—The colour reactions with ferric chloride which de Jong and Tromp de Haas (A., 1904, ii, 762) have shown to be characteristic of the latex of certain plants resemble the reactions with the chlorogenic acid obtained from coffee (A., 1908, i, 186). A delicate test for this acid is now described. It consists in boiling the suspected substance with dilute hydrochloric acid for an hour, extracting with ether, and shaking the washed and not too concentrated extract with very dilute ferric chloride, when a violet coloration is produced. By this means it is shown that chlorogenic acid is present in the latex of *Ficus elastica* and of *Castilloa elastica*. It has actually been isolated from the latter substance, 300 grams of the latex yielding 0·3 gram chlorogenic acid, m. p. 208°, $[\alpha]_D^{26}$ $-35·2°$. The latex of *Ficus elastica* contains, in addition, an organic magnesium salt, which has now been isolated and given the formula

$$C_6H_8O_8Mg,3H_2O.$$

The free acid has $[\alpha]_D^{26}$ $+36·5°$, and gives a sparingly soluble potassium salt, which closely resembles potassium disaccharate, and a diphenylhydrazone, m. p. 210°, which is identical with that derived from *d*-saccharic acid. This magnesium salt is the first indication of the occurrence of *d*-saccharic acid in nature. J. C. W.

The Carboxylase of Higher Plants. W. ZALESKI and ELISABETH MARX (*Biochem. Zeitsch.*, 1912, 47, 184—185).—Neuberg has shown that yeast can ferment pyruvic acid with evolution of carbon dioxide. The authors now show that the addition of this acid to powdered pea-seeds causes an increase of the post-mortal production of carbon dioxide, which takes place with equal energy in air and hydrogen. S. B. S.

Basic Constituents of Fly Agaric. E. BUSCHMANN (*Chem. Zentr.*, 1912, ii, 613; from *Pharm. Post*, 1912, 45, 453—454).—A methyl alcohol extract of fly agaric (*Amanita muscaria*) by precipitation with phosphotungstic acid and silver nitrate yielded hypoxanthine and xanthine, the former predominating (compare Zellner, *Chemie der höheren Pilze*, 1907). T. A. H.

The Inulin Metabolism of Cichorium Intybus (Chicory). II. The Formation and Storage of Inulin. VIKTOR GRAFE and V. VOUK (*Biochem. Zeitsch.*, 1912, 47, 320—330. Compare A., 1912, ii, 977).—From estimations of reducing sugar and inulin in different

parts of the plant collected at different periods, the following conclusions were drawn. The inulin is not merely a reserve material, but is intimately connected with the general carbohydrate metabolism, as it can be readily detected macrochemically in the parenchymatous cells of the leaves of young plants. No difference in the inulin and lævulose content of leaves of plants collected in the morning and afternoon could be detected. From this fact the conclusion is drawn that new carbohydrate is formed during the day in such quantity that an equilibrium is maintained between the lævulose and inulin. As the development of the root progresses there is a constant increase in the inulin content, accompanied at first by a diminution of the lævulose; the latter increases in quantity again as the roots ripen.

S. B. S.

The Organic Phosphoric Acid of Cotton-seed Meal. R. J. ANDERSON (*J. Biol. Chem.*, 1912, **13**, 311—324).—The organic phosphorised substance from cotton-seed meal is probably either phytin or an isomeride; this is to be ascertained by further work.

W. D. H.

Pigments of the Fucoideæ. HARALD KYLIN (*Zeitsch. physiol. Chem.*, 1912, **82**, 221—230).—The fucoidæe contain carrotene and a crystalline, yellow pigment probably identical with xanthophyll. They further contain a yellow pigment, phycoxanthin, which differs from xanthophyll in being soluble in light petroleum. E. F. A.

Presence of Gentiopicrin, Gentianose, and Sucrose in the Fresh Roots of Gentiana Asclepiadea. MARC BRIDEL (*Compt. rend.*, 1912, **155**, 1164—1166).—The author has isolated and characterised gentiopicrin, gentianose, and sucrose from the fresh roots of *Gentiana Asclepiadea*, and has obtained indications of the presence of another carbohydrate, hydrolysable by invertin. W. G.

The Constituents of Ipé tabaco Wood (Bignonia tecoma). OTTO A. OESTERLE (*Chem. Zentr.*, 1912, ii, 1666—1667; from *Schweiz. Woch. Chem. Pharm.*, 1912, **50**, 529—532).—In order to investigate the nature of Lee's tecomin (T., 1901, **79**, 284), the alcoholic extract of *B. tecoma* wood has been freed from resinous matter by means of benzene and light petroleum, leaving a mixture which was partly soluble in boiling sodium carbonate solution. The soluble substance crystallised in yellow needles or leaflets, m. p. 142—143°, soluble in alkalis and alkali carbonates with intense red colours which disappeared on reduction, but soon reappeared in the air. Tecomin is possibly identical with lapachol. From the substance which remained undissolved by sodium carbonate, light yellow needles, m. p. 242°, were obtained. J. C. W.

Variations of the Fatty Matters, Sugars, and Saponin during the Maturation of Seeds of Lychnis Githago. (Mlle.) MARIE KORSAKOV (*Compt. rend.*, 1912, **155**, 1162—1164).—The fatty matters, sugars, and saponin have been estimated in the seeds of *Lychnis Githago*

at three stages in their development: (*a*) just after flowering, when young and white; (*b*) further advanced but still white; (*c*) almost ripe and black. The results show a marked decrease in the content of fatty matters and sugars, reducing and non-reducing, and an increase in the saponin content with advance in development. The young seeds only contain traces of saponin, and the amount of saponin in the other organs of the plant being practically nil, it seems that the glucoside must be formed in the seed itself. W. G.

Presence of Gentiopicrin in Swertia perennis. MARC BRIDEL (*Compt. rend.*, 1912, **155**, 1029—1031; *J. Pharm. Chim.*, 1912, [vii], **6**, 481—484).—*Swertia perennis* contains the glucoside gentiopicrin, which can be isolated in the pure state and hydrolysed by emulsin (compare Bourquelot and Bridel, A., 1910, ii, 234). There are also indications of the presence of a carbohydrate, which is only very slowly hydrolysed by emulsin. W. G.

Occurrence of Trehalose, Vanillin, and *d*-Sorbitol. EDMUND O. VON LIPPMANN (*Ber.*, 1912, **45**, 3431—3434).—After exposure to a sudden sharp frost in July, the flowers of some blooming rushes, *Carex brunescens*, growing in a sheltered spot, were observed to be covered with minute, hard, white crusts, which proved to be hydrated trehalose, $C_{12}H_{24}O_{11},2H_2O$.

The flowers of an orchid, *Gymnadenia albida*, growing last summer on the heights above Davos, were observed by the author to have a strong odour of vanilla; vanillin was isolated from them. Under normal conditions of growth, the flowers of this orchid contain little or no vanillin.

During last year's wet summer, many fungi in the fields near Kissingen grew in enormous quantities and to prodigious size, in particular, a variety of *Boletus bovinus*, which reached the dimensions of a dinner plate. After fine weather had set in, a number of the tops of these fungi, which had been struck off by a passer-by and had partly dried, were found to be covered with a network of a crystalline substance which on examination proved to be hydrated *d*-sorbitol. C. S.

Chemical means of Protecting Plants from Frost. N. A. MAXIMOV (*Ber. Deut. bot. Ges.*, 1912, **30**, 504—416. Compare A., 1912, ii, 476).—The supposition that the protective action of the substances employed depends on the eutectic point of the solution is confirmed by the results of further experiments in which mixtures instead of single substances were used. A mixture of mannitol and potassium nitrate considerably increased the power of resisting cold, whilst the two substances, singly, have very little effect.

As regards the connexion between the protective action and the permeability of the plasma for the protective substance, it is now shown that the action takes place immediately, and that the result depends on the action of the solution on the surface of the plasma. From this it follows that the death of plants by freezing is due to injury to the surface of the plasma. N. H. J. M.

Alfalfa. IV. Enzymes Present in Alfalfa Seeds. C. A. JACOBSON (*J. Amer. Chem. Soc.*, 1912, **34**, 1730—1740).—In continuation of the investigation of alfalfa (*Medicago sativa*) (A., 1912, ii, 80, 239, 976), a study has been made of the enzymes contained in the seeds. The results show that the seeds contain enzymes, which, like amylase and emulsin, are capable of hydrolysing starch and amygdalin respectively; an enzyme which coagulates milk, like rennin; an enzyme, which like the peroxydases, precipitates purpurogallin from a pyrogallol solution containing hydrogen dioxide, and an enzyme, resembling proteases in being able to digest casein and Witte peptone. This protease is found to be a vegetable erepsin, since it will not begin the digestion of egg-albumin, blood-serum, legumin, or conglutin, and its digestion of casein and Witte peptone is checked to some extent by the presence of egg-albumin or blood-serum. The seeds do not appear to contain invertase or lipase. E. G.

Comparative Efficiency for Growth of the Total Nitrogen from Alfalfa Grass and Corn Grain. EDWIN B. HART, GEORGE C. HUMPHREY, and F. B. MORRISON (*J. Biol. Chem.*, 1912, **13**, 133—154). —Experiments on heifers show that the utilisation of nitrogen for growth is as efficient when the source is alfalfa hay as when it is corn kernel. There was no sudden increase or decrease in the nitrogen of urine or fæces when the animals were suddenly changed from one ration to the other. The amide-nitrogen, which is high in the grass, is therefore not valueless. The effect on milk production will be treated later. In growing heifers, the creatinine output rises with increased storage of nitrogen. W. D. H.

Observations on the Action of Fluorine in Nature. UGO ALVISI (*Gazzetta*, 1912, **42**, ii, 450—452).—The author confirms the presence of fluorine in wheat (when ripe) and in human teeth. He suggests the employment of calcium silicofluoride as a manure.
R. V. S.

Reducing Substances Present in Fresh Sugar Beets. Their Influence on the Direct Estimation of Sucrose in the Beet. HENRI PELLET (*Bull. Assoc. chim. Sucr. Dist.*, 1912, **30**, 239—253).—Freshly harvested sugar beets always contain a small quantity of reducing sugar, amounting to 0·05—0·27 gram per 100 c.c. of the sap. This amount is independent of the initial richness of the beet in sucrose, and does not vary in different parts of the same beet. The estimation is made in the sap clarified by treatment with neutral lead acetate; basic lead acetate precipitates some of the reducing sugar. Beets of inferior quality contain 2—2·5 grams of reducing sugar per 100 c.c. of sap. Beets stored in silos lose some of their sucrose, but the amount of reducing sugar does not increase. Beets damaged during harvesting or transport contain 0·3—0·35 gram of reducing sugar; in sickly beets the quantity increases to 0·4—0·5 gram per 100 c.c. of sap.

Reducing sugar is not formed during diffusion. The amount arising

during the processes of manufacture is very small when proper care is exercised.

The presence of this reducing sugar renders the polarimetric estimation of the sucrose in the beet-juice inaccurate. E. F. A.

Sesame Cake. ACH. GRÉGOIRE and EM. CARPIAUX (*Bull. Soc. chim. Belg.*, 1912, **26**, 479—485).—A number of samples of sesame cake have been examined with respect to the content of pure ash, lime, fat, acidity of fat, and oxalic acid. The results show great variations in the composition of the commercial products.

The pure ash contains, as a mean value, 34·5% of lime, the extreme values being 28·4% and 39·8% respectively. This determination may be employed for controlling the purity of sesame cake, since the great majority of other seeds yield an ash relatively poor in lime. Sesame cake, free from oil and earth, contains an average of 1·99% anhydrous oxalic acid, the individual determinations varying between 1·44% and 2·96%. This value is not sensibly altered when the oil becomes rancid. Free oxalic acid could not be detected. H. W.

The Black Earths of the Valley of l'oued R'Dom in Morocco. G. GIN (*Compt. rend.*, 1912, **155**, 1166—1167).—An account of a black arable earth from a fertile valley traversed by l'oued R'Dom. A description of the earth and results of chemical analyses are given. It is found to support vegetation even in the warm, dry months, and this is supposed to be due to the presence of a trihydrated aluminium oxide in the clay, which supplies the necessary water during the dry months, and recoups itself at the next wet season. The black colour is due to an amorphous humic substance, which is partly soluble to a brown solution in potassium hydroxide.

W. G.

Agronomic Study of Manganese. P. NOTTIN (*Compt. rend.*, 1912, **155**, 1167—1169).—A study of the behaviour of different soils towards soluble manganese salts. Soil has the power of rendering the manganese insoluble and fixing it, the constituents of the soil, however, having different absorbent powers. Silica and humus play no part in the manganese fixation. Chalk produces fixation of the manganese by interchange of the calcium and manganese. Natural clay also has a marked absorbent power, independent of the lime present.

W. G.

Nitrolim and its Decomposition in the Soil. III. C. J. MILO (*Chem. Zentr.*, 1912, ii, 1393; from *Med. Proefstat. Java-Suikerind*, 1912, 601—634. Compare A., 1912, i, 16).—Nitrolim is hygroscopic, and absorbs water and carbon dioxide with liberation of nitrogen. The calcium cyanamide decomposes into cyanamide and carbamide, which, with the help of micro-organisms, gives rise to ammonium carbonate. In soils which are only slightly absorptive, the calcium cyanamide gives basic salts and cyanamide, and further decomposition proceeds very slowly. J. C. W.

Organic Chemistry.

Purification of Saturated Hydrocarbons by means of Potassium Permanganate. NICOLAI M. KISHNER (*J. Russ. Phys. Chem. Soc.* 1912, **44**, 1748—1753).—Saturated hydrocarbons, when prepared by the reduction of their halogen derivatives, are usually contaminated with unsaturated hydrocarbons, and the same is the case with trimethylenic hydrocarbons prepared by Gustavson's method. The removal of these impurities is an easy matter when the saturated hydrocarbons are stable to concentrated sulphuric acid or to fuming nitric acid; but in some cases the unsaturated hydrocarbons are converted into saturated ones by these reagents, and in certain others the carbon-atom skeleton undergoes isomerisation.

The author has investigated the efficacy of potassium permanganate as a means of purification in these exceptional instances. The results show that the complete removal of small admixtures of the unsaturated compounds in this way is very difficult, and is accompanied by the loss of much of the saturated hydrocarbons. As the concentration of the unsaturated hydrocarbon in the mixture diminishes, its rate of oxidation decreases, until finally it may become less than that at which the saturated compound oxidises; thus a mixture containing 15 parts of menthane and 5 parts of menthene is converted into one containing 11·5 and 2·5 parts respectively by one oxidation, these amounts becoming 7·2 and 0·8, and 3·7 and 0·3 after successive oxidations. Somewhat similar results are obtained with mixtures of menthane and limonene. T. H. P.

Fractional Distillation of Coal. LÉO VIGNON (*Compt. rend.*, 1912, **155**, 1514—1517).—The author has distilled various samples of coal at successive temperatures of 400°, 600°, 850°, 1000° and 1200°, and analysed the gaseous mixtures evolved at these temperatures. The results show (1) that the unsaturated hydrocarbons (acetylene, ethylene, etc.) almost all pass over below 600° and disappear entirely at higher temperatures; (2) methane and its homologues are very abundant (60—80% of total gas) up to 800°, after which they decrease rapidly with rise in temperature; (3) from 800—1000° hydrogen predominates, but in its turn diminishes above 1000°; (4) very high temperatures favour the formation of carbon monoxide.

Rise in distillation temperature produces an increase in the total volume of gas evolved, but a diminution in its calorific power.

W. G.

A New Method for Determining the Position of the Double Bond. JOH. JEGOROV (*J. pr. Chem.*, 1912, [ii], **86**, 521—539).—The method consists in combining the unsaturated compound with nitrogen peroxide, and heating the resulting additive compound with concentrated hydrochloric acid, whereby the molecule becomes ruptured at the position originally occupied by the double linking with the forma-

tion of two carboxylic acids: $R\cdot CH{:}CHR^1 \longrightarrow NO\cdot O\cdot CHR\cdot CHR^1\cdot NO_2$, or $NO_2\cdot CHR\cdot CHR^1\cdot O\cdot NO \longrightarrow R\cdot CO_2H + R^1\cdot CO_2H$.

The transformation of a nitrite into a carboxylic acid has been investigated in the case of amyl nitrite, which, under the influence of hydrochloric acid, yields amyl alcohol and an ester, presumably amyl valerate, the valeric acid being formed by the oxidising action of the nitrite on the amyl alcohol.

When heated with water at 160—170°, the light yellow, oily, additive compound of oleic acid and nitrogen peroxide yields pelargonic acid, *ω-nitrononane*, azelaic acid, and *θ-nitrononoic acid*. The nitro-compounds could not be isolated in a state of purity, and therefore were identified by reducing them to the corresponding amino-compounds.

θ-Aminononoic acid, $NH_2\cdot CH_2\cdot[CH_2]_7\cdot CO_2H$, was isolated in the form of its *platinichloride* from the above mixture by distillation in steam, and reduction of the residual nitrononoic and azelaic acids with tin and hydrochloric acid.

Nonylamine is a viscid liquid, and forms a *hydrochloride* which becomes black when heated without showing a definite m. p.; the *platinichloride*, $2C_9H_{19}\cdot NH_2,H_2PtCl_6$, crystallises in golden-yellow needles.

When heated with concentrated hydrochloric acid, the additive compound of oleic acid and nitrogen peroxide yields pelargonic and azelaic acids, together with hydroxylamine.

From these results the conclusion is drawn that the additive compound consists of a mixture of two isomerides (I) and (II), which, when heated with water, undergo the transformations shown in the following scheme:

$$\text{(I.)}\ 2C_8H_{17}\cdot CH(NO_2)\cdot CH(O\cdot NO)\cdot C_7H_{14}\cdot CO_2H \longrightarrow H_2O + N_2O +$$
$$2C_8H_{17}\cdot CH(NO_2)\cdot CO\cdot C_7H_{14}\cdot CO_2H \xrightarrow{H_2O} C_9H_{19}\cdot NO_2 + C_7H_{14}(CO_2H)_2.$$
$$\text{(II.)}\ 2C_8H_{17}\cdot CH(O\cdot NO)\cdot CH(NO_2)\cdot C_7H_{14}\cdot CO_2H \longrightarrow H_2O + N_2O +$$
$$C_8H_{17}\cdot CO\cdot CH(NO_2)\cdot C_7H_{14}\cdot CO_2H \longrightarrow C_8H_{17}\cdot CO_2H + NO_2\cdot C_8H_{16}\cdot CO_2H.$$

The action of hydrochloric acid on θ-nitrononoic acid gives rise to azelaic acid: $NO_2\cdot CH_2\cdot[CH_2]_7\cdot CO_2H \longrightarrow$
$$HO\cdot N{:}C(OH)\cdot[CH_2]_7\cdot CO_2H \longrightarrow NH_2\cdot OH + C_7H_{14}(CO_2H)_2.$$
In a similar manner nitrononane yields pelargonic acid.

The above method has been applied to the determination of the position of the double linking in a number of unsaturated compounds. In all cases the unsaturated compound was allowed to combine with nitrogen peroxide in light petroleum solution at a low temperature, and the resulting oily additive compounds were heated with concentrated hydrochloric acid at 130—140°.

Undecenoic acid gave sebacic and formic acids. *iso*Oleic acid decomposes into octoic and sebacic acids, corresponding with the structure $CH_2Me\cdot[CH_2]_5\cdot CH{:}CH\cdot[CH_2]_8\cdot CO_2H$; erucic acid into nonoic and brassylic acids.

From the behaviour of the hexylene, prepared from mannitol, which yielded formic, acetic, butyric and valeric acids, the author draws the conclusion that the hydrocarbon consists of a mixture of two isomerides, $CHMe{:}CHPr^a$ and $CH_2{:}CH\cdot CH_2Pr^a$.

Methoxy- and ethoxy-undecenoic acids, obtained by the action of alcoholic alkali hydroxides on the dibromide of undecenoic acid, gave results in agreement with the structure:

$$OMe\cdot CH_2\cdot[CH_2]_7\cdot CH\colon CH\cdot CO_2H.$$

The unsaturated acids from linseed oil were also examined and found to consist of a mixture of the two following compounds:

$$CHEt\colon CH\cdot CH_2\cdot CH\colon CH\cdot CH_2\cdot CH\colon CH\cdot[CH_2]_7\cdot CO_2H.$$
$$CH_3\cdot[CH_2]_4\cdot CH\colon CH\cdot CH_2\cdot CH\colon CH\cdot[CH_2]_7\cdot CO_2H.$$

F. B.

The Theory of the Asymmetric Carbon Atom and Pasteur's Principle. ERNST MOHR (*J. pr. Chem.*, 1912, [ii], **87**, 91—95).—A theoretical paper in which the author shows that, contrary to his previous views (A., 1904, i, 1), a compound of the formula $C(dR)_2(lR)_2$, where dR and lR represent structurally identical, univalent groups of enantiomorphous configuration does not contain an asymmetric carbon atom, and is therefore incapable of existing in two enantiomorphous forms. F. B.

The Melting Point of Ethylene Dibromide. EUGEN VON BIRON (*Zeitsch. physikal. Chem.*, 1913, **81**, 590).—Moles (A., 1912, ii, 533) states that ethylene dibromide has m. p. 9·975°. Biron has shown that when purified by repeated fractional crystallisation it has m. p. 10·012° and D_4^{20} 2·1804 (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 1609). He points out that the work must be carried out in the absence of light. J. F. S.

The History of Distillation and of Alcohol. EDMUND O. VON LIPPMANN (*Chem. Zeit.*, 1913, **37**, 1—2. Compare A., 1912, i, 824).—The author combats the statement attributed to Davidsohn (*Mitt. Ges. Med. Naturwiss.*, 1912, **12**, 102) that the Celts first submitted fermented liquors to distillation and that the knowledge of the process passed from them to other nations. D. F. T.

Ethyl Ether by Catalysis. CHARLES BASKERVILLE (*J. Amer. Chem. Soc.*, 1913, **35**, 93—96).—Sabatier and Mailhe (A., 1910, i, 294) have shown that several metallic oxides, including that of thorium, exert a catalytic action on alcohols between 300° and 350°. In the case of ethyl alcohol, the action appears to consist almost entirely of dehydration with formation of ethylene, but at a lower temperature the dehydration is said to be capable of limitation to the production of ether.

Experiments are described in which alcohol vapour was passed over pure thorium oxide at about 250°, but although the conditions specified by Sabatier and Mailhe were carefully observed, little or no ether was obtained. E. G.

Esters and Amides of the Phosphoric Acids. IV. Reaction between Esters of Metaphosphoric Acid and Uni- and Multi-valent Alcohols. Synthesis of Glycero-mono- and -di-phosphoric Acid. Preparation of Pure Silver Metaphosphate. KURT LANGHELD, F. OPPMANN, and E. MEYER (*Ber.*, 1912, **45**, 3753—3760).—In part polemical (compare Grün and Kade, this vol.,

i, 159). When ethyl metaphosphate reacts with ethyl alcohol and benzyl alcohol, the following three products are formed:

$PO(OEt)_2 \cdot O \cdot C_7H_7$, $PO(OH)_2 \cdot O \cdot C_7H_7$, $OEt \cdot PO(O \cdot C_7H_7) \cdot OH$.

The mono- and tri-esters are obtained in molecular proportions. The same result is obtained with glycerol, in which case the excess prevents the determination of the relative proportions of the esters.

Barium glycerophosphate is obtained in stellar aggregates of small platelets containing a molecule of water, which is slowly removed on drying in a vacuum. On exposure of the anhydrous substance, $\frac{1}{2}H_2O$ is absorbed quickly and the second $\frac{1}{2}H_2O$ only slowly. The solubility in water at 220° is 8·4%, and approaches that of the natural product.

Barium glycerodiphosphate, $2H_2O$, crystallises well.

To prepare pure silver metaphosphate, $(AgPO_3)_2,H_2O$, sodium ammonium phosphate is converted into metaphosphate by cautious heating in a vacuum at 320°. About half the product is soluble in water, from which it is precipitated in crystalline form on the addition of alcohol. This product, $2NaPO_3,H_2O$, reacts with silver nitrate.

Silver metaphosphate crystallises in large octahedra. E. F. A.

The Glycerotriphosphoric Acid of Contardi. PAUL CARRÉ (*Compt. rend.*, 1912, **155**, 1520—1521*).—A reply to Contardi (compare A., 1912, i, 743), in which the author maintains that the esterification of 1 mol. of glycerol with 3 mols. of phosphoric acid gives glycerodiphosphoric acid, $C_3H_5(PO_4H_2)_2 \cdot OH$, glycerophosphoric acid, and a di-ester of the form PO_4R_2H, about 50% of the phosphoric acid remaining unaltered and no glycerotriphosphoric acid being formed.

He further maintains his views, already expressed (compare A., 1904, i, 133, 215; 1905, i, 184), that, on heating an equimolecular mixture of glycerol and phosphoric acid in a vacuum, the mixture is transformed quantitatively into the normal tri-ester. W. G.

Crystalline Forms of Salts of Ethanedisulphonic Acid. K. BLEICHER (*Zeitsch. Kryst. Min.*, 1912, **51**, 502—520).—Detailed crystallographic constants are given for the following salts of ethanedisulphonic acid: Sodium ($2H_2O$), monoclinic;

$$a:b:c = 0·7893:1:0·4624;$$

$\beta = 91°34'$. Lithium ($2H_2O$), monoclinic; $a:b:c = 1·5717:1:2·5939$; $\beta = 111°7'$. Potassium, monoclinic; $a:b:c = 1·2594:1:5816$; $\beta = 126°18'$. Ammonium, monoclinic; $a:b:c = 1·1647:1:0·6959$; $\beta = 120°21'$. Potassium sodium ($2H_2O$), rhombic;

$$a:b:c = 0·7467:1:0·5563.$$

Disodium ammonium, $Na_4(NH_4)_2(C_2H_4S_2O_6)_3$, monoclinic; $a:b:c = 1·5637:1:0·5906$; $\beta = 101°17'$. Lithium potassium ($1H_2O$), monoclinic; $a:b:c = 1·2401:1:1·2753$; $\beta = 104°41'$. Lithium ammonium, monoclinic; $a:b:c = 0·7627:1:0·7799$; $\beta = 96°46'$. Barium, rhombic; $a:b:c = 0·7678:1:0·9062$. Barium (H_2O), rhombic; $a:b:c = 0·9374:1:0·4051$. Strontium (H_2O), monoclinic;

$$a:b:c = 0·5347:1:0·0641;$$

$\beta = 101°3'$. Cadmium ($2H_2O$), triclinic; $a:b:c = 1·7421:1:1·0515$; $\alpha = 90°1'$, $\beta = 101°56'$, $\gamma = 100°54'$. Zinc ($3H_2O$), triclinic; $a:b:c =$

* and *Bull. Soc. chim.*, 1913, [iv], **13**, 66—69.

0·5718 : 1 : 0·7813; $a = 94°0'$, $\beta = 110°28'$, $\gamma = 90°30'$. Magnesium ($4H_2O$), triclinic; $a : b : c = 0·6546 : 1 : 0·4066$; $a = 96°18'$, $\beta = 102°9'$, $\gamma = 94°14'$. Copper ($4H_2O$), triclinic; $a : b : c = 0·6527 : 1 : 0·4350$; $a = 95°15'$, $\beta = 96°39'$, $\gamma = 94°32'$. L. J. S.

Phenomenon of Double Melting for Fats. ANDREAS SMITS and S. C. BOKHORST (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 681—683).—According to Guth (A., 1903, i, 225), tristearin melts at 71·5°, but if allowed to solidify in a capillary tube it melts at 55°, solidifies again, and melts a second time at 71·5°. In view of the improbable explanation of these results, the authors have made a further examination of the behaviour of the substance, and find that the above phenomena are due to the existence of two crystalline modifications. Of these, the metastable form appears most readily. If, however, the liquid is kept for some time at a temperature between the two melting points, the stable form crystallises out, although very slowly.

When the metastable form is heated, it melts at 54·5°, and when the temperature is then raised to 63° the stable form is deposited. The stable unary melting point is 70·8°. It is probable that the double melting phenomena, observed for other fats, are to be explained in the same way. H. M. D.

Anomalies in the Consistency and Melting Points of Fats. ADOLF GRÜN (*Ber.*, 1912, **45**, 3691—3701).—It has already been observed that glycerides can exist in two modifications (Kast, A., 1906, i, 922; Grün and Schacht, A., 1907, i, 462). To this phenomenon is attributable the variation in the m. p. recorded for certain fats with the age or method of preparation of the sample. The present investigation endeavours to extend the present limited knowledge of this phenomenon.

[With A. CUSTODIS].—$\alpha\gamma$-Dilaurin, obtained from $\alpha\gamma$-dichlorhydrin and potassium laurate, is a mixture of two modifications; the product of higher m. p., 57°, *acetyl* derivative, m. p. 34°, or after one year 32°, is obtained in better yield the lower the reaction temperature (140—150°), whilst the other modification, m. p. 40°, preponderates when the temperature of formation is somewhat higher (170—180°); the latter modification very easily remains in a supercooled condition. Both forms, on keeping, finally attain a m. p. 45°, which is also the temperature observed for a mixed m. p. It is probable that the two substances are structurally identical.

When the two forms of $\alpha\gamma$-dilaurin are treated with lauryl chloride at 100°, two modifications of trilaurin are obtained, one m. p. 45°, the other forming soft needles which melt in the hand. The former, obtained from the less fusible dilaurin, is identical with natural trilaurin; the latter, obtained from the more fusible dilaurin, resembles its parent substance in having in benzene a molecular weight only one-half that expected from the formula; the less fusible di- and tri-laurins are of normal molecular weight.

$\alpha\gamma$-Dibenzoin, $OBz{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OBz$, by warming with glycerol and sulphuric acid, can be converted into a modification

which remains oily at the ordinary temperature; the molecular weight of the substance in benzene solution is, however, approximately normal.

$\alpha\beta$-Dibenzoin, obtained from anhydrous potassium benzoate and $\alpha\beta$-dibromohydrin, and also in a purer condition by the use of silver benzoate, is also a viscous, uncrystallisable oil.

In an addendum it is remarked that lack of recognition of the above peculiarities of glycerides may lead to considerable errors, as, for example, the reported formation of $\alpha\beta$-dilaurin from $\alpha\gamma$-dichlorohydrin (van Eldik Thieme, A., 1912, i, 333). D. F. T.

The Synthesis of Fats. DAVID HOLDE (*Ber.*, 1912, **45**, 3701—3702. Compare Kremann and Schoulz, A., 1912, ii, 1152).—The author draws attention to the manner in which the results of Kremann and Schoulz (*loc. cit.*) support his views (A., 1903, i, 140) that the stearic and palmitic acids in olive oil must be present in the form of "mixed" glycerides, and not as tripalmitin and tristearin.

D. F. T.

Diglyceride-phosphoric Acids. ADOLF GRÜN and FRITZ KADE (*Ber.*, 1912, **45**, 3358—3367).—When phosphoric oxide acts on distearin at temperatures above 100°, or in the absence of moisture, blackening takes place. When the requisite amount of water is added, esters of pyrophosphoric acid or primary orthophosphoric acid esters are obtained. The former decompose into phosphoric acid and the ortho-acid esters, which are transformed in turn into secondary and tertiary esters and finally into the stable form, pentadistearin phosphate. In addition the reaction product contains free phosphoric acid and distearin. The changes are expressed by the scheme:

$$PO(OR)(OH)\cdot O\cdot PO(OH)_2 \longrightarrow PO(OR)(OH)_2 \longrightarrow PO(OR)_2(OH) \longrightarrow PO(OR)_3 \longrightarrow P(OR)_5.$$

$\alpha\beta$-Distearin pyrophosphate, $C_3H_5(O\cdot CO\cdot C_{17}H_{35})_2\cdot O\cdot P_2H_3O_6$, is a colourless, crystalline, fatty substance, m. p. about 65°; primary *$\alpha\beta$-distearin orthophosphate* forms colourless, somewhat lustrous, matted crystals, m. p. 71°. The *secondary* ester yields soft crystals, m. p. about 67°; it forms a waxy, pale yellow *silver* salt with silver acetate, and a *potassium* salt separating in colourless platelets. The *tertiary* ester is very similar to the other esters, but the solution is neutral.

Pentadistearin phosphate, $P[O\cdot C_3H_5(O\cdot CO\cdot C_{17}H_{35})_2]_5$, forms colourless, brittle crystals, m. p. 70°. All the compounds described are very ill-defined. E. F. A.

Alleged Synthesis of Lecithins. ADOLF GRÜN and FRITZ KADE (*Ber.*, 1912, **45**, 3367—3376).—To effect the synthesis of lecithins it is proposed to allow the components of choline to act in turn on diglyceride-phosphoric acid. Ethylene glycol and phosphoric oxide acting on distearin produce almost quantitatively *distearin ethylene-glycol orthophosphate*,

$$C_3H_5(O\cdot CO\cdot C_{17}H_{35})_2\cdot O\cdot PO(OH)\cdot O\cdot C_2H_4\cdot OH.$$

When ethylene chlorohydrin is used, the reaction takes place in two directions, the glycol ester as well as the *β-chloroethyl* ester,

$$C_3H_5(O\cdot CO\cdot C_{17}H_{35})_2\cdot O\cdot PO(OH)\cdot O\cdot C_2H_4Cl,$$

being formed. This compound reacts with trimethylamine, forming the *trimethylammonium* salt,

$$C_3H_5(O{\cdot}CO{\cdot}C_{17}H_{35})_2{\cdot}O{\cdot}PO(O{\cdot}C_2H_4Cl){\cdot}O{\cdot}NHMe_3,$$

and on more energetic action of excess of trimethylamine this undergoes rearrangement to lecithin hydrochloride,

$$C_3H_5(O{\cdot}CO{\cdot}C_{17}H_{35})_2{\cdot}O{\cdot}PO(O{\cdot}C_2H_4{\cdot}NMe_3Cl){\cdot}OH.$$

The final product obtained was a mixture of both compounds together with an intermediate product.

The *β-chloroethyl* ester, from αβ-distearinphosphoric acid, forms colourless crystals, which sinter at 60°, m. p. 65—66°; the isomeric αγ-distearin compound is very similar.

The *ethyleneglycol* ester of *αβ-distearinphosphoric* acid has m. p. 65—70°, and is a typically fatty substance. It reacts faintly acid.

The *trimethylammonium* salt forms tough crystals which sinter at 60°, m. p. 69°.

The synthetic lecithin hydrochloride (αβ-distearincholinephosphoric acid ester) product is a soft, waxy compound, which sinters at 60° to a clear, viscid oil, which becomes mobile at 64—65° and opaque at 74°.

E. F. A.

Preparation of Mixed αβ-Diglycerides. Adolf Grün and B. Schreyer (*Ber.*, 1912, **45**, 3420—3426).—Glycerol-α-monochlorohydrin is converted by the action of myristoyl chloride into the ester, $CH_2Cl{\cdot}CH(OH){\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}C_{13}H_{27}$, which reacts with stearyl chloride to form myristostearochlorohydrin,

$$CH_2Cl{\cdot}CH(O{\cdot}CO{\cdot}C_{17}H_{38}){\cdot}CH_2(O{\cdot}CO{\cdot}C_{13}H_{27}).$$

On treatment with silver nitrite the chlorine atom is replaced by hydroxyl and α-myristo-β-stearin obtained.

α-Myristo-γ-chlorohydrin is a yellow, mobile oil; it is converted by silver nitrite into α-monomyristin, m. p. 68°.

β-Myristo-αγ-dichlorohydrin forms colourless, transparent, glass-like crystals, m. p. 20°. The *β-monomyristin* obtained from it gives colourless, lustrous, crystalline plates, m. p. 69°.

α-Myristo-β-stearo-γ-chlorohydrin forms colourless crystals, m. p. 31°.

α-Myristo-β-stearin crystallises in slender platelets, m. p. 58°.

E. F. A.

Alcoholysis and the Composition of Cocoanut Oil. George D. Elsdon (*Analyst*, 1913, **38**, 8—11).—Cocoanut oil when boiled in a reflux apparatus with absolute methyl alcohol containing 2% of hydrogen chloride for about twenty hours deposits on cooling a large quantity of methyl esters; the remainder may be obtained by diluting the alcoholic solution with water and agitating with ether.

When the mixture of the esters is submitted to distillation at 14 mm. pressure, seven fractions may be isolated (b. p. 63—76°, 76—100°, 100—128°, 128—153°, 153—182°, 182—204°, 204—216°).

From the results obtained on weighing, refractionating, and further identification of the fractions, the author considers that the composition of the fatty acids and of cocoanut oil may be represented approximately

by hexoic acid 2%, octoic acid 9%, decoic acid 10%, lauric acid 45%, myristic acid 20%, palmitic acid 7%, stearic acid 5%, and oleic acid 2%.

L. DE K.

Preparation of Ethyl Acrylate. FREDERICK G. TROBRIDGE (*Proc. Univ. Durham, Phil. Soc.*, 1912, 4, 223—224).—Ethyl acrylate is obtained in 80% yield by the action of the zinc–copper couple on ethyl $\alpha\beta$-dibromopropionate in ethereal solution. F. B.

Action of Zinc on a Mixture of Pinacolin and Ethyl α-Bromopropionate. NICOLAI N. BUNGE (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1776—1788).—This incomplete investigation is published owing to the appearance of Umnova's paper (this vol., i, 7), and is a continuation of work begun by Lazarkevitsch and proceeded with by Reformatski and Agafonov.

The products of the action of zinc on a mixture of pinacolin (1 mol.) and ethyl bromopropionate (1 mol.) vary with the conditions of the reaction. If the latter takes place at the ordinary temperature and the viscous mass obtained after three or four days is decomposed with water, a yield of 30% of ethyl β-hydroxy-$\alpha\beta\gamma\gamma$-tetramethylvalerate is obtained. At 50—70°, however, this ester is accompanied by (1) a lactone, $C_9H_{16}O_2$, which may also be obtained by boiling either the ester or the corresponding acid for some hours with 20% sulphuric acid solution; (2) ethyl propionylpropionate, which yields diethyl ketone on hydrolysis.

β-Hydroxy-$\alpha\beta\gamma\gamma$-tetramethylvaleric acid,

$$CMe_3\cdot CMe(OH)\cdot CHMe\cdot CO_2H,$$

forms large, colourless crystals (? rhombohedra), m. p. 109·5—110·5°, and has the normal molecular weight in freezing acetic acid. Its *ethyl ester*, $C_{11}H_{22}O_3$, is a colourless, viscous liquid, b. p. 117°/20 mm., D_4^{20} 0·96034, n_D^{20} 1·44039, and exhibits normal cryoscopic behaviour in benzene. The *potassium, barium, calcium* ($+H_2O$), and *silver* salts were analysed.

The *lactone*, $CMe_3\cdot CH<\begin{matrix}CHMe\cdot CO\\ CH_2-O\end{matrix}$ or $CMe_2<\begin{matrix}CHMe\cdot CO\\ CMe_2-O\end{matrix}$, forms large crystals, m. p. 65—66°, and exhibits the normal molecular weight in freezing acetic acid; when boiled with water it yields a neutral solution and does not combine with it. T. H. P.

Uranium Salts. ARRIGO MAZZUCCHELLI and OLGA GRECO D'ALCEO (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 620—626).—The paper deals with complex uranium salts. Additive products are practically not formed in the following cases: mercuric cyanate, carbamide or thiocarbamide with uranyl nitrate; carbamide or hexamethylenediamine with uranyl oxalate; hexamethylenediamine, aniline or pyridine with the complex sodium uranyl pyrophosphate, malonate or succinate. Attempts to prepare complex salts from aminoacetic, aspartic, aminobenzoic and sulphanilic acids were unsuccessful. The *aspartate*,

$$UO_2(C_4H_5O_4N)_2,3H_2O,$$

was prepared, but it is not a complex derivative. The *aminobenzoate*, $UO_2(C_7H_6O_2N)_2,4H_2O$, was obtained, and also the basic *sulphanilate*, $UO_3\cdot C_6H_7O_3NS,H_2O$.

The uranous salts also appear to have little tendency to form aminic

complexes. Diurano-oxalic acid gives ordinary *salts* with *pyridine* $[2U(C_2O_4)_2 \cdot C_2O_4(C_5H_5N)_2]$ and with *aniline* $[2U(C_2O_4)_2 \cdot C_2O_4(C_6H_7N)_2]$. Indications were obtained of the formation of a complex salt in the case of uranous aminoacetate. The basic *succinate*, $UO \cdot C_4H_4O_4, 2H_2O$, was prepared, and also the analogous *malonate*, $UO \cdot C_3H_2O_4, 6H_2O$. When a solution of sodium uranylmalonate with an excess of malonic acid is electrolytically reduced, the anodic liquid being an acid solution of sodium malonate separated from it by a parchment, dark green, dichroic crystals of the complex *salt*, $U(C_3H_2O_4)_3Na_2, 2H_2O$, are obtained on subsequent concentration of the cathodic liquid in a vacuum. A basic *uranous phthalate*, $UO{:}C_8H_4O_4, 3H_2O$, and *uranous trichloroacetate*, $UO(C_2O_2Cl_3)_2, 3H_2O$, were also prepared.

R. V. S.

Molecular Rearrangements in the Camphor Series. XI. Derivatives of *iso*Camphoric Acid: *iso*Aminocamphonanic Acid and Its Decomposition Products. WILLIAM A. NOYES and LEONIDAS R. LITTLETON (*J. Amer. Chem. Soc.*, 1913, **35**, 75—81).—It has been shown in earlier papers (A., 1895, i, 295 ; 1909, i, 133) that aminocamphonanic acid (aminolauronic acid) is decomposed by nitrous acid with formation of lauronolic acid, laurolene, and *iso*campholactone. The present work was undertaken with the object of preparing *iso*aminocamphonanic acid and studying its behaviour with nitrous acid.

sec.-Methyl *iso*camphorate (α-methyl *iso*camphorate),

$$CO_2H \cdot C_8H_{14} \cdot CO_2Me,$$

has m. p. 89·5—90°, and $[\alpha]_D$ $-58·4°$ in 10% alcoholic solution (compare Noyes and Knight, A., 1911, i, 111). The tert.-*methyl* ester, prepared by boiling a solution of the dimethyl ester in methyl alcohol with sodium hydroxide, was obtained as a very viscous oil; it has $[\alpha]_D$ $-53·1°$ in 10% alcohol solution. The terms "secondary" and "tertiary" are used here to indicate the carboxyl containing the methyl group.

Methyl sec.-iso*camphoramate*, $CO_2Me \cdot C_8H_{14} \cdot CO \cdot NH_2$, m. p. 126—127°, prepared from the *sec.*-methyl ester by converting it into the chloride and treating the latter with ammonia, crystallises in rectangular plates, and has $[\alpha]_D$ $-54·1°$ in 10% solution in methyl alcohol. When this ester is warmed with sodium hypobromite solution it yields *methyl* iso*aminocamphonanate*, b. p. 239° (corr.), m. p. 230° (decomp.), which forms white crystals; the *hydrochloride*,

$$CO_2Me \cdot C_8H_{14} \cdot NH_2, HCl, H_2O,$$

has $[\alpha]_D$ $-32·03°$ in 10% solution in water, and $-42·03°$ in 10% solution in alcohol. If this hydrochloride is warmed with solution of sodium hydroxide and subsequently acidified with hydrochloric acid, the *hydrochlo ide* of iso*aminocamphonanic acid*,

$$\begin{array}{l} CH_2{-}CH_2 \\ | \\ NH_2 \cdot CH \cdot CMe_2 \end{array} \!\!>\! CMe \cdot CO_2H, HCl,$$

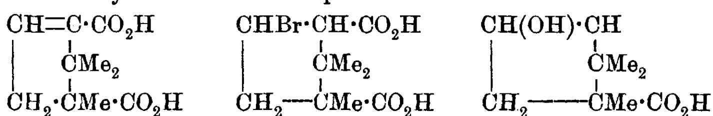
m. p. 320° (corr.), is obtained, which is decomposed by nitrous acid with formation of *cis*-camphonolactone, together with small quantities of an unsaturated *acid*, b. p. 150°/60 mm. (decomp.), and a saturated acid which decomposes at 160°.

E. G.

New Methods of Preparation of Camphonenic (γ-Lauronolic) Acid and the Relation of the Latter to Laurolenic (Lauronolic) Acid. JULIUS BREDT [and, in part, PAUL LEVY and S. LINK] (*J. pr. Chem.*, 1913, [ii], 87, 1—11).—The first part of this paper is mainly a summary of the authors' views on the constitution and relationships of the lauronolic acids and allied compounds, together with suggestions concerning their nomenclature (compare A., 1911, i, 417).

When submitted to slow distillation, dehydrocamphoric acid (A., 1902, i, 374) loses carbon dioxide, yielding γ-lauronolic (camphonenic) acid (I). It is accompanied by *iso*dehydrocamphoric anhydride, from which it may be separated by distillation in steam. When purified by the calcium salt, $C_{18}H_{26}O_4Ca,H_2O$, and repeatedly crystallised from dilute acetic acid it is obtained in feather-like crystals, m. p. 155—156° (compare Noyes, A., 1912, i, 159).

Dehydrocamphoric acid combines with hydrobromic acid, yielding a mixture of two stereoisomeric *hydrobromides* (II), of which the *cis*-form has m. p. 168—170°, and is reduced by zinc and acetic acid to *cis*-camphoric acid, whilst the *cis-trans*-modification has m. p. 232°, and on reduction yields *cis-trans*-camphoric acid:



(I.) (II.) (III.)

When boiled in aqueous solution the sodium salt of the *cis-trans*-hydrobromide yields as main product a *hydroxy-acid* (III), which is accompanied by γ-lauronolic acid (10%).

Oxidation of γ-lauronolic acid with nitric acid, or of its calcium salt with potassium permanganate, gives rise to camphoronic acid. F. B.

A New Method of Preparation of Laurolenic (Lauronolic) Acid and the Decomposition of Camphanic Acid in an Electric Reflux Heater under Diminished Pressure. JULIUS BREDT and AUGUST AMANN (*J. pr. Chem.*, 1913, [ii], 87, 12—26).—Lauronolic acid, which the authors now terms laurolenic acid, is obtained by boiling γ-camphonanic acid (A., 1912, i, 113) for a short time with aqueous sodium carbonate. It is accompanied by camphonololactone, and has also been prepared (1) by distillation of camphanic acid under diminished pressure in a specially constructed, electrically heated apparatus, a sketch of which is given, and (2) by heating chlorocamphoric anhydride (A., 1912, i, 411) with aqueous sodium carbonate. The m. p. of the acid varies from 5·5—7° to 8·5—10° according to its method of preparation, and $[\alpha]_D$ from 181·3° to 195·2°.

The calcium salt separates from its aqueous solution at the ordinary temperature with $2H_2O$, and not $3H_2O$, as stated by Noyes and Burke (A., 1912, i, 159). F. B.

Methods for the Preparation of Neutral Solutions of Ammonium Citrate. JAMES M. BELL and CHARLES F. COWELL (*J. Amer. Chem. Soc.*, 1913, 35, 49—54).—The methods at present

employed for the preparation of neutral solutions of ammonium citrate are not satisfactory and two new methods have therefore been devised. In one of these methods, the excess of ammonia is estimated by extracting the solution with chloroform, and titrating the chloroform with 0·1*N*-hydrochloric acid in presence of methyl-red as indicator. In the other method, the rise of temperature due to the heat of neutralisation is observed as the citric acid solution is titrated with ammonia, the end-point being at the break in the heating curve. Both these methods are considered to be simpler than that involving the determination of the conductivity of solutions at constant temperature.

E. G.

Thio-γ-valerolactone. KARL FRIES and H. MENGEL (*Ber.*, 1912, **45**, 3408—3411).—On heating valerolactone with phosphorus pentasulphide, *thio-γ-valerolactone*, $CHMe\begin{cases}CH_2\cdot CH_2\\ S\text{——}CO\end{cases}$, is obtained as a colourless oil of pleasant aromatic odour, b. p. 94—95°/20 mm. It is readily hydrolysed by alkali hydroxides to γ-mercaptovaleric acid, which is reconverted into the thiolactone on treatment with mineral acids.

A further product of the action of the pentasulphide is *dithio-γ-valerolactone*, $CHMe\begin{cases}CH_2\cdot CH_2\\ S\text{——}CS\end{cases}$, an orange-coloured, viscid oil of unpleasant odour. Condensing agents such as sodium methoxide convert it very readily into *trithio-di-γ-valerolactone*,

$$CHMe\begin{cases}CH_2\cdot CH_2 & CS\cdot S\text{—}\\ S\text{——}C & \!\!\!=\!=C\cdot CH_2\end{cases}\!\!>CHMe,$$

which crystallises in bunches of large, red prisms, m. p. 77°.

E. F. A.

Maleindialdehyde. ALFRED WOHL and BRUNO MYLO (*Ber.*, 1912, **45**, 1746—1756).—Maleindialdehyde diethylacetal, an intermediate product in the preparation of tartardialdehyde (A., 1912, i, 162), has been hydrolysed by means of dilute sulphuric acid, and the maleindialdehyde has been characterised. The most striking property of this compound is its yellow colour, which is more intense than that of diacetyl and may be accounted for by the grouping together of conjugated double bonds and the conveying of the influence of one carbonyl group to the other by an ethylenic linking. Oxidation by silver carbonate gives maleic and also fumaric acids, and since the original acetal yields a tartardialdehyde acetal of the type of mesotartaric acid (*ibid.*), it is suggested that this is the real maleindialdehyde, whereas that obtained by Marquis from nitrosuccinaldehyde monoacetin (A., 1905, i, 224) is fumardialdehyde, especially as the nitrous acid which is formed at the same time has a great tendency to convert maleic into fumaric acid.

For the preparation of *maleindialdehyde*, $CHO\cdot CH\!:\!CH\cdot CHO$, 35 grams of the acetal are shaken with 150 c.c. of *N*/10-sulphuric acid and the faintly yellow, pungent smelling solution is exactly neutralised with barium hydroxide. After removing the barium sulphate by centrifugation, the solution is evaporated at 40° in a vacuum with a

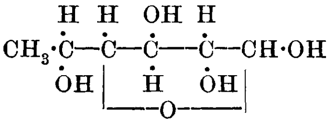
fractionating column which, however, does not prevent the loss of some aldehyde, since it is volatile in steam, and the residue is extracted with chloroform and dried. The extract is evaporated in the same way and the syrupy residue is maintained at 105—115°/9 mm., when the polymeric substances slowly decompose and the aldehyde distils over. The distillate is collected in a Claisen flask in a freezing mixture and redistilled from a bath already heated to 75°, when the mobile, yellow, pungent-smelling aldehyde boils at 56—59°/9·5 mm. It dissolves in water and organic solvents, and probably forms hydrates and alcoholates, since yellow aqueous or alcoholic solutions soon become colourless. It is only slowly affected by oxygen or bromine water, but it immediately reduces permanganate or ammoniacal silver oxide. At the ordinary temperature it very quickly changes to a syrup with less intense colour and odour, and it is then only slightly soluble in ether, benzene or warm water. From the aqueous solution an amorphous solid separates out; probably a syrupy and a solid polymeride exist.

Derivatives of the dialdehyde have been prepared by hydrolysing the acetal, exactly neutralising with sodium carbonate, and precipitating with the free base in the cold. The *diphenylhydrazone*, NHPh·N:CH·CH:CH·CH:N·NHPh, forms unstable, yellow, quadratic leaflets from hot alcohol, m. p. 198—199°; Marquis's dihydrazone melts at 236—237° (*ibid.*). It gives a reddish-violet compound on oxidation, which is similar to, but not identical with, Marquis's "tetrazone"; they are probably not tetrazones at all. The *dioxime*, $C_4H_6O_2N_2$, forms pure white needles from hot methyl alcohol which decompose with violence at 150—155°; Marquis's compound decomposes at 220° (*ibid.*). The *disemicarbazone*, $C_6H_{10}O_2N_6$, is only very slightly soluble, and crystallises best from a large volume of boiling water in slender needles, m. p. 246—247° (corr.). J. C. W.

The Isomeric Changes of Dextrose Produced by Alkalis. Theory of Catalytic Action. LEONOR MICHAELIS and PETER RONA (*Biochem. Zeitsch.*, 1912, **47**, 447—461).—The changes in dextrose (measured chiefly polarimetrically) produced by alkalis (in presence of phosphates, etc., added to keep the hydrogen-ion concentration constant during the experiment) is directly proportional to the hydroxyl-ion concentration. The acid nature of dextrose was demonstrated, and its dissociation constant was found to be $5 \cdot 10^{-13}$. This was measured by ascertaining the changes in the hydroxyl-ion concentration of sodium hydroxide solutions (measured electrometrically) produced by the addition of dextrose. From these facts, the hypothesis is put forward, that the "catalytic" action of the hydroxyl ions increases the number of sugar ions, according to theory of mass action, and it is the latter which spontaneously undergo isomeric change. S. B. S.

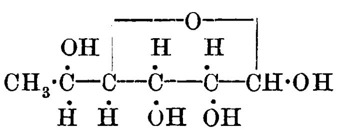
Conversion of *d*-Glucose [Dextrose] into a Methylpentose. EMIL FISCHER and KARL ZACH (*Ber.*, 1912, **45**, 3761—3773).—Triacetylmethylglucoside bromohydrin (Fischer and Armstrong, A., 1902, i, 263), $CH_2Br\cdot CH(OAc)\cdot \underbrace{CH\cdot CH(OAc)\cdot CH(OAc)\cdot CH}_{O}(OMe)$,

is converted on reduction with acetic acid and zinc dust into a triacetyl derivative which on alkaline hydrolysis yields *β-methyl*-d-*iso-rhamnoside*, $CH_3 \cdot CH(OH) \cdot CH \cdot CH(OH) \cdot CH(OH) \cdot CH \cdot OMe$. This is



hydrolyed by acids to *d-iso*rhamnose (annexed formula), which is identical with the *iso*rhodeose described by Votoček (A., 1911, i, 354), and obtained by him from purgic acid. Since no asymmetric carbon atom is concerned in the series of reactions, no Walden rearrangement is possible, and the methylpentose has the same configuration as *d*-glucose.

Accordingly the annexed formula of *l*-rhamnose (methyl-*l*-mannose), which was hitherto uncertain, is established.



β-Methyl-*d-iso*rhamnoside, like *β*-methylglucoside, is hydrolysed by emulsin, whereas *β*-methylxyloside is not attacked. Renewed emphasis is laid on this remarkable difference in view of the similarity in structure of the three glucosides.

Triacetyl-methyl-d-*isorhamnoside* crystallises in well-formed, colourless needles, m. p. 100° (corr.), $[\alpha]_D^{20}$ − 20·22°.

β-Methyl-d-iso*rhamnoside* forms slender, colourless needles, m. p. 133° (corr.), $[\alpha]_D^{20}$ − 55·3°, which taste bitter.

*d-iso*Rhamnose separates in hard, colourless crystals in a variety of forms, m. p. 139—140° (corr.). The rotation changes from $[\alpha]_D^{20}$ + 73·3° to + 29·7° in aqueous solution.

*d-iso*Rhamnosephenylosazone crystallises in yellow needles, m. p. 185° (corr.), to a dark red liquid (compare Votoček, *loc. cit.*), $[\alpha]_D^{20}$ − 95° in white light; it is the optical antipode of *l*-rhamnosephenylosazone.

*d-iso*Rhamnonolactone has m. p. 151—152° (corr.), $[\alpha]_D^{20}$ changing from + 66·88° to + 5·35°. E. F. A.

Properties of Phytin. M. A. Egorov (*Bied. Zentr.*, 1912, **42**, 66—67; from *J. Exper. Landw.*, 1912, **12**, 361).—The phosphoric acid of phytin, which is precipitated by acid molybdate solution, is not precipitated under ordinary conditions in ammonium citrate solution by magnesia mixture.

When phytin is boiled with water for fourteen to sixteen hours it is completely decomposed with production of inositol and inorganic phosphoric acid compounds. The yield of phosphoric acid is about 100%. N. H. J. M.

Formation of Humus and Combustible Minerals without the Intervention of Atmospheric Oxygen, Micro-organisms, High Temperatures, or Great Pressure. Louis C. Maillard (*Compt. rend.*, 1912, **155**, 1554—1556).—A theoretical discussion of work previously described (compare A., 1912, i, 13, 169). The author has now shown that oxidation does not intervene in any way in

the generation of carbon dioxide and the production of humic substances by the interaction of sugars and amino-acids. He has further obtained a jet black substance, rich in carbon and containing nitrogen, which exhibits a remarkable resistance to reagents, and he suggests that this reaction should be taken into account in framing theories as to the formation of combustible minerals. W. G.

Some Unstable Nitrites Fixed by means of Organic Bases. III. GINO SCAGLIARINI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 640—643).—The author describes stable compounds of the nitrites of mercury, zinc, and cadmium with hexamethylenetetramine. The substances were prepared by adding sodium nitrite to a solution of a salt of the metal in the presence of hexamethylenetetramine. The *compound*, $2Hg(NO_2)_2,8H_2O,3C_6H_{12}N_4$, forms white crystals with a greenish lustre. The *compound*, $Zn(NO_2)_2,2H_2O,C_6H_{12}N_4$, forms colourless prismatic crystals, as does also the *compound*, $Cd(NO_2)_2,2H_2O,C_6H_{12}N_4$. R. V. S.

Alloxan Anhydride and Its Methyl Derivatives. HEINRICH BILTZ (*Ber.*, 1912, **45**, 3659—3675).—By heating under reduced pressure it is found possible completely to dehydrate alloxan and its methyl and dimethyl derivatives; the anhydrous substances have an intense yellow colour and can be sublimed unchanged in a vacuum.

Alloxan anhydride, $C_4H_2O_4N_2$, obtained by heating the monohydrate for an hour at 210—220° in a vacuum produced by a mercury pump, forms yellow, rhombic crystals ($a:b:c = 0·9974:1:1·6841$), m. p. 256° (decomp.). A partial dehydration of the monohydrate is also effected by recrystallising from acetic acid.

Methylalloxan anhydride, obtained from the monohydrate by similar treatment to the previous but at 160°, separates from acetic acid in leafy crystals (rhombic system, $a:b:c = 0·6766:1:?$), m. p. 154—156° (decomp.).

Dimethylalloxan anhydride (compare Holleman, A., 1897, i, 599) could be obtained from the monohydrate by heating in a water-pump vacuum at 210—220°; it crystallises from benzyl cyanide in short, yellow columns (rhombic system, $a:b:c = 0·6847:1:?$).

[With E. TOPP.]—The above anhydrous compounds separated from alcohols containing a little hydrogen chloride in the form of alcoholates which are analogous to the phenolates described earlier (Boehringer & Söhne, D.R.P. 1898, 107720; 1899, 113722). *Alloxan ethyl alcoholate*, $CO<\begin{matrix}NH-CO\\NH-CO\end{matrix}>C(OH)·OEt$, prisms; *alloxan methyl alcoholate*, prisms; *alloxan benzyl alcoholate*, prisms.

Methylalloxan ethyl alcoholate, tablets.

Dimethylalloxan ethyl alcoholate, tetragonal prisms, m. p. 95°; *dimethylalloxan methyl alcoholate*, m. p. *circa* 90°, hexagonal tablets; *dimethylalloxan benzyl alcoholate*, crystals, m. p. 185—188°.

All these alcoholates when heated eliminate the molecule of alcohol, giving a residue which has approximately the m. p. of the pure anhydride.

The following compounds were prepared by crystallisation from a

solution of the anhydride and a phenol with hydrogen chloride in acetic acid ; *alloxan phenolate*, decomposing at 240—245° ; alloxan *p*-cresolate decomposing at 228—230° (compare Boehringer & Söhne, *loc. cit.*) ; *dimethylalloxan* p-*cresolate*, hexagonal prisms, m. p. 105°.

[With J. KARTTE.]—An aqueous solution of dimethylalloxan dihydrate when saturated with sulphur dioxide and evaporated in a vacuum desiccator deposits *dimethylalloxan sulphite*,

$$CO<\begin{matrix}NMe\cdot CO\\NMe\cdot CO\end{matrix}>C(OH)\cdot SO_3\cdot C(OH)<\begin{matrix}CO\cdot NMe\\CO\cdot NMe\end{matrix}>CO,$$

colourless prisms, which decompose at 75°. *Methylalloxan sulphite*, obtained in an analogous manner, crystallises in prisms with $4H_2O$. *Alloxan sulphite* forms rhombic leaflets, decomposing near 184°.

Alloxan anhydride condenses in alcoholic acetic acid solution with dimethylcarbamide producing 7 : 9-dimethyluric acid glycol (compare Biltz and Krebs, A., 1910, i, 526), but the product from dimethylalloxan anhydride and dimethylcarbamide was allocaffeine (compare Biltz and Krebs, *loc. cit.*, i, 521).

Working details are given of the methods found most suitable for the preparation of di- and tetra-methylalloxantin and their conversion into methyl- and dimethyl-alloxans. D. F. T.

The System Ammonium Thiocyanate–Thiocarbamide–Water. ANDREAS SMITS and A. KETTNER (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 683—686).—The investigation of the melting-point diagram of the pseudo-binary system ammonium thiocyanate–thiocarbamide has given results which indicate the existence of a compound $NH_4CNS,4CS(NH_2)_2$, whereas Atkins and Werner (T., 1912, **101**, 1167) are of the opinion that the compound has the composition $NH_4CNS,3CS(NH_2)_2$. The evidence for the former is supported by the results of the determination of the solubility isotherms at 25° and the examination of the co-existing solid phases by the residue method. The solubility curves afford a simple explanation of the method of preparation of thiocarbamide from ammonium thiocyanate recommended by Reynolds and Werner (T., 1903, **83**, 1), which up to the present has not been satisfactorily accounted for. H. M. D.

Selective Catalysis of Dehydrogenation. NICOLAI D. ZELINSKI (*Ber.*, 1912, **45**, 3678—3682).—The catalytic dehydrogenation of *cyclo*hexane compounds by palladium or platinum at 300° and the inactivity of these metals towards *cyclo*pentane compounds under the same conditions can be applied to the separation of *cyclo*hexane and *cyclo*pentane hydrocarbons.

[With (Frl.) A. HERZENSTEIN.]—After a mixture of equal volumes of methyl*cyclo*pentane and *cyclo*hexane has been thrice submitted to the action of platinum black at 300°, no further liberation of hydrogen occurs, and the hydrogen collected amounts to more than 90% of the theoretical. After removal of the benzene from the resultant hydrocarbon mixture by treatment at the ordinary temperature with sulphuric acid (two volumes of acid, D 1·84, mixed with one volume of fuming acid containing 7% of anhydride), the residual liquid was pure methyl*cyclo*pentane.

*cyclo*Heptane resembles *cyclo*pentane (Zelinski, A., 1911, i, 958) in resisting the above catalytic dehydrogenation.

A specimen of naphtha, b. p. 102—104°, D^{18} 0·7647, n^{18} 1·4215, from Baku petroleum, by the above treatment gave a liquid which could be separated by distillation into two fractions. The less volatile fraction, b. p. 105—107°, contained much toluene, whilst the other fraction, b. p. 104—105°, after one more treatment with platinum black followed by the removal of any aromatic hydrocarbons by means of the special sulphuric acid mentioned above, gave a hydrocarbon, C_7H_{14}, b. p. 101—102·5°/747 mm., D_4^{20} 0·7488, n^{20} 1·4101, which is probably a *cyclo*pentane or *cyclo*butane derivative.

[With W. Dobrochotov.]—Another specimen of naphtha, b. p. 100—100·5°, D^{18} 0·766, $n^{20.5}$ 1·4210, when submitted to the action of platinum black at 300°, liberated much hydrogen, and after the removal of toluene and redistillation had b. p. 100—101°, D_4^{18} 0·7490, n^{18} 1·4142. The original hydrocarbon, a "heptanaphthene," which had been previously treated with a mixture of nitric and sulphuric acids, had therefore yielded a *cyclo*paraffin product very similar to that obtained from the above naphtha fraction (b. p. 102—104°), which had not been first treated with nitric and sulphuric acids. D. F. T.

Formation of Dimethylstyrene [β-Phenyl-Δ^β-butylene] from Phenyldimethylethyl Alcohol [β-Phenyl*iso*butyl Alcohol]. Albin Haller and Édouard Bauer (*Compt. rend.*, 1912, **155**, 1581—1585).—By the action of sodamide on phenylacetonitrile (1 mol.) in ethereal solution followed by the addition of methyl iodide (1 mol.), a liquid, b. p. 115—120°/19—20 mm., is obtained, which on further treatment with sodamide and methyl iodide gives α-phenyl*iso*butyronitrile (compare Wallach, A., 1900, i, 229). This substance on hydrolysis with 85% sulphuric acid on a water-bath furnishes the corresponding amide, which by reduction with sodium in absolute alcohol yields *β-phenyl*iso*butyl alcohol*, $CPhMe_2\cdot CH_2\cdot OH$, b. p. 122—123°/20 mm., which gives a *phenylurethane*, white needles, m. p. 59—60°. During the reduction there is produced at the same time some β-phenyl*iso*butylamine, b. p. 115—116°/20 mm. (compare Wallach, *loc. cit.*), which forms a *platinichloride*, insoluble in water.

By acting on β-phenyl*iso*butyl alcohol with thionyl chloride in slight excess at 0°, a liquid is obtained separable into two fractions, of which one is β-phenyl-Δ^β-butylene, CPhMe:CHMe (compare Klages, A., 1902, i, 666; 1903, i, 19), and the other a *chloride*, $C_{10}H_{13}Cl$, b. p. 104—105°/20 mm., the constitution of which has not yet been established. With silver acetate, it gives an *acetate*, which on saponification gives an *alcohol*, b. p., 115—117°/15 mm., isomeric with the alcohol from which the chloride was derived. W. G.

2 : 4 : 6-Tribromo-1-iodo-3-nitrobenzene. C. Loring Jackson and Webster N. Jones (*Amer. Chem. J.*, 1913, **49**, 46—55).—2 : 4 : 6-Tribromo-3-nitroaniline (Körner, A., 1876, i, 210) has m. p. 101·5°. Remmers (A., 1874, 696) assigned the m. p. 214—215° to this compound, but it is now shown that his substance was probably 2 : 4 : 6-tribromo-3-nitroacetanilide. 2 : 4 : 6 - Tribromo - 3 - nitrodiacetanilide

(Remmers, *loc. cit.*) has m. p. 168—169°, and seems to be identical with the substance supposed by Wheeler (A., 1896, i, 157) to be the monoacetanilide. 2 : 4 : 6-*Tribromo-3-nitroacetanilide*, m. p. 208—209°, forms white, rhombic crystals.

2 : 4 : 6-*Tribromo-1-iodo-3-nitrobenzene*, $C_6HBr_3I\cdot NO_2$, m. p. 144—145°, obtained by the action of potassium iodide on the diazotisation product of 2 : 4 : 6-tribromo-3-nitroaniline, crystallises in white, rectangular plates. When this substance is treated with a solution of sodium ethoxide, it is converted into a *dibromoiodonitrophenetole*,

$$NO_2\cdot C_6HBr_2I\cdot OEt,$$

m. p. 121°, which forms long, white, rectangular prisms; other compounds are produced in this reaction, one of which has m. p. 149°.

E. G.

The Nitration of the Chlorotoluenes. ARNOLD F. HOLLEMAN and J. P. WIBAUT (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 594—599).—The position assumed by a third substituent in a benzene ring depends on the relative velocities of substitution caused by the two substituents already present. The hydroxyl, amino-, halogen and methyl groups which cause ortho-para substitution are placed in the order of decreasing velocity.

In order to obtain further knowledge of the relative substitution velocity caused by different groups, the author has re-investigated the nitration products of *o*-chlorotoluene (Goldschmidt and Hönig, A., 1886, 1022). All four possible chloronitrotoluenes, 2 : 3, 2 : 4, 2 : 5, 2 : 6, were found to be present in the product, although the 2 : 4-isomeride proved difficult of detection. For the estimation of the relative amounts of the isomerides in the nitration product, Valeton's modification of the m.-p. method was used, and indicated in a product obtained at 0° from 10 grams of chlorotoluene and 40 grams of nitric acid (D 1·52), 19·2, 17·0, 43·3, and 20·5% respectively, in the above order.

In extending a similar investigation to the nitration of *m*-chlorotoluene, 3 : 6-, 3 : 5-, 3 : 4-, and 3 : 2-chloronitrotoluenes were prepared in a high state of purity, and had m. p. 24·9°, 58·4°, 24·2°, and 23·4° respectively. Analysis of the reaction product indicated no appreciable quantity of the 3 : 5-isomeride, and 58·9, 32·3, and 8·8% of the remaining three.

By a calculation involving the composition of the nitration products of toluene, chlorobenzene and *p*-chlorotoluene, it is deduced that chlorine causes a velocity of substitution 1·491 times as great as that caused by the methyl radicle. The knowledge of this number allows the calculation of the proportion in which the various isomeric products should be formed in the nitration of *o*- and *m*-chlorotoluenes, and the theoretical proportions exhibit a gratifying concordance with the experimental.

D. F. T.

αα-Dihalogenoarylsulphonylacetonitriles, $R\cdot SO_2\cdot CX_2\cdot CN$, and a Peculiar Reduction of these Halogen Compounds. JULIUS TRÖGER and W. KROSEBERG (*J. pr. Chem.*, 1913, [ii], **87**, 67—84. Compare A., 1905, i, 336, 870; 1908, i, 633, 798).—It has been shown previously that αα-dibromoarylsulphonylacetonitriles may be

obtained readily by the action of bromine on the sodium salts of arylsulphonyl-α-oximinoacetonitriles, $SO_2R\cdot C(:NOH)\cdot CN$, in aqueous solution. Attempts to prepare the corresponding dichloro- and di-iodo-compounds in a similar manner were unsuccessful. The dichloro-compounds may, however, be obtained by the addition of bleaching powder to a glacial acetic acid solution of the corresponding arylsulphonylacetonitriles, $SO_2R\cdot CH_2\cdot CN$.

The following compounds were prepared in this manner: *αα-dichlorobenzenesulphonylacetonitrile*, $SO_2Ph\cdot CCl_2\cdot CN$, lustrous prisms, m. p. 57°; *αα*-p-*trichlorobenzenesulphonylacetonitrile*, white needles, m. p. 96—97°; *αα-dichloro*-p-*bromobenzenesulphonylacetonitrile*, stout needles, m. p. 105—106°; *αα-dichloro*-p-*iodobenzenesulphonylacetonitrile*, flat prisms, m. p. 111—112°; *αα-dichloro*-p-*toluenesulphonylacetonitrile*, broad, lustrous needles, m. p. 92°; *αα-dichloro*-p-*methoxybenzenesulphonylacetonitrile*, m. p. 121°; *αα-dichloro*-p-*ethoxybenzenesulphonylacetonitrile*, m. p. 95°; *αα-dichloro-ψ-cumenesulphonylacetonitrile*, m. p. 103—104°, and *αα-dichloro-α-naphthalenesulphonylacetonitrile*, m. p. 118°.

The benzenesulphonyl derivative may also be prepared by directly chlorinating benzenesulphonylacetonitrile in glacial acetic acid solution. When dissolved in aqueous sodium hydroxide and the solution treated with a large excess of sodium hypochlorite, benzenesulphonylacetonitrile yields phenyl dichloromethyl sulphone, $CHCl_2\cdot SO_2Ph$.

αα-Dibromo-p-*toluenesulphonylacetonitrile*, prepared from *p*-toluenesulphonylacetonitrile and bromine in glacial acetic acid solution, crystallises in long, white prisms, m. p. 121°; *αα-dibromo*-o-*methoxybenzenesulphonylacetonitrile* forms small prisms, m. p. 123°; *αα-dibromo*-p-*ethoxybenzenesulphonylacetonitrile*, stout, white needles, m. p. 118°; *αα-dibromo-ψ-cumenesulphonylacetonitrile* crystallises in prisms, m. p. 123°; *αα-dibromo-α-naphthalenesulphonylacetonitrile*, in pale yellow needles, m. p. 146°.

Attempts have been made to prepare compounds of the type $SO_2R\cdot CO\cdot CN$: (1) by hydrolysing the α-oximinoarylsulphonylacetonitriles with dilute acids; (2) by the action of silver oxide on the above dihalogen compounds, and (3) by oxidising the arylsulphonylacetonitriles with potassium permanganate, but so far these attempts have not met with success.

When heated with sodium benzenesulphinate in alcoholic solution, αα-dihalogenoarylsulphonylacetonitriles undergo a remarkable reduction to arylsulphonylacetonitriles, thus: $SO_2R\cdot CX_2\cdot CN + 2SO_2PhNa + 2H_2O = 2NaX + 2SO_2Ph\cdot OH + SO_2R\cdot CH_2\cdot CN$.

The action of iodine dissolved in aqueous potassium iodide on the sodium salt of α-oximinobenzenesulphonylacetonitrile leads to the formation of the corresponding *potassium* salt, $SO_2Ph\cdot C(CN):NOK$, which crystallises in lustrous, golden-yellow leaflets.

The authors also record unsuccessful attempts to prepare compounds of the type $SO_2R\cdot C(CN):NO\cdot ONa$ by the condensation of ethyl nitrate and arylsulphonylacetonitriles by means of sodium ethoxide in alcoholic solution; in the case of *p*-chlorobenzenesulphonylacetonitrile, the product of the reaction consisted of the *sodium* salt,

$$C_6H_4Cl\cdot SO_2\cdot CHNa\cdot CN.$$

F. B.

Spontaneous Formation of Iodonium Bases Containing Iodine in a Pentatomic Heterocyclic Nucleus. LUIGI MASCARELLI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 617—620).—When 2:2′-di-iodosodiphenyl, $IO{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}IO$, or 2:2′-di-iododiphenyl tetrachloride, $ICl_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}ICl_2$, are kept in water for some months, the aqueous solution yields diphenyleneiodonium iodide, $\begin{matrix}C_6H_4\\ | \\ C_6H_4\end{matrix}\!\!>\!I{\cdot}I$, when treated with sulphur dioxide. In the case of the tetrachloride, the di-iodoso-derivative is probably first formed, together with hydrogen chloride. By subsequent simultaneous oxidation and reduction of the di-iodoso-compound, all the following substances may be produced: $C_6H_4I{\cdot}C_6H_4I$, $IO_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}IO_2$, $C_6H_4I{\cdot}C_6H_4{\cdot}IO_2$, $IO{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}IO_2$, and $C_6H_4I{\cdot}C_6H_4{\cdot}IO$. By rearrangement of the compound

$$IO{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}IO_2,$$

diphenyleneiodonium iodate, $\begin{matrix}C_6H_4\\ | \\ C_6H_4\end{matrix}\!\!>\!I{\cdot}IO_3$, is produced, and this, by the action of sulphur dioxide, is reduced to the iodide (compare Forster and Schaeppi, T., 1912, **101**, 1359). R. V. S.

$\omega\omega'$-Diarylated Aliphatic Hydrocarbons. WALTHER BORSCHE and J. WOLLEMANN (*Ber.*, 1912, **45**, 3713—3725. Compare A., 1912, i, 23).—The method for the synthesis of $\alpha\kappa$-diphenyldecane has now been extended to the preparation of other members of the series, with certain modifications in the case of the pentane, heptane, and nonane.

Adipyl chloride, from adipic acid and phosphorus trichloride, condenses with benzene to form $\alpha\zeta$-diphenylhexan-$\alpha\zeta$-dione, m. p. 107° (Etaix, A., 1898, i, 124), *δ-benzoylvaleric acid*, $COPh{\cdot}[CH_2]_4{\cdot}CO_2H$, being formed at the same time in white needles, m. p. 70—72°. The diketone has been converted into the dioxime, m. p. 222—223° (*ibid.*), which on reduction yields *$\alpha\zeta$-diamino-$\alpha\zeta$-diphenylhexane*,

$$NH_2{\cdot}CHPh{\cdot}[CH_2]_4{\cdot}CHPh{\cdot}NH_2,$$

as a colourless oil, b. p. 250—254°/16 mm., the *carbamide* of which, $C_{20}H_{26}O_2N_4$, melts at 121°, and the *benzoyl* derivative, $C_{33}H_{32}O_2N_2$, at 238°. The conversion of the diamine into Rupe and Bürgin's $\alpha\zeta$-diphenyl-$\Delta^{\alpha\epsilon}$-hexadiene (A., 1910, i, 161) gives a poor result, but the method of von Braun and Deutsch (A., 1912, i, 687) provides a better way of obtaining the desired $\alpha\zeta$-diphenylhexane.

In the same way, suberyl chloride has been converted into the corresponding dioxime (Etaix, *loc. cit.*), and this has been reduced and the phosphate of the diamine has been distilled. A good yield of *$\alpha\theta$-di-phenyl-$\Delta^{\alpha\eta}$-octadiene*, $CHPh\colon CH{\cdot}[CH_2]_4{\cdot}CH\colon CHPh$, is thus obtained in colourless leaflets, m. p 61—62°, b. p. 210—220°/11 mm.; it gives a *tetrabromide*, $C_{20}H_{22}Br_4$, m. p. 196°, and absorbs hydrogen in the presence of palladium, yielding $\alpha\theta$-diphenyloctane (compare Braun and Deutsch, *loc. cit.*).

A characteristic derivative of $\alpha\kappa$-diphenyldecane (*loc. cit.*) is the nitration product, 2:4:2′:4′-*tetranitro-$\alpha\kappa$-diphenyldecane*,

$$C_{10}H_{20}[C_6H_3(NO_2)_2]_2;$$

it forms yellowish-white needles, m. p. 63°.

n 2

The acid chlorides for the corresponding pentane, heptane, and nonane are difficult to obtain, and the diamines would probably yield ring compounds. Hence, the necessary ketones have been prepared by the reduction of available unsaturated ketones (compare A., 1912, i, 194) and reduced to alcohols, which, on dehydration with zinc chloride, give the olefines. The reduction of distyryl ketone to di-β-phenylethyl ketone is usually accompanied by by-products, the nature of which seems to depend on the condition of the palladium employed. The substance, $C_{34}H_{34}O_2$, m. p. 126° (*ibid.*), has not since been encountered; instead, the $\alpha\epsilon\zeta\kappa$-tetraphenyldecane-$\theta$-dione, $C_{34}H_{34}O_2$, m. p. 173—174°, of Harries and Gollnitz (A., 1904, i, 427), and, apparently, its unsaturated *ketone*, $C_{34}H_{30}O_2$, a white powder, m. p. 207—208°, which dissolves with a purple colour in concentrated sulphuric acid, have been isolated. The required di-β-phenylethyl ketone can be more conveniently prepared from phenylethyl methyl ketone by saturating its benzylidene compound (Harries and Gollnitz, *loc. cit.*) with hydrogen in presence of palladium. On reduction with sodium and alcohol, *$\alpha\epsilon$-diphenylpentan-γ-ol*, $OH\cdot CH(CH_2\cdot CH_2Ph)_2$, is obtained as a very soluble, crystalline mass, m. p. 47—48°, b. p. 218°/11 mm., which, on distillation with zinc chloride, yields *$\alpha\epsilon$-diphenyl-Δ^{β}-pentene* as a colourless oil, b. p. 184—185°/10 mm. Reduction readily results in the $\alpha\epsilon$-diphenylpentane of Braun and Deutsch (A., 1912, i, 435). The same series of reactions has also been carried out with phenyl δ-phenylbutyl ketone (A., 1912, i, 194), which has been obtained in colourless needles, m. p. 47°. *$\alpha\epsilon$-Diphenylpentan-α-ol*, $OH\cdot CHPh\cdot[CH_2]_3\cdot CH_2Ph$, is a colourless oil, b. p. 217°/12 mm., which gives a poor yield of *$\alpha\epsilon$-diphenyl-Δ^{α}-pentene*, a colourless, mobile liquid, b. p. 186°/11 mm., which polymerises when heated. The $\alpha\epsilon$-diphenylpentane forms a *tetranitro*-derivative, $C_{17}H_{16}O_8N_4$, in slender, yellow needles, m. p. 126°.

$\alpha\eta$-Diphenylheptan-γ-one is best obtained by the reduction of *$\alpha\eta$-diphenyl-Δ^{α}-hepten-γ-one*, $CHPh\colon CH\cdot CO\cdot[CH_2]_3\cdot CH_2Ph$, which is formed in colourless leaflets, m. p. 25°, b. p. 240°/12 mm., by the condensation of benzaldehyde with methyl-δ-phenylbutyl ketone (A., 1911, i, 880). Its reduction product, *$\alpha\eta$-diphenylheptan-γ-ol*, m. p. 42—43°, b. p. 233°/11 mm., is very readily dehydrated, and the heptene is also easily reduced to *$\alpha\eta$-diphenylheptane*, b. p. 207—208°/12 mm.

In the same way, $\alpha\iota$-diphenylnonan-ϵ-one (A., 1912, i, 194) has been reduced to *$\alpha\iota$-diphenylnonan-ϵ-ol*, a viscous, colourless liquid, b. p. 251°/11 mm., which yields the *$\alpha\iota$-diphenyl-Δ^{δ}-nonene* as a highly refractive oil, b. p. 231—233°/12 mm. Reduction of the latter to *$\alpha\iota$-diphenylnonane*, a colourless oil, b. p. 235°/12 mm., proceeds very readily. J. C. W.

Pyrosulphates of Sodium and Potassium as Condensing Agents. ALLAN F. ODELL and CLEVE W. HINES (*J. Amer. Chem. Soc.*, 1913, **35**, 81—84).—The alkali pyrosulphates have been used as condensing agents by Bogojavlenski and Narbutt (A., 1905, i, 854) in the preparation of certain esters. The salts are readily converted into the hydrogen sulphates by the addition of water, and should,

therefore, be efficient agents for the abstraction of water in organic synthesis; they are easily prepared and convenient to handle.

The pyrosulphates have now been applied to the preparation of triphenylbenzene, benzylideneaniline, benzylidenemalonic acid, phenylstyryl ketone and acetanilide, and have given good results. They cannot be employed, however, to effect the condensation of phenols with other substances. E. G.

Nitro-derivatives of *m*-Cresyl Oxide [*m*-Tolyl Ether]. ALPHONSE MAILHE (*Compt. rend.*, 1912, **155**, 1524—1526).—A study of the nitration of *m*-tolyl ether prepared by the aid of thorium oxide (compare A., 1912, i, 767). Nitration in acetic acid solution at the ordinary temperature yields *nitro*-m-*tolyl ether*,

$$C_6H_4Me\cdot O\cdot C_6H_3Me\cdot NO_2,$$

b. p. 245—250°/50 mm., m. p. 48°, which on reduction with iron and acetic acid gives the corresponding *amine*, giving a violet coloration with calcium chloride. If during the nitration the temperature rises to 80—90°, *dinitro*-m-*tolyl ether*, $O(C_6H_3Me\cdot NO_2)_2$, prisms, m. p. 112°, is obtained, in which the nitro-groups are probably para to the oxygen.

By gradually adding tolyl ether to fuming nitric acid, kept cold, and then adding water, a paste is obtained, which, after extraction of the above dinitro-compound, is added to a mixture of sulphuric and nitric acids and yields 2 : 4 : 2′ : 4′-*tetranitro*-m-*tolyl ether*,

$$O[C_6H_2Me(NO_2)_2]_2,$$

a white, amorphous powder, m. p. 203°, which on boiling with concentrated aqueous potassium hydroxide yields *dinitrodihydroxy*-m-*tolyl ether*, a black, crystalline powder, m. p. 300° (decomp.).

If the original tolyl ether is nitrated in sulphuric acid solution by the gradual addition of fuming nitric acid, the temperature being gradually raised to 90° towards the end of the reaction, 2 : 6 : 2′ : 6′-*tetranitro*-m-*tolyl ether*, hexagonal plates, m. p. 147°, is obtained together with a large proportion of its isomeride. Attempts to carry the nitration further have, as yet, not been successful. W. G.

Preparation and Oxidation of Styrolene Alcohol [Phenylethylene Glycol]. WM. LLOYD EVANS and LOU HELEN MORGAN (*J. Amer. Chem. Soc.*, 1913, **35**, 54—68).—This investigation was undertaken with the object of determining the mechanism of the oxidation of phenylethylene glycol (styrolene alcohol) with different reagents, and of establishing the conditions under which mandelaldehyde might be isolated as an intermediate product. Zincke (*Annalen*, 1883, **216**, 303) has shown that on oxidising the glycol with chromic acid, benzaldehyde, formaldehyde, and formic acid are produced, that with potassium permanganate a quantitative yield of benzaldehyde may be obtained, and that with nitric acid, benzoylcarbinol and benzoylformic acid are formed.

Phenylethylene glycol is best prepared by the hydrolysis of the corresponding diacetate (Zincke, *loc. cit.*). On oxidation with potassium permanganate, either alone or in presence of alkali hydroxide, it yields benzoic acid, but not phenylglyoxylic acid, the reaction taking place

in accordance with the equation: (1) $C_6H_5 \cdot CH(OH) \cdot CH_2 \cdot OH \rightarrow C_6H_5 \cdot CHO + CH_3 \cdot OH$ or

(2) $C_6H_5 \cdot CH(OH) \cdot CH_2 \cdot OH \rightarrow C_6H_5 \cdot CH_2 \cdot OH + \colon CH \cdot OH$.

When the glycol is oxidised with potassium ferricyanide, benzoic acid is the chief product, but mandelic acid is not formed, and the reaction proceeds according to equation (1) or (2). With silver oxide, in presence of alkali hydroxide, the oxidation takes place, with formation of benzoylcarbinol as the first product of the reaction, in one of the following ways: (3) $C_6H_5 \cdot CH(OH) \cdot CH_2 \cdot OH \rightarrow C_6H_5 \cdot \overset{|}{\underset{|}{C}} \cdot CH_2 \cdot OH + H_2O$; and $C_6H_5 \cdot \overset{|}{\underset{|}{C}} \cdot CH_2 \cdot OH + H_2O \rightarrow C_6H_5 \cdot CO \cdot CH_2 \cdot OH + 2H$; or (4) $C_6H_5 \cdot CH(OH) \cdot CH_2 \cdot OH \rightarrow C_6H_5 \cdot CH(OH) \cdot CH\colon + H_2O$, and

$C_6H_5 \cdot CH(OH) \cdot CH\colon + H_2O \rightarrow C_6H_5 \cdot CH(OH) \cdot CHO + 2H$;

at 60°, both reactions occur. If silver oxide is employed alone at 20°, the reaction seems to proceed entirely in accordance with equation (3). The oxidation of phenylethylene glycol by bromine in presence of potassium carbonate yields benzoylcarbinol. Aqueous solutions of copper salts do not exert any marked action on the glycol even at 100°. E. G.

Preparation of Benzyl Mercaptan. JOHN A. SMYTHE (*Proc. Univ. Durham, Phil. Soc.*, 1912, **4**, 220—222).—Benzyl mercaptan may be prepared from benzyl sulphide by reduction with iron filings in acetic acid solution. When dissolved in glacial acetic acid, and the solution saturated simultaneously with hydrogen chloride and sulphur dioxide, it yields benzyl disulphide and trisulphide in equal amounts. F. B.

Derivatives of Ethylene Dimercaptan, $SH \cdot CH_2 \cdot CH_2 \cdot SH$, *s*-Dithiolethylene, $SH \cdot CH\colon CH \cdot SH$, and of Dithiolacetylene, $SH \cdot C\colon C \cdot SH$. EMIL FROMM, HANS BENZINGER, and FRITZ SCHÄFER (*Annalen*, 1912, **394**, 325—337).—s-*Diethylthiolethylene*,

$SEt \cdot CH\colon CH \cdot SEt$,

b. p. 170°/13 mm., is obtained by the slow addition of dichloroethylene to ethyl mercaptan and potassium hydroxide in alcohol, the mixture being finally heated on the water-bath. The addition of dichloroethylene to benzyl mercaptan in boiling 7·5% alcoholic potassium hydroxide yields s-*dibenzylthiolethylene*, $C_{16}H_{16}S_2$, m. p. 61°, colourless needles, which decomposes by heating into hydrogen sulphide, toluene, benzyl mercaptan, and stilbene, and forms a *dibromide*, $C_{16}H_{16}Br_2S_2$, m. p. 73—74°, with bromine in carbon disulphide. By heating with alcoholic potassium hydroxide, this dibromide yields *dibenzylthiolacetylene*, $CH_2Ph \cdot S \cdot C\colon C \cdot S \cdot CH_2Ph$, m. p. 53°, straw-yellow needles or flesh-coloured leaflets.

s-*Dibenzylthiolethane*, $CH_2Ph \cdot S \cdot CH_2 \cdot CH_2 \cdot S \cdot CH_2Ph$, m. p. 38°, prepared from ethylene dibromide and sodium benzyl mercaptide, is oxidised by cold nitric acid (D 1·34) to the *disulphoxide*, $C_{16}H_{18}O_2S_2$, m. p. 198°, white leaflets; the *disulphone*, $C_{16}H_{18}O_4S_2$, pearly leaflets subliming at 304°, is obtained by oxidising the disulphoxide by 5% potassium permanganate, or the sulphide by chromic and acetic acids.

s-*Di*-o-*nitrophenylthiolethylene*, $C_{14}H_{10}O_4N_2S_2$, m. p. 215°, golden-yellow leaflets, prepared from dichloroethylene, *o*-nitrophenyl mercaptan, and alcoholic potassium hydroxide, forms a *dibromide*,

$$C_{14}H_{10}O_4N_2Br_2S_2,$$

m. p. 132°, citron-yellow prisms, which is converted into *di*-o-*nitrophenylthiolacetylene*, m. p. 225°, yellow needles, by hot alcoholic potassium hydroxide. This acetylene derivative absorbs only one mol. of bromine in chloroform, forming *dibromodi*-o-*nitrophenylthiolethylene*, $C_2Br_2(S{\cdot}C_6H_4{\cdot}NO_2)_2$, m. p. 209°, yellow leaflets. Sodium *o*-nitrophenyl mercaptide and di-*o*-nitrophenylthiolethylene dibromide react in alcohol to form *glyoxaltetra*-o-*nitrophenylmercaptal*,

$$CH(S{\cdot}C_6H_4{\cdot}NO_2)_2{\cdot}CH(S{\cdot}C_6H_4{\cdot}NO_2)_2,$$

yellow needles, m. p. 178°.

s-*Di*-o-*aminophenylthiolethylene*, $C_2H_2(S{\cdot}C_6H_4{\cdot}NH_2)_2$, m. p. 67°, colourless leaflets, obtained by the reduction of the nitro-compound by alkaline sodium hyposulphite, forms a *dibenzoyl* derivative, m. p. 132°, *diacetyl* derivative, m. p. 159°, and a sparingly soluble *dihydrochloride*, m. p. 201°; the last reacts with only one mol. of sodium nitrite during its diazotisation.

s-*Di*-o-*nitrophenylthiolethane*, $C_2H_4(S{\cdot}C_6H_4{\cdot}NO_2)_2$, m. p. 207°, yellow prisms, prepared by treating moist *o*-nitrophenyl mercaptan and ethylene dibromide with hot alcoholic potassium hydroxide, is oxidised to the *disulphoxide*, $C_{14}H_{12}O_6N_2S_2$, m. p. 145°, pale yellow needles, by chromic and warm glacial acetic acids, and to the *disulphone*, m. p. 164°, almost colourless prisms, by chromic and boiling glacial acetic acids, and yields s-*di*-o-*aminophenylthiolethane*, m. p. 74° (*dibenzoyl* derivative, m. p. 153°; *diacetyl* derivative, m. p. 194—195°), by reduction with tin and hydrochloric acid.

s-*Di*-p-*nitrophenylthiolethylene*, m. p. 126°, prepared like the ortho-isomeride, forms a *dibromide*, $C_{14}H_{10}O_4N_2Br_2S_2$, m. p. 137°, yellow needles, and yields by reduction the *diamino*-compound (*diacetyl* derivative, m. p. 194°), which can be readily tetrazotised. s-*Di*-p-*nitrophenylthiolethane*, m. p. 134°, crystallises in yellow prisms.

Di-2 : 4-*dinitrophenyl disulphide*, $S_2[C_6H_3(NO_2)_2]_2$, yellow needles, exploding at 280°, is obtained by heating alcoholic 2 : 4-dinitrochlorobenzene with aqueous sodium sulphide and sulphur.

2 : 4-Dinitrophenyl benzyl sulphide yields the *sulphoxide*,

$$C_6H_3(NO_2)_2{\cdot}SO{\cdot}CH_2Ph,$$

m. p. 144° (decomp.), straw-yellow needles, by oxidation with 30% hydrogen peroxide in glacial acetic acid, and the *sulphone*, m. p. 177°, by oxidation with chromic and warm glacial acetic acids.

2 : 4-*Dinitrophenyl methyl sulphide*, m. p. 126°, prepared from 2 : 4-dinitrophenyl mercaptan, methyl iodide, and methyl alcoholic sodium methoxide, yields the *sulphoxide*, m. p. 159°, yellow leaflets, and the *sulphone*, m. p. 184° (decomp.), colourless needles, by oxidation with hydrogen peroxide and chromic acid respectively. C. S.

Decomposition of Benzyl Disulphide by Alkalis. EMIL FROMM and AQUILA FORSTER (*Annalen*, 1912, **394**, 338—343).—In addition to the substances identified by Price and Twiss among the products of decomposition of benzyl disulphide by alkalis (T., 1910, **97**,

1175), the authors have detected thiobenzoic acid and dithiobenzoic acid. *Benzyl dithiobenzoate*, $Ph\cdot CS_2\cdot CH_2Ph$, m. p. 55°, is prepared by heating the acid and benzyl chloride with alcohol and 10% sodium hydroxide.

When the preceding decomposition is effected in the presence of benzyl chloride, the authors could obtain only about 5% of the benzylmercaptal of benzaldehyde instead of 50%, as stated by Price and Twiss (*loc. cit.*), and they suggest that the latters' benzyl chloride was highly contaminated with benzylidene chloride, which reacts with the sodium benzyl mercaptide to form the benzylmercaptal.

[With MAX KLINGER.]—The substance, m. p. 164°, obtained by Fromm and Schmoldt by the dry distillation of benzoyl sulphide, benzoyl disulphide, or thiobenzoic acid, and stated to be tolane tetrasulphide (A., 1907, i, 702), is now shown to be a mixture. By treatment with ammonium sulphide or with ether and petroleum, it is separated into sulphur and tetraphenylthiophen, m. p. 184°. The substance described as tolane disulphide (*loc. cit.*) is probably also a mixture of sulphur and tetraphenylthiophen. C. S.

Some Mercaptals and Mercaptols and their Derivatives. EMIL FROMM, AQUILA FORSTER, and BORIS VON SCHERSCHEWITZKI (*Annalen*, 1912, **394**, 343—349).—The *benzylmercaptal* of formaldehyde, $CH_2(S\cdot CH_2Ph)_2$, m. p. 55°, obtained by saturating with hydrogen chloride a solution of benzyl mercaptan and excess of 40% formaldehyde in glacial acetic acid, is oxidised to the *sulphoxide*, $CH_2(SO\cdot CH_2Ph)$, m. p. 189°, by hydrogen peroxide and to the *sulphone*, $CH_2(SO_2\cdot CH_2Ph)_2$, m. p. 216°, by acidified 5% potassium permanganate. The *benzylmercaptal* of acetaldehyde,

$$CHMe(S\cdot CH_2Ph)_2,$$

b. p. 200—205°/5 mm., is oxidised to the *sulphone*, $CHMe(SO_2\cdot CH_2Ph)_2$, m. p. 176°, by 5% potassium permanganate.

The *benzylmercaptole* of acetone, $CMe_2(S\cdot CH_2Ph)_2$, b. p. 195°/5 mm., yields the *sulphoxide*, m. p. 105°, and *sulphone*, m. p. 125°, by oxidation as above. This sulphone and also αα-dibenzylsulphone-ethane are produced when dibenzylsulphonemethane is heated with alcoholic methyl iodide and aqueous sodium hydroxide. When αα-dibenzylsulphonepropane is similarly treated, benzylmethylsulphone is obtained, owing to the intermediate formation of benzylsulphinic acid. The following substances are also described: the p-*tolylmercaptal* of formaldehyde and its *sulphoxide*, m. p. 45°, and *sulphone*, m. p. 135°; the p-*tolylmercaptole* of acetone, m. p. 64—65°, and its *sulphoxide*, m. p. 75—76°, and *sulphone*, m. p. 147—148°; *αα-di* p-*tolylsulphone-ethane*, m. p. 156°, and *αα-di*-p-*tolylsulphonepropane*, m. p. 189°. C. S.

Catalysis of Dehydrogenation of Hexahydrobenzoic [*cyclo*-Hexanecarboxylic] Acid. NICOLAI D. ZELINSKI and N. UKLONSKAJA (*Ber.*, 1912, **45**, 3677—3678).—An extension of the process which proved successful with *cyclo*hexane and its methyl derivative to simple derivatives which are not hydrocarbons (Zelinski, A., 1911, i, 958).

When *cyclo*hexanecarboxylic acid is added gradually to palladium

black at 300° in an atmosphere of hydrogen at 20—25 mm. pressure, the vapours which pass away on condensation give crystals of benzoic acid in a smaller quantity of unchanged liquid *cyclo*hexanecarboxylic acid.

If ethyl *cyclo*hexanecarboxylate (b. p. 195—197°, n^{17} 1·4424) is submitted twice to the above treatment, the liquid product can be separated by distillation into two fractions, the smaller one consisting of a mixture of ethyl benzoate and ethyl benzoate (n^{18} 1·5071), whilst the main fraction is of pure ethyl *cyclo*hexanecarboxylate. The progress of the dehydrogenation can be conveniently followed by the change in the refractive index.

As with *cyclo*pentane and its methyl derivative, no dehydrogenation was observed when methyl*cyclo*pentanecarboxylic acid was treated in a similar manner. D. F. T.

Study of Double Linkings. ANTONIO MADINAVEITIA and JOSÉ SUREDA BLANES (*Anal. Fis. Quim.*, 1912, **10**, 381—389).—Under the influence of platinum black, cinnamic acid in glacial acetic acid solution is fully hydrogenised to Zelinski's *cyclo*hexylpropionic acid, whilst palladium black and colloidal palladium determine reduction to phenylpropionic acid. *Octahydroeugenole*, prepared by the hydrogenation of eugenole with platinum black as catalyst, has b. p. 125° at 12 mm., and forms an oil soluble in acetic acid, alcohol and ether, and insoluble in water and light petroleum. In the presence of palladium black, eugenole is reduced to hydroeugenole. G. D. L.

Some Para-derivatives of Phenylacetic Acid. S. ROBSON (*Proc. Univ. Durham Phil. Soc.*, 1912, **4**, 225—227).—*p*-Bromophenylacetic acid, m. p. 114—115°, has been prepared from *p*-nitrophenylacetonitrile by reduction with stannous chloride, followed by replacement of the amino-group by bromine by means of the diazo-reaction, and finally hydrolysing the resulting *p*-bromophenylacetonitrile, m. p. 112°, with sulphuric acid; on nitration it yields 4-bromo-3-nitrophenylacetic acid (Bedson, T., 1880, **37**, 100).

p-Chloro- and *p*-iodo-phenylacetic acids have been prepared in a similar manner. F. B.

Walden's Inversion and Substitution Processes. II. EMIL FISCHER (*Annalen*, 1912, **394**, 350—362. Compare A., 1911, i, 418).—Mainly a reply to Biilmann (A., 1912, i, 420) and to Noyes and Potter (*ibid.*, 786).

Phenylpropiolic acid is reduced to cinnamic acid by zinc dust in alkaline as well as in acid solution (compare A., 1912, i, 187); consequently, the presence of the acid is not the cause of the presumably abnormal course of the reduction. C. S.

Behaviour Towards Light of Cinnamylideneacetonitrile of α-Phenylcinnamylideneacetic Acid, and of the Two Cinnamylideneacetic Acids. HANS STOBBE [and NICOLAUS BARBASCHINOV] (*Ber.*, 1912, **45**, 3396—3408).—When the dark yellow

α-phenylcinnamylideneacetonitrile, CHPh:CH·CH:CPh·CN, is exposed to light in benzene or chloroform solution, a resin is formed, together with benzoic acid and a colourless dimeride, $C_{34}H_{26}N_2$, m. p. 197°. It thus behaves very similarly to cinnamylidenemalonic acid (Riiber, A., 1902, i, 617), which is polymerised by light to diphenyltetramethylenediethenyldicarboxylic [diphenyl*cyclo*butyldiacrylic] acid. The dimeride, when cautiously oxidised by potassium permanganate in aqueous alkaline methylacetate solution, is converted into benzoyl cyanide and α-truxillic acid, $CO_2H\cdot CH<{CHPh \atop CHPh}>CH\cdot CO_2H$. This establishes the dimeride as 1 : 3-*diphenyltetramethylene*-2 : 4-*diethenyl*-β-*phenyl*-β-*cyanide* [1 : 3-*diphenyl*cyclo*butane*-2 : 4-*diatroponitrile*],

$$CN\cdot CPh{:}CH\cdot CH<{CHPh \atop CHPh}>CH\cdot CH{:}CPh\cdot CN.$$

It combines with bromine to a colourless tetrabromide, indicating the absence of a conjugated double bond system, whereas phenylcinnamylidene acetic acid forms only a colourless dibromide. The polymerisation of the cyanide is accompanied by bleaching, the absorption field of the dimeride being displaced some 800 wave-lengths towards the ultraviolet.

On heating at 200°, the dimeride is depolymerised, yielding simply unimolecular cyanide. This behaviour, which is shared by α-truxillic acid, is not in accordance with that of other *cyclo*butane derivatives, and throws some uncertainty on the four-ring formulæ adopted.

A second colourless dimeride, m. p. 215°, is formed during exposure to light. This is also produced as a by-product of the action of bromine on the first dimeride. It does not unite with bromine, and it is not so easily depolymerised; the constitution has not been determined.

α-Phenylcinnamylideneacetic acid, whether used in the form of the acid, its sodium salt or methyl ester, is stable towards light in the absence of oxygen, but in presence of air it is oxidised to benzaldehyde and benzoic acid. No polymerisation product is formed. The methyl ester is more readily oxidised than the acid, whilst the sodium salt is still more resistant.

Similarly under no conditions could a polymeride be obtained from the isomeric cinnamylideneacetic acids. Some oxidation takes place, also the *allo*-acid is converted into its isomeride.

The dimeric acid, $C_{22}H_{20}O_4$, obtained by Riiber (*loc. cit.*) on heating the dimeride of cinnamylidenemalonic acid could not be depolymerised to cinnamylideneacetic acid. The sodium salt and methyl ester behave similarly to the acid; the ester is more easily oxidised under the influence of light; the salt is more stable than the acid. The different behaviour of the compounds studied is not due to any differences in the selective absorption of light by them.

The *dibromide*, $C_{17}H_{13}NBr_2$, from phenylcinnamylideneacetonitrile, crystallises in colourless needles, m. p. 118°. The *tetrabromide* $C_{34}H_{26}N_2Br_4$, of the dimeride has m. p. 276°.

Cinnamylidenemalonic acid forms a *dibromide*, $C_{12}H_{10}O_4Br_2$, m. p. 180°. The *tetrabromide* of the dimeride has decomp. above 100°.

Methyl allo*cinnamylideneacetate* is an oil, solidifying below −80°.

E. F. A.

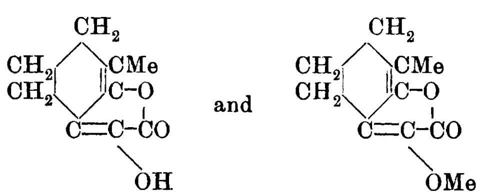
Some Pharmaceutical Incompatibilities of Salol [Phenyl Salicylate]. ITALO BELLUCCI (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 610—616. Compare Caille, A., 1909, i, 594).—In pharmaceutical practice it is not infrequently observed that two dry, solid drugs yield a pasty or liquid mixture. This phenomenon is not due in all cases to the occurrence of a chemical reaction, but results in some cases from the formation of an eutectic mixture of low m. p. In the present paper the author gives tables and curves which exhibit the results of the thermal analysis of the binary mixtures of salol with the substances mentioned in the following list:

	Eutectic.			Eutectic.	
	Temp.	% Salol.		Temp.	% Salol.
β-Naphthol	34°	90	Chloral hydrate ...	17°	61
Antipyrine	30	83	Thymol	13	66
Urethane	29	86	Camphor	6	56
Menthol	28	45	Guaiacol	3	53
β-Bromocamphor..	21	64			

In the system salol-menthol there is complete miscibility in the solid state, the curve being Roozeboom's type III. with a minimum at about 28° and 45% of salol. From the temperature given it follows that some of the above binary mixtures are pasty at ordinary temperatures, others liquid. R. V. S.

Condensation of Cyclic Ketones with Ethyl Oxalate. ARTHUR KÖTZ, K. BLENDERMANN, and J. MEYER (*Ber.*, 1912, **45**, 3702—3705. Compare A., 1906, **88**, 668).—Active 1-methyl*cyclo*hexan-3-one condenses in the cold with ethyl oxalate and sodium ethoxide, and when the dry product is treated with methyl iodide and subsequently hydrolysed, 1:4-dimethyl*cyclo*hexan-2-one is obtained, b. p. 51°/10 mm. Its *oxime*, $C_8H_{15}ON$, has m. p. 97—98°.

Inactive 1-methyl*cyclo*hexan-2-one condenses to form a *methyl*-cyclo*hexenolpyruvolactone*, $C_9H_{10}O_3$, m. p. 141°, alcohol being eliminated. When this is treated with methyl iodide, a *dimethyl* compound, $C_{10}H_{12}O_3$, m. p. 87°, is formed, which absorbs 4 atoms of hydrogen and yields 1-methyl*cyclo*hexan-2-one on hydrolysis. Since these compounds give no reactions for ketones, and since Claisen has shown that the formation of lactones is possible in such circumstances (A., 1895, i, 373), they may be represented by the annexed formulæ.



J. C. W.

Melting Point of Ethyl Gallate. HENRY C. BIDDLE (*J. Amer. Chem. Soc.*, 1913, **35**, 96).—Biddle and Kelley (A., 1912, i, 714) suggested that the peculiar behaviour of ethyl gallate on melting might be due to the existence of two crystalline forms. It has now been found, however, that by continued purification the ester can

be obtained in long, colourless needles, melting fairly sharply at 160°. E. G.

Kojic Acid, a New Organic Acid Formed by Aspergillus oryzæ. T. YABUTA (*J. Coll. Agric. Imp. Univ. Tokyo*, 1912, 5, 51—58).—*Kojic acid*, $C_{10}H_8(OH)_4(CO_2H)_2$, obtained from finely powdered *Aspergillus oryzae*, forms colourless needles or prisms, m. p. 152°. The acid gives a strong red colour with ferric chloride; it has no action on alkaline diazobenzenesulphonic acid, on Millon's reagent, or on Fehling's solution. The aqueous solution absorbs much bromine. Methoxyl and ethoxyl groups are not present. The *copper* salt, $C_{12}H_{12}O_8Cu$, forms light green, rhombic crystals. The *acetyl* derivative, $C_{12}H_{10}O_4(OAc)_4$, crystallises from alcohol in colourless needles, m. p. 102°. The *dibenzoyl* derivative, $C_{12}H_{10}O_4(OH)_2(OBz)_2$, m. p. 137°, and the *tetrabenzoyl* derivative, $C_{12}H_{10}O_4(OBz)_4$, m. p. 135°, were prepared.

The acid also occurs in *Aspergillus albus*, *A. candidus*, and *A. nidulans*, but was not found in thirteen other varieties or in *Penicillium* or *Mucor*.

The production of the acid seems to depend on the food supplied to the *Aspergillus*. It was found in *Aspergillus* grown on certain cereals and potatoes, but not with leguminous seeds. N. H. J. M.

Synthesis of β-Glucosidogallic Acid. EMIL FISCHER and HERMANN STRAUSS (*Ber.*, 1912, 45, 3773—3779).—Ethyl gallate combines with acetobromoglucose, forming *ethyl tetra-acetylglucosidogallate*, which is completely hydrolysed by cold barium hydroxide solution to *glucosidogallic acid*, $C_6H_{11}O_5{\cdot}C_6H_2(OH)_2{\cdot}CO_2H$. This crystallises in colourless, interlaced needles, m. p. 193° (decomp.), after sintering from 155°, $[\alpha]_D^{20}$ $-22°$. It is monobasic and is hydrolysed by emulsin into dextrose and gallic acid. With ferric chloride a brownish-red coloration is produced, indicating that the *p*-hydroxyl group of the gallic acid is attached to the sugar residue. It differs from the supposed glucosides of gallic acid described by Gibson (A., 1903, i, 355) and by Feist (A., 1912, i, 566, 888).

Ethyl tetra-acetylglucosidogallate crystallises in colourless needles, m. p. 180—181° (corr.), $[\alpha]_D^{20}$ $-10{\cdot}6°$. E. F. A.

Some Reduction Products of Ellagic Acid. MAXIMILIAN NIERENSTEIN and FREDERIC W. RIXON (*Annalen*, 1912, 394, 249—258).—The electrolytic reduction of ellagic acid in a divided cell with mercury cathode and nickel anode yields different products at different temperatures. By reduction in $4N$-sodium hydroxide at the ordinary temperature, ellagic acid yields chiefly *leucoellagic acid*,

$$C_6H(OH)_2{<}\begin{matrix}CH(OH){\cdot}O\\O{\cdot}CH(OH)\end{matrix}{>}C_6H(OH)_2,$$

m. p. 294—296° (decomp.), small needles. This substance is colourless, does not possess any tinctorial properties, forms a *hexa-acetyl* derivative, m. p. 272—275° (decomp.), and a *hexabenzoyl* derivative, m. p. 300—305° (decomp.), and is reconverted into ellagic acid by oxidation with hydrogen peroxide. By boiling with aqueous potassium hydroxide and carbon tetrachloride, leucoellagic acid is converted into the

potassium salt, long rhombohedra, of the *dicarboxylic acid*,

$$CO_2H\cdot C_6(OH)_2\langle\begin{matrix}CH(OH)\cdot O\\ O\cdot CH(OH)\end{matrix}\rangle C_6(OH)_2\cdot CO_2H,$$

m. p. 123—124° (decomp.), small needles. A solution of the dicarboxylic acid in ethyl acetate has been separated by strychnine into the two (impure) active acids and the meso-modification. The impure d-*acid* has m. p. 122—124° and $[\alpha]_D^{17}$ +19·9°; the impure l-*acid* has m. p. 127—131° and $[\alpha]_D^{17}$ −2·3°, and the meso-*acid* has m. p. 143—146° (decomp.).

The electrolytic reduction of ellagic acid in alkaline solution at 70° yields pentahydroxydiphenylmethylolide (A., 1908, i, 548), whilst its reduction in concentrated sodium hydroxide at 110° yields 2 : 3 : 4 : 2′ : 3′ : 4′-hexahydroxydiphenyl. C. S.

New Basic Component of the Muscle of the Dog and Its Relation to Hexamethylornithine. DANKWART ACKERMANN (*Zeitsch. Biol.*, 1912, **59**, 433—440).—*Myokynine*, a basic substance obtained from dog's muscle, is probably *l*-hexamethylornithine. Both substances give precipitates with phosphotungstic acid and with alcoholic mercuric chloride solution.

The *aurichloride* from myokynine contains $2H_2O$ and is lævorotatory, that from *hexamethylornithine*, m. p. 204—205°, is anhydrous. Myokynine *platinichloride* ($2H_2O$) has m. p. 232—234°; the isomeride (H_2O) has m. p. 232—233°.

Hexamethylornithine is obtained from ornithine by means of methyl sulphate; it is dextrorotatory. E. F. A.

The Bromination of *cyclo*Pentanone. MARCEL GODCHOT and FÉLIX TABOURY (*Compt. rend.*, 1912, **155**, 1522—1524).—When bromine (4 mols.) dissolved in carbon tetrachloride is added to a solution of *cyclo*pentanone (1 mol.) in the same solvent, either with or without the presence of aluminium bromide, the mixture being kept cold, there is obtained, on evaporating off the solvent, an abundant crop of crystals with more or less oil. The crystals are separated, and on purification yield *tetrabromo*cyclo*pentanone*, $C_5H_4OBr_4$, large plates, m. p. 99°. It is very soluble in ether, ethyl acetate, etc., and when left to itself slowly loses hydrogen bromide and is converted into a yellow oil. This change takes place rapidly in solution in ethyl acetate, and the product when purified is *tribromo*cyclo*pentenone*, $C_5H_3OBr_3$, colourless prisms, m. p. 57—58°. This substance on bromination in carbon tetrachloride solution adds on two atoms of bromine, giving *pentabromo*cyclo*pentanone*, $C_5H_3OBr_5$, m. p. 93°.

The oil obtained in the original bromination slowly loses hydrogen bromide, and on boiling the product with water and extracting with ether, a *compound* is obtained, m. p. 147°, which analysis shows to be either $C_5H_3O_2Br$ or $C_5H_5O_2Br$, the amount of material to hand not allowing of definite distinction between the two formulæ. The substance functions both as an alcohol and a ketone. W. G.

2 : 2-Dimethyl*cyclo*heptanone. P. JOSEPH TARBOURIECH (*Compt. rend.*, 1913, **156**, 75—77).—The dehydration of *cyclo*hexanoldimethylcarbinol gives rise to a hydrocarbon, C_9H_{14}, and two isomeric ketones,

$C_9H_{16}O$, one of which has been shown to be 1-acetyl-1-methyl*cyclo*hexane (compare A., 1910, i, 557), and the other is now proved to be 2 : 2-*dimethyl*cyclo*heptanone*, $Me_2C<\begin{matrix}CH_2\cdot CH_2\cdot CH_2 \\ CO-CH_2-CH_2\end{matrix}$, the :CO group having been introduced into the hexatomic ring. By purification through its oxime, it is obtained as a colourless liquid, b. p. 82°/18 mm., giving a *carbanilino-oxime*, m. p. 94°, and a *semicarbazone*, m. p. 176°. On oxidation with weak alkaline permanganate, it yields *a-keto-ββ-dimethylpimelic acid*, $CO_2H\cdot CO\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO_2H$, m. p. 67°, giving a *semicarbazone*, m. p. 185°, and an *oxime*, m. p. 140—141°, which on heating further decomposes, losing carbon dioxide and water, giving *δ-cyano-δδ-dimethylpentoic acid*,

$$CN\cdot CMe_2\cdot[CH_2]_3\cdot CO_2H,$$

m. p. 34—35°, which on hydrolysis with alcoholic potassium hydroxide is converted into αα-dimethyladipic acid. W. G.

Electrolysis of *cyclo*Pentanone. MARCEL GODCHOT and FÉLIX TABOURY (*Bull. Soc. chim.*, 1913, [iv], **13**, 12—17. Compare A., 1912, i, **34**, 552).—On electrolysis in alkaline solution, *cyclo*pentanone yields *cyclo*pentylidene*cyclo*pentanone (Wallach, A., 1897, i, 160) and two other products, which appear to be tetra*cyclo*pentane derivatives. It is probable that the *cyclo*pentylidene*cyclo*pentanone is formed by the condensation of two mols. of *cyclo*pentanone in presence of alkali, and that the other two products are formed from the condensation product by electrolytic action, the first being the corresponding pinacone and the second the corresponding pinacolin. These supposed tetra*cyclo*pentane derivatives have the following characters. The first, m. p. 160—162°, has the formula $C_{20}H_{30}O_2$, and is probably identical with the substance obtained by Meiser (A., 1899, i, 741). It probably has the annexed constitution, which makes it the pinacone corresponding with *cyclo*pentylidene*cyclo*pentanone. This substance probably loses 1 mol. of water, giving rise to the second *product*, $C_{20}H_{28}O$, b. p. 320°/25 mm., a yellow liquid which gives no typical carbonyl derivatives, although it probably has the following constitution, being formed in a manner analogous to the transformation of the pinacone of *cyclo*pentanone into the corresponding pinacolin (Meiser, *loc. cit.*), $\begin{matrix}CH_2-CH_2 \\ CH_2\cdot C(C_5H_8)\end{matrix}>C<\begin{matrix}CH_2-CH_2 \\ CO\cdot C(C_5H_8)\end{matrix}>CH_2$.

$$\begin{matrix}CH_2\cdot CH_2 \\ CH_2\cdot CH_2\end{matrix}>C:C<\begin{matrix}CH_2-CH_2 \\ C(OH)\cdot CH_2\end{matrix}$$
$$\begin{matrix}CH_2\cdot CH_2 \\ CH_2\cdot CH_2\end{matrix}>C:C<\begin{matrix}C(OH)\cdot CH_2 \\ CH_2-CH_2\end{matrix}$$

T. A. H.

Terpenes and Ethereal Oils. CXII. Condensation Products of Cyclic Ketones and Acetone. OTTO WALLACH and WOLFGANG VON RECHENBERG (*Annalen*, 1912, **394**, 362—384).—Many years ago a substance, $C_{10}H_{16}O$, isomeric with pulegone, was obtained by the condensation of acetone and methyl*cyclo*hexan-3-one, but its constitution could not be definitely settled (A., 1896, i, 310; 1898, i, 484). An extensive examination of similar condensations now leads to the generalisation that the acetone attacks the carbonyl group of *cyclo*hexanones, but a nuclear methylene group of *cyclo*-

pentanones; thus equal molecular quantities of *cyclo*pentanone and acetone are kept in alcoholic sodium ethoxide for some hours at 0°, and then for two to three days at the ordinary temperature, whereby, in addition to a little mesityl oxide, *propylidene*cyclo*pentan*-2-*one*,

$$CMe_2:C<\begin{matrix}CO-CH_2\\ CH_2\cdot CH_2\end{matrix},$$

b. p. 195—199°, D^{20} 0·9565, n_D^{20} 1·4932, is obtained (*semicarbazone*, m. p. 215—218°; *oxime*, m. p. 77°), by the reduction of which by hydrogen and colloidal palladium, iso*propyl*cyclo*pentan*-2-*one*, b. p. 176·5—177·5°, D^{21} 0·9000, n_D^{21} 1·4419 (*semicarbazone*, m. p. 197°; *benzylidene* derivative, m. p. 79—80°), is formed. In a similar manner, i-*methyl*cyclo*pentan*-3-*one*, b. p. 144—144·5°, D^{22} 0·913, n_D 1·4329 (*semicarbazone*, m. p. 185°; *benzylidene* derivative, m. p. 157°; m-*nitrobenzylidene* derivative, m. p. 174°; *anisylidene* derivative, m. p. 197—198°; *piperonylidene* derivative, m. p. 166—167°; *cinnamylidene* derivative, m. p. 148° [compare A., 1904, i, 752; 1908, i, 424]), prepared from *i*-*β*-methyladipic acid, condenses with acetone to form 1-*methyl*-4-*propylidene*cyclo*pentan*-3-*one*, $CMe_2:C<\begin{matrix}CH_2\cdot CHMe\\ CO-CH_2\end{matrix}$, b. p. 203—205°, D^{21} 0·9315, n_D^{21} 1·4846 (*semicarbazone*, m. p. 210°; *oxime*, m. p. 89°). The constitution of this compound is determined by its exalted molecular refraction, and by the fact that 1-*methyl*-4-iso*propyl*-cyclo*pentan*-3-*one*, b. p. 186—187°, D^{20} 0·8850, n_D^{20} 1·4392 (*semicarbazone*, m. p. 179°; *oxime*, m. p. 66°), obtained from it by Paal's method, yields by oxidation with chromic and dilute sulphuric acids a *keto-acid*, $CHMe_2\cdot CO\cdot CH_2\cdot CHMe\cdot CH_2\cdot CO_2H$ (*semicarbazone*, m. p. 164°; *oxime*, m. p. 76—77°), by the further oxidation of which *i*-*β*-methylglutaric acid is produced.

*cyclo*Hexanone and acetone condense to form Δ^1-cyclo*hexenylacetone*, $C_6H_9\cdot CH_2\cdot COMe$, b. p. 203—204°, D^{19} 0·9375, n_D 1·4736 (*semicarbazone*, m. p. 144—145°; *oxime*, b. p. 135°/20 mm.), the constitution of which follows from its molecular refraction and from its reduction by Paal's method to *cyclo*hexylacetone, m. p. 171—172° (not 165—166°, A., 1907, i, 616). cyclo*Hexyltrimethylcarbinol*, $C_6H_{11}\cdot CH_2\cdot CMe_2\cdot OH$, b. p. 208°, D^{20} 0·902, n_D^{20} 1·4627, is prepared from *cyclo*hexylacetone and magnesium methyl iodide in the usual manner.

Methyl*cyclo*hexan-4-one and acetone yield 1-*methyl*-Δ^3-cyclo*hexenyl*-4-*acetone*, $C_6H_8Me\cdot CH_2\cdot COMe$, b. p. 216—217°, D^{21} 0·916, n_D^{21} 1·4672 (*semicarbazone*, m. p. 122—123°), by the reduction of which 1-*methyl*-cyclo*hexyl*-4-*acetone*, b. p. 214—215°, D^{21} 0·8930, n_D^{21} 1·4499 (*semicarbazone*, m. p. 166°), is formed.

The compound $C_{10}H_{16}O$, obtained from active methyl*cyclo*hexan-3-one and acetone (*loc. cit.*), is now proved to be 1-*methyl*-$\Delta^{2(\text{or }3)}$-cyclo*hexenyl*-3-*acetone*, $C_6H_8Me\cdot CH_2\cdot COMe$, or a mixture of both. By reduction by Paal's method, it yields 1-*methyl*cyclo*hexyl*-3-*acetone*, $C_6H_{10}Me\cdot CH_2\cdot COMe$, b. p. 212—214°, $D^{21.5}$ 0·8915, $n_D^{21.5}$ 1·4496 (*semicarbazone*, m. p. 154°), which is converted by alkaline hypobromite into 1-methyl*cyclo*hexyl-3-acetic acid, and by magnesium methyl iodide ultimately into 1-*methyl*cyclo*hexyltrimethylcarbinol*,

$$C_6H_{10}Me\cdot CH_2\cdot CMe_2\cdot OH,$$

b. p. 117°/20 mm. (*phenylurethane*, m. p. 126°). By the elimination of water, the carbinol yields a *hydrocarbon*, $C_{11}H_{20}$, b. p. 186·5—187·5°, D^{20} 0·8120, n_D^{20} 1·4546. *i*-Methyl*cyclo*hexan-3-one condenses with acetone in the same manner as the active substance, yielding a *compound*, $C_{10}H_{16}O$, b. p. 214—217°, D^{21} 0·918, n_D 1·4704 (*semicarbazone*, m. p. 150—151°).

1-Methyl*cyclo*hexan-2-one and acetone, after keeping with alcoholic sodium ethoxide for four weeks, yield mesityl oxide and 1-*methyl*-Δ^1-cyclo*hexenyl*-2-*acetone*, b. p. 216—217°, D^{19} 0·936, n_D^{19} 1·4778 (*semicarbazone*, m. p. 173—174°); the latter yields by reduction by Paal's method, 1-*methyl*cyclo*hexyl*-2-*acetone*, b. p. 212—214°, D^{21} 0·9050, n_D^{21} 1·4546 (*semicarbazone*, m. p. 179°), from which 1-*methyl*cyclo*hexyl*-2-*acetic acid* (*silver* salt, $C_9H_{15}O_2Ag$; *amide*, m. p. 160—161°) is obtained by oxidation by alkaline hypobromite. C. S.

Studies in the *cyclo*Pentadiene Series. II. 5-Nitro-2:3-dibenzoyl*cyclo*pentadiene. WILLIAM J. HALE and LAMBERT THORP (*J. Amer. Chem. Soc.*, 1913, 35, 68—75).—It has been shown by Hale (A., 1912, i, 566) that acetonylacetone condenses with nitromalonaldehyde to form 5-nitro-2 : 3-diacetyl*cyclo*pentadiene. A similar condensation has now been effected with diphenacyl.

When diphenacyl (1 mol.) is added to a solution of sodium nitromalonaldehyde (1 mol.) and sodium hydroxide (2 mols.), and the mixture is left for eight to ten days at 40°, 5-*nitro*-2 : 3-*dibenzoyl*cyclo*pentadiene*, $NO_2\cdot CH<\begin{matrix}CH:CBz\\ \vert \\ CH:CBz\end{matrix}$, m. p. 237—238° (decomp.), is obtained in a yield of 75% of that calculated from the amount of aldehyde used. The compound crystallises in yellow prisms; its *sodium*, *barium*, and *silver* salts are described. The *oxime*, m. p. 155—156° (decomp.), and the *anil*, m. p. 264—265°, form slender, yellow needles. The *phenylhydrazone* crystallises in yellow needles; it is unstable and readily undergoes an intramolecular condensation.

If 5-nitro-2:3-dibenzoyl*cyclo*pentadiene is boiled with dilute nitric acid, it undergoes oxidation with production of carbon dioxide, oxalic acid, and benzoic acid. A similar result is obtained by means of an alkaline solution of potassium permanganate, 1 mol. of the compound yielding carbon dioxide (3 mols.), oxalic acid (1 mol.), nitric acid (1 mol.), and benzoic acid (2 mols.). E. G.

Thio-derivatives of Ketones. EMIL FROMM (*Annalen*, 1912, 394, 290—309).—[With FRITZ HAAS.]—The substance previously described as duplobenzylidenethioacetone by Fromm and Höller (A., 1907, i, 710) is now shown to be a mixture of stereoisomeric bases, the *duplobenzylidenethioacetoneamines*, $C_{20}H_{23}NS_2$, and its extraordinary additive compounds with acids are simply salts of these bases; consequently, the theories advanced by Fromm and Höller to explain the formation of these additive compounds are abandoned. The *hydrochloride*, $C_{20}H_{23}NS_2,HCl$, has m. p. 238°, the *sulphate* has m. p. 192°, and the *nitrate* has m. p. 211°. The substance previously described as duplobenzylidenethioacetone hydrate, and the two additive compounds

with ammonia, m. p. 142° and 148° respectively, are simply duplobenzylidenethioacetoneamine.

The neutral by-product, duplobenzylideneoxythioacetone, m. p. 186°, obtained by Fromm and Höller in the preparation of their so-called duplobenzylidenethioacetone (*loc. cit.*), becomes the main product when sodium sulphide is employed instead of ammonium sulphide. It is now shown to be *duplobenzylideneacetone sulphide*, $C_{20}H_{22}O_2S$. It forms a *dibromo*-derivative, $C_{20}H_{20}O_2SBr_2$, m. p. 164°, rhombic leaflets, with bromine in chloroform, and is oxidised by 5% potassium permanganate, by fuming nitric acid, or by 30% hydrogen peroxide in glacial acetic acid, to *duplobenzylideneacetone sulphoxide*, $C_{20}H_{22}O_3S$, m. p. 308°, prisms, which forms a *dibromo*-derivative, $C_{20}H_{20}O_3SBr_2$, m. p. 214°, felted needles, with bromine. By treating a not too concentrated solution of styryl methyl ketone in alcohol with ammonium polysulphide, *duplobenzylideneacetone disulphide*, $C_{20}H_{22}O_2S_2$, m. p. 125°, is obtained.

Since duplobenzylidenethioacetoneamine yields hydrogen sulphide, ammonia, and styryl methyl ketone-phenylhydrazone by treatment with phenylhydrazine at a temperature not exceeding 140—150°, it probably has the formula $NH[CMe(SH)\cdot CH\dot{:}CHPh]_2$, despite its insolubility in alkalis. Moreover, since it yields duplobenzylideneacetone disulphide by oxidation by hydrogen peroxide or by iodine, the disulphide probably has the formula $S_2[CMe(OH)\cdot CH\dot{:}CHPh]_2$. By moistening with a little alcohol and then shaking with dilute sodium hydroxide, the disulphide is converted into the sulphide. The latter, therefore, is probably $S[CMe(OH)\cdot CH\dot{:}CHPh]_2$, and the sulphoxide is $SO[CMe(OH)\cdot CH\dot{:}CHPh]_2$. The disulphide and the sulphide cannot be benzoylated or acetylated, but both, and also the sulphoxide, yield styryl methyl ketone-phenylhydrazone by treatment with phenylhydrazine.

[With EMIL HUBERT.]—*Benzylideneacetophenone hydrosulphide*, $CHPh\dot{:}CH\cdot CPh(OH)\cdot SH$, m. p. 107°, is obtained by the action at 0° of hydrogen sulphide on an alcoholic solution of phenyl styryl ketone containing a little potassium hydroxide. It forms a S-*benzoyl* derivative, $CHPh\dot{:}CH\cdot CPh(OH)\cdot SBz$, m. p. 125°, which is not oxidised to a disulphide by iodine. *Dibenzylideneacetophenone disulphide*,

$$S_2[CPh(OH)\cdot CH\dot{:}CHPh]_2,$$

m. p. 159°, is obtained by oxidising the preceding hydrosulphide by iodine in alcohol-chloroform solution, or by adding cold alcoholic phenyl styryl ketone to alcoholic sodium sulphide saturated with sulphur and with hydrogen sulphide.

The amorphous α- and β-duplobenzylideneacetophenone sulphides, m. p. 96° and 181° respectively, described by Fromm and Lambrecht (A., 1908, i, 989), are not pure. The pure substances are crystalline, have m. p. 109° and 186° respectively, and have the formula $C_{30}H_{26}O_2S$, not $C_{30}H_{24}OS$. The views previously advanced to explain their isomerism are withdrawn. The pure substances are obtained by the action of alcoholic ammonia on phenyl styryl ketone hydrosulphide in chloroform, an excess of ammonia producing the β-isomeride, m. p. 186°, a little ammonia forming the α-isomeride, m. p. 109°. This method of formation, together with the fact that the two sulphides

yield hydrogen sulphide and 1 : 3 : 5-triphenylpyrazolone by boiling with phenylhydrazine in glacial acetic acid, leads to the formula $S[CPh(OH)\cdot CH:CHPh]_2$ for the two isomerides. *a*-Duplobenzylideneacetophenone sulphide is converted into the *β*-isomeride, not by iodine as stated by Fromm and Lambrecht (*loc. cit.*), but by ammonia. The stereoisomerism of the two substances is probably similar to that of dioximes, consequently *cis-*, *trans-*, and *amphi*-modifications

```
        Ph Ph                          Ph Ph
CH——Ċ·S·Ċ————CH          CH——Ċ·S·Ċ——CH
C̈HPh  ȮH ȮH  PhHC̈        PhC̈H   ȮH ȮH  C̈HPh
        cis.                            trans.

              Ph  Ph
      CH——Ċ·S·Ċ————CH
     PhC̈H    ȮH ȮH   PhHC̈
              amphi.
```

should exist. This view of the stereoisomerism receives strong support by the discovery of the third modification required by the theory. *a*-Duplobenzylideneacetophenone sulphide, m. p. 109° (sulphone, m. p. 198°, is obtained by passing hydrogen sulphide, without cooling, into an alcoholic solution of phenyl styryl ketone containing a little potassium hydroxide. *β*-Duplobenzylideneacetophenone sulphide, m. p. 186° (sulphone, m. p. 216°), is prepared by saturating an alcoholic solution of phenyl styryl ketone with ammonia and then with hydrogen sulphide. *γ-Duplobenzylideneacetophenone sulphide*, m. p. 212° (*sulphone*, $C_{30}H_{26}O_4S$, m. p. 276°), is obtained by adding an alcoholic solution of phenyl styryl ketone to alcohol saturated with anhydrous sodium sulphide and with sulphur. C. S.

Stereoisomerism of Derivatives of Phenacyl Sulphide. Emil Fromm and Julius Flaschen (*Annalen*, 1912, **394**, 310—324).—Phenacyl sulphide is obtained in almost quantitative yield by Tafel and Mauritz's method (A., 1891, 302) when the solution is kept at 0° during the reaction. In addition to the diphenylhydrazone described by these authors, a *phenylhydrazone*, $C_{22}H_{20}ON_2S$, m. p. 126°, yellow needles, can be prepared. Phenacyl sulphide in glacial acetic acid is oxidised to *diphenacyl sulphoxide*, $SO(CH_2\cdot COPh)_2$, m. p. 98°, and in benzene is oxidised by a faintly acidified solution of potassium permanganate to *diphenacylsulphone*, m. p. 120°, colourless prisms. The sulphone yields *diphenacylsulphone dibenzylmercaptole*, $SO_2[CH_2\cdot CPh(S\cdot C_7H_7)_2]_2$, m. p. 110°, by treatment with an excess of benzyl mercaptan in glacial acetic acid saturated with hydrogen chloride, and forms only a *dimethyl* derivative, $SO_2(CHMe\cdot COPh)_2$, m. p. 178°, with methyl iodide and sodium ethoxide in alcohol. In boiling glacial acetic acid, phenacylsulphone and the calculated quantity of phenylhydrazine yield *diphenacylsulphonediphenylhydrazone*,

$$SO_2(CH_2\cdot CPh:N\cdot NHPh)_2.$$

This crystallises from glacial acetic acid in yellow needles, m. p. 148°, and from alcohol or from benzene and petroleum in pale yellow needles, m. p. 160°. This second modification, which can also be obtained by

the interaction of diphenacylsulphone and phenylhydrazine in alcohol containing a little sodium hydroxide, is converted into the first modification, m. p. 148°, by crystallisation from glacial acetic acid. A third *isomeride*, m. p. 170°, is obtained from diphenacylsulphone and phenylhydrazine in alcohol, *anhydrodiphenacylsulphonephenylhydrazone*,

$$C_{22}H_{18}O_2N_2S,$$

m. p. 187°, being also produced. *Diphenacylsulphonephenylhydrazone*, m. p. 193°, yellow needles, is prepared by crystallising the preceding anhydride from glacial acetic acid or by boiling equal molecular quantities of diphenacylsulphone and phenylhydrazine in the same solvent. Reasons are given for regarding this phenylhydrazone as *trans*-diphenacylsulphonephenylhydrazone and the anhydride as a derivative of the *cis*-isomeride; the diphenylhydrazones, m. p. 148°, 160°, and 170°, are regarded as having the *trans*-, *amphi*-, and *cis*-configurations respectively.

Anhydrodiphenacylsulphonedioxime,

$$\begin{matrix} CPh{\cdot}CH \\ \| \\ N\text{———}O \end{matrix}\!\!>\!SO{\cdot}CH_2{\cdot}CPh{:}NOH,$$

m. p. 167° white needles, prepared from diphenacylsulphone and hydroxylamine hydrochloride (2 mols.) in alcohol in the presence of sodium carbonate or acetate, yields *acetyldiphenacylsulphoneoxime*, $C_{18}H_{17}O_5NS$, m. p. 110°, by boiling with acetic anhydride. cis-*Diphenacylsulphonedioxime*, m. p. 204° (*acetyl* derivative, m. p. 158°), is obtained from diphenacylsulphone and an excess of hydroxylamine hydrochloride in boiling alcohol containing a drop of hydrochloric acid. trans-*Diphenacylsulphonedioxime*, m. p. 190° (*acetyl* derivative, m. p. 146°), is obtained together with the monoxime, m. p. 173°, by heating diphenacyl sulphone with hydroxylamine hydrochloride (2 mols.) and calcium carbonate (1 mol.) in alcohol through which carbon dioxide is being passed. cis-*Diphenacylsulphoneoxime*, $C_{16}H_{15}O_4NS$, m. p. 144°, is obtained from equal molecular quantities of diphenacylsulphone and hydroxylamine hydrochloride in the presence of sodium carbonate or acetate. trans-*Diphenacylsulphoneoxime*, m. p. 173°, is obtained from equal molecular quantities of diphenacylsulphone and hydroxylamine hydrochloride in boiling alcohol in the presence of calcium carbonate. The monoximes each yield the same acetyl derivative, m. p. 110°, as that obtained from anhydrodiphenacylsulphonedioxime. The *cis*-oxime, m. p. 144°, yields anhydrodiphenacylsulphonedioxime by further treatment with hydroxylamine hydrochloride and sodium carbonate, and the *cis*-dioxime by treatment with hydroxylamine hydrochloride and calcium carbonate. The *trans*-oxime, m. p. 173°, yields only anhydrodiphenacylsulphonedioxime by treatment with hydroxylamine hydrochloride and sodium carbonate or calcium carbonate. Since the anhydrodioxime is produced from each of the monoximes, it is certainly derived from the *amphi*-dioxime. The configurations of the other substances are not established with certainty, C. S.

Transformations of Thujane. II. Nicolai M. Kishner (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1759—1762. Compare A., 1911, i, 71, 996).—Decomposition by means of aniline or alcoholic potassium hydroxide of the unstable bromide obtained by shaking thujane with

fuming hydrobromic acid for a comparatively short time (two to three hours) yields a mixture of two isomeric hydrocarbons, $C_{10}H_{18}$, the one with the higher boiling point predominating when alkali is employed. The properties of various preparations of these hydrocarbons are as follows: (1) b. p. 160—161·5°/753 mm., D_0^{20} 0·8085 (or 0·8082), n_D 1·4490, $[\alpha]_D$ +17·86° (or +15·59°); (2) b. p. 166—168°/754 mm., D_0^{20} 0·8159 (or 0·8188), n_D 1·4538, $[\alpha]_D$ +6·13° (or +2·8°). If the action of the hydrobromic acid on thujane is prolonged for fifteen hours, distillation of the bromide yielded with aniline gives hydrocarbons with the constants: (1) b. p. 160—162°/762 mm., D_0^{20} 0·8093, n_D 1·4494, $[\alpha]_D$ +3·67°; (2) b. p. 167·5—170°/761 mm., D_0^{20} 0·8171, n_D 1·4555, $[\alpha]_D$ +2·4°.

Both hydrocarbons contain the same carbon-atom nucleus, since reduction of them by Sabatier's method leads to one and the same hydrocarbon, $C_{10}H_{20}$, b. p. 161—163°/753 mm. (or 759 mm.), D_0^{20} 0·7904 (or 0·7902), n_D 1·4319 (or 1·4336), $[\alpha]_D$ −1·29° (or −1·21°)

T. H. P.

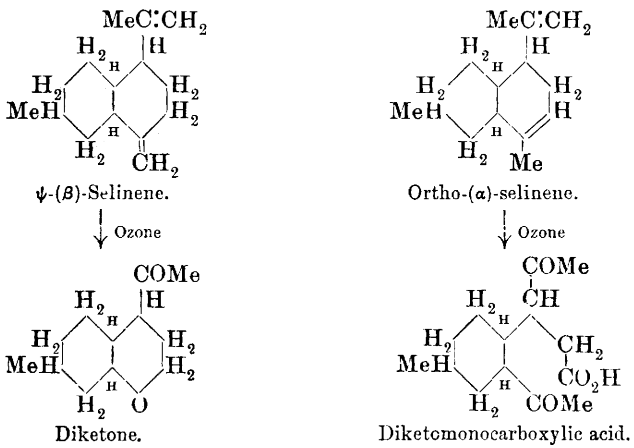
A Special Case of Racemism. MAURIZIO PADOA and G. ROTONDI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 626—631).—The paper deals with the thermal analysis of the system formed by the two modifications (namely, the stable, m. p. 75°, and the labile, m. p. 45°) of optically active bromocamphor (*d*- or *l*-). This presents a case not considered by Roozeboom in his analysis of the criteria for the characterisation of inactive mixtures, because each enantiomorph exists in two modifications. Mixtures containing more than about 58% of *d*-bromocamphor, or more than 58% of *l*-bromocamphor, have an initial m. p., with separation of pure solvent. As the cooling is continued the composition mentioned is reached and the labile form then appears. At this point the whole mass solidifies and pure solvent separates along a curve shown until the inactive conglomerate is reached, which possesses the lowest transformation point. Below the curve just mentioned and the m.-p. curve of the labile modification, only conglomerates of the two bromocamphors are stable. Fused mixtures which contain less than 58% of *d*-bromocamphor and less than 58% of *l*-bromocamphor crystallise in the labile form, and when cooling is continued they are transformed into conglomerates. The labile forms have therefore a small area of stability, bounded by the curve of the labile modification and the curve of the separation of conglomerates already mentioned.

As regards the characterisation of the racemism, the racemic compound exists between 44° and 50·5°; below that it is split into inactive conglomerates. This is analogous to the behaviour of sodium ammonium racemate studied by van't Hoff. R. V. S.

The Constituents of Essential Oils (The Constitution of Selinene). FRIEDRICH W. SEMMLER and FELIX RISSE (*Ber.*, 1912, 45, 3725—3731. Compare this vol., i, 66).—In the former communication, the sesquiterpene, selinene, was shown to give a dihydrochloride from which a regenerated selinene with slightly higher rotation, due perhaps to a different arrangement of the unsaturated linkings, could be obtained. In order to elucidate the constitution of these isomerides, they have been oxidised with ozone.

Natural ψ-(β)-selinene on oxidation gave a very small amount of an acid, but chiefly an indifferent product which was purified by conversion into a *disemicarbazone*, $C_{13}H_{20}(N\cdot NH\cdot CO\cdot NH_2)_2$, m. p. 228°, from which the saturated *diketone*, $C_{13}H_{20}O_2$, b. p. 178—180°/11 mm., D^{20} 1·0566, n_D 1·49994, $a_D+15°$, was recovered by means of oxalic acid. The fact that two carbon atoms have been eliminated by this process, whereas the acid resulting from the oxidation by hypobromite contains only one carbon atom less, indicates the presence in selinene of one methylene group attached directly to the ring and another in a side-chain.

Regenerated selinene, *ortho*-(α)-selinene, b. p. 128—132°/11 mm., D^{20} 0·9190, n_D 1·50920, $a_D+61°36'$, gives much less of the diketone on treatment with ozone, the chief product being the acid, which has been characterised as *methyl selinenediketomonocarboxylate*, $C_{15}H_{24}O_4$, b. p. 185—190°/11 mm., D^{20} 1·0635, n_D 1·47889, $a_D+4°24'$. The formation of this acid is explained by assuming that the elimination of hydrogen chloride from the dichloride has resulted in the displacement of a double bond into the ring. A consideration of other sesqui-terpenes leads to the adoption of the annexed formulæ.



J. C. W.

Chemical Investigation of the Oil of Chenopodium. II. E. K. NELSON (*J. Amer. Chem. Soc.*, 1913, **35**, 84—90. Compare A., 1911, i, 797).—It has been found that when the glycol anhydride formed by the molecular rearrangement of ascaridole is treated with dilute sulphuric acid, ascaridole α-glycol is produced together with two other crystalline substances, one of which, termed *ascaridole β-glycol*, $C_{10}H_{18}O_3$, crystallises with $1H_2O$; the anhydrous substance has m. p. 103—105°; when this glycol is warmed with dilute sulphuric acid, thymol is produced. The other *substance*, termed the "erythrite," $C_{10}H_{20}O_4$, also crystallises with $1H_2O$, and when anhydrous has m. p. 128—130°; it is decomposed by boiling dilute sulphuric acid with formation of a *ketone*, with a strong menthone-like odour, and a

phenolic substance, m. p. 80—81°; the *semicarbazone* of the ketone has m. p. 182—184°. On oxidising the "erythrite" with alkaline potassium permanganate, an *acid*, $C_{10}H_{18}O_6$, m. p. 190—191°, is produced, which forms rhombic prisms; when this acid is heated at 210°, it is converted into its anhydride, and on further heating yields ascaridic anhydride, m. p. 70—71°. If the acid $C_{10}H_{18}O_6$ is oxidised with potassium permanganate in presence of sulphuric acid, it yields β-methylheptane-$\gamma\zeta$-dione, and it is therefore probable that it is a modification of $\alpha\alpha$-dihydroxy-α-methyl-α-*iso*propyladipic acid. The "erythrite" therefore probably has the structure

$$OH\cdot CMe{<}\begin{matrix}CH_2\text{———————}CH_2\\CH(OH)\cdot CH(OH)\end{matrix}{>}C(C_3H_7)\cdot OH.$$

The acid, $C_{10}H_{16}O_5$, obtained by the oxidation of the α-glycol, is converted by further oxidation into β-methylheptane-$\gamma\zeta$-dione. When the glycol anhydride is boiled with a saturated solution of oxalic acid, a small quantity of the phenolic substance, m. p. 80—81°, is produced, which is formed on boiling the "erythrite" with dilute sulphuric acid and is also obtained by treating the α-glycol with strong dehydrating agents. On heating the glycol anhydride with benzoic anhydride at 150°, an ester of carvacrol is produced.

From the results of this work, it is considered that the α-glycol has the constitution $CMe{<}\begin{matrix}CH_2\text{———————}CH_2\\ \text{————}O\text{————}\\CH(OH)\cdot CH(OH)\end{matrix}{>}C\cdot C_3H_7$, and that the acid obtained by its oxidation has the structure of $\alpha\delta$-cineolic acid, $CO_2H\cdot \underbrace{CMe\cdot CH_2\cdot CH_2\cdot C}_{O}(C_3H_7)\cdot CO_2H$. E. G.

Action of Gaseous Oxygen on Caoutchouc. STANLEY J. PEACHEY (*J. Soc. Chem. Ind.*, 1912, **31**, 1103—1104).—When purified caoutchouc, in the form of a thin film, is exposed to an atmosphere of oxygen at a temperature of 85°, oxidation commences after a few hours' heating, and then proceeds rapidly to completion. Results of experiments with Ceylon caoutchouc show that, under these conditions, each $C_{10}H_{16}$ unit of the molecule combines with 4 atoms of oxygen. This result is not in agreement with that obtained by Herbst (A., 1906, i, 196), and it may be assumed that the reaction which takes place when caoutchouc in benzene solution is oxidised by air (as in Herbst's experiments) differs from that which occurs when caoutchouc itself is oxidised by pure oxygen. The oxidation most probably results in the formation of additive products. W. P. S.

The Nitrogenous Constituent of Para Caoutchouc and Its Bearing on the Nature of Synthetic Caoutchouc. CLAYTON BEADLE and HENRY P. STEVENS (*J. Soc. Chem. Ind.*, 1912, **31**, 1099—1101. Compare A., 1912, i, 789).—It is shown that the removal of insoluble (nitrogenous) constituents from caoutchouc results in deterioration of the latter, although it is open to question how far the quality of caoutchouc is improved by the presence of more than a certain proportion of insoluble matter. In the vulcanisation process the insoluble matter appears to play the part of a sulphur carrier.

The authors have also made experiments on the influence of the resinous constituents on the vulcanising properties of caoutchouc, and find that the removal of the resins results in a marked deterioration of the quality of the caoutchouc. The absence of nitrogenous substances and resins in synthetic caoutchouc should make the latter inferior to natural rubber. W. P. S.

Chemistry of Caoutchouc. VI. Theory of Vulcanisation. IV. DAVID SPENCER and C. A. WARD (*Zeitsch. Chem. Ind. Kolloide*, 1912, **11**, 274—280. Compare A., 1912, i, 706).—Experiments have been made to ascertain whether the so-called "depolymerisation" of caoutchouc, which is brought about by mechanical or thermal treatment, is accompanied by a change in the rate at which it reacts with sulphur in the process of vulcanisation. For this purpose comparative measurements were made with two exactly similar mixtures of 100 parts of caoutchouc and 10 parts of sulphur. In the one case the caoutchouc was kneaded for thirty minutes at a moderate temperature, the sulphur being then added, and the mixing effected by a further kneading for ten minutes. In the second case, the treatment was similar, except that the caoutchouc was subjected to the mechanical treatment for ninety minutes at a much higher temperature.

From the observations made on the rate of vulcanisation at 135°, it appears that there is no appreciable difference between the two samples, and the authors draw the conclusion that "depolymerisation" has no influence whatever on the chemical result of the vulcanisation process. The conclusions arrived at by Axelrod (*Gummi Zeit.*, 1909, **24**, 352) are therefore not confirmed by these experiments. H. M. D.

The Action of Chloroacetyl Chloride on Ethyl Malonate; Iminotetronic Acid. ERICH BENARY (*Ber.*, 1912, **45**, 3682—3686).—As the substance described as the ester-amide of tetramic acid (Benary, A., 1911, i, 672) is in reality ethyl iminotetron-α-carboxylate (Anschütz, A., 1912, i, 836), the compound $C_9H_{12}O_5$, from which it is obtained by the action of ammonia, is presumably ethyl *iso*tetron-α-carboxylate; this view is supported by the action of organic bases which give compounds similar to that produced by ammonia; these compounds are probably ketonic, but do not yield phenylhydrazones (compare Wolff, A., 1900, i, 582); they frequently yield salts, however, derived from the enolic structure.

Ethyl phenyliminotetron-α-carboxylate, $\begin{matrix} CH_2\text{—}CO \\ | \\ O\cdot C(:NPh) \end{matrix}\!\!>\!CH\cdot CO_2Et$, obtained by the interaction of equivalent quantities of ethyl *iso*tetron-α-carboxylate and aniline, crystallises in needles, m. p. 116—117°; it exhibits both acidic and basic properties.

Ethyl phenylhydrazinotetron-α-carboxylate (already described) yields a *potassium* salt.

Ethyl piperidinoisotetron-α-carboxylate, $\begin{matrix} CH_2\text{——}CO \\ | \\ O\cdot C(C_5NH_{10}) \end{matrix}\!\!>\!C\cdot CO_2Et$, m. p. 107—108°, from equal weights of piperidine and ethyl *iso*tetron-

a-carboxylate, as might be expected from the structure, has no acidic properties.

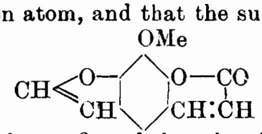
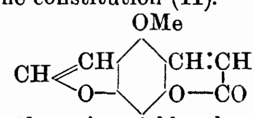
When iminotetronic acid in benzene solution is treated with rather more than an equimolecular quantity of bromine, *bromoiminotetronic acid*, $\begin{matrix} CH_2\cdot C(OH) \\ | \\ O{-}C(:NH) \end{matrix}\!\!>\!CBr$, needles, m. p. 182°, is obtained; it gives a red coloration with ferric chloride.

On adding ice to the reaction mixture from iminotetronic acid and nitric acid, aci-*nitroiminotetronic acid*, $\begin{matrix} CH_2{-}CO \\ | \\ O\cdot C(:NH) \end{matrix}\!\!>\!C:NO_2H$, is precipitated, leaflets, m. p. 255—258° (decomp.); it is a strongly acidic substance, which gives a *phenylhydrazone*, yellow tablets, m. p. 211—212°.

The conclusion is drawn that the action of chloroacetyl chloride on ethyl sodiomalonate consists of two concurrent processes, one of which produces unstable ethyl chloroacetylmalonate, which undergoes spontaneous change into ethyl tetron-a-carboxylate, whilst the other process involves the enolic form of ethyl sodiomalonate, which reacts with the acid chloride producing ethyl *iso*tetron-a-carboxylate. D. F. T.

Hydroxymethylfurfuraldehyde. FRANCESCO ANGELICO and A. COPPOLA (*Gazzetta*, 1912, **42**, ii, 583—589).—The authors confirm the formula for this substance given by Fenton and Gostling (T., 1889, **75**, 423), and by the application of the Angeli-Rimini reaction they have prepared from it *a-hydroxymethylfuranhydroxamic acid*, $C_6H_7O_4N$, which crystallises in pink, lustrous, soapy scales, m. p. 139°, the free acid being prepared from the *copper* salt, $(C_6H_6O_4N)_2Cu,H_2O$. When the acid is hydrolysed with 25% sulphuric acid, it yields hydroxylamine and hydroxypyromucic acid (m. p. 165°). R. V. S.

Constitution of Bergapten. HERMANN THOMS and E. BAETCKE (*Ber.*, 1912, **45**, 3705—3712).—Bergapten, which Pomeranz showed to be a coumarin-coumarone derivative of phloroglucinol (A., 1892, 71; 1893, 342), was found to occur in certain fruits accompanied by an isomeride, xanthotoxin (A., 1912, i, 40), to which the formula (I) was assigned. Bergapten has now been converted into an amine, and this into a quinone containing no methoxy-group, from which the conclusion is drawn that the methoxy-group is *para* to the unsubstituted carbon atom, and that the substance has the constitution (II).

I.  II. 

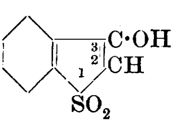
This is confirmed by the fact that xanthotoxin yields the same quinone.

Aminobergapten, $C_{12}H_7O_4\cdot NH_2$, is obtained by the reduction of the nitro-derivative (Pomeranz, *loc. cit.*) with tin and hydrochloric acid, in slender, pale yellowish-green needles, m. p. 198°, and yields an *acetyl* compound, m. p. 208°. When oxidised with sodium dichromate the

methoxy-group is replaced, and the golden-yellow *quinone*, $C_{11}H_4O_5$, m. p. 248—250°, is formed. *Aminoxanthotoxin* is prepared in the same way, and is similar in appearance to its isomeride; it melts, however, at 236°, is more easily acetylated, yielding an *acetyl* compound, m. p. 246—247°, and is much less soluble in cold sulphuric acid, but it yields the same quinone.

The *quinol*, $C_{11}H_4O_3(OH)_2$, crystallises with $2H_2O$ in light green needles, which lose water at 110°, and yield a *diacetyl* compound, m. p. 208—209°, and a *diphenylurethane* derivative, $C_{11}H_4O_3(O{\cdot}CO{\cdot}NPh_2)_2$, m. p. 229—230°. J. C. W.

Action of Hydrogen Peroxide on Hydroxythionaphthen, Hydroxythionaphthen Carboxylic Acid, and "Thioindigo." MAURICE LANFRY (*Compt. rend.*, 1912, **155**, 1517—1519. Compare A., 1912, i, 293).—Hydroxythionaphthen in alkaline solution gives a blue precipitate on the addition of hydrogen peroxide, leaving a brown liquid, from which only gummy substances could be extracted. The blue precipitate on solution in water and addition of strong acid gives a red, flocculent precipitate, which resembles "thioindigo" in all its properties. The addition of hydrogen peroxide to a boiling solution of hydroxythionaphthen in acetic acid gives a red precipitate of "thioindigo," which slowly dissolves and the solution becomes colourless. Extraction with benzene separates out 3-*hydroxy*-1-*dioxythionaphthen* (annexed constitution), m. p. 139°, which in its chemical properties closely resembles the hydroxythionaphthen from which it is prepared.



The effect of hydrogen peroxide on the sodium salt of hydroxythionaphthencarboxylic acid is to destroy its phenolic character with the formation of a small quantity of "thioindigo." The major part of the salt is resinified.

In the presence of hydrogen peroxide, finely divided "thioindigo" slowly dissolves in acetic acid to a red solution, which gradually becomes decolorised. The only products of extraction were gummy substances. W. G.

"Bisphenylthiophenindigo" [5 : 5′-Diphenyl-$\Delta^{2,2'}$-bisthiophen-3-one]. PAUL FRIEDLAENDER and ST KIELBASINSKI (*Ber.*, 1912, **45**, 3389—3396).—Although *m*-hydroxydiphenyl shows no tendency to pass over into an ortho-quinonoid compound, the analogous 3-hydroxy-5-phenylthiophen behaves entirely differently, readily forming "*bisphenylthiophenindigo*," $CH{<}\begin{matrix}CO{-}C{=}C{\cdot}CO{-}\\ CPh{\cdot}S\quad S{\cdot}CPh\end{matrix}{>}CH$.

The dye is prepared by the following series of operations. On heating ethyl cinnamate with sulphur, a disulphide, thiobenzoylthioacetic acid, $S{<}\begin{matrix}S{-}{-}CO\\ CPh{:}CH\end{matrix}$ (Baumann and Fromm, A., 1897, i, 191), is formed. The ring is opened by sodium sulphide, and by the action of chloroacetic acid a compound,

$$CO_2H{\cdot}CH_2{\cdot}S{\cdot}CPh{:}CH{\cdot}CO{\cdot}S{\cdot}CH_2{\cdot}CO_2H$$

is formed, which when boiled with acetic anhydride is converted into acetoxyphenylthiophen, $S<\begin{matrix}CH-C\cdot O\cdot CO\cdot CH_3\\ CPh:CH\end{matrix}$ On hydrolysis, 4-hydroxy-2-phenylthiophen is obtained.

This condenses with aromatic aldehydes or with isatin to dyes, forms a quinoneoxime with nitrous acid, and is converted by alkaline or acid oxidising agents into "bisphenylthiophenindigo."

The *disulphide* crystallises in broad needles, m. p. 156°.

4-*Hydroxy*-2-*phenylthiophen* separates in slender needles, m. p. 78°; the *acetyl* derivative forms broad, colourless, compact platelets, m. p. 75°.

The *quinone oxime*, $S<\begin{matrix}CPh{=\!=\!=}CH\\ C(:N\cdot OH)\cdot CO\end{matrix}$, prepared by interaction with sodium nitrite, forms broad faint, brownish-yellow needles, m. p. 216°.

On bromination, a *product*, $CPh<\begin{matrix}CBr\cdot CO\\ S-CBr_2\end{matrix}$, is obtained, crystallising in brownish-yellow plates, m. p. 134°. It does not react simply with aniline: on warming with sodium acetate, slender, red needles or ruby-red prisms of a brominated diphenylthiophenindigo are obtained.

4-Hydroxy-2-phenylthiophen reacts with piperonal, the *condensation* product crystallising in long, yellow needles, m. p. 196°.

"*Bis*-5-*phenyl*-2-*thiophenindigo*" [5 : 5'-*diphenyl*-$\Delta^{2,2'}$-*bisthiophen*-3-*one*] separates in brownish-red, lustrous needles, m. p. 280°.

" 5-*Phenyl*-2-*thiophen*-3-*indoleindigo* " [5-phenyl-2-(3'-indoxyl)-thiophen-3-one], produced on condensation with isatin, crystallises in sealing wax-red needles, m. p. 281°.

" 5-*Phenyl*-2-*thiophen*-2-*indoleindigo* " [5-phenyl-2-(2'-indoxyl)-thiophen-3-one], $\begin{matrix}CH\cdot CO\\ CPh\cdot S\end{matrix}>C:C<\begin{matrix}CO\\ NH\end{matrix}>C_6H_4$, obtained on boiling isatin-anilide with phenylhydroxythiophen in acetic anhydride, crystallises in slender, dark violet needles. E. F. A.

Methylation of Histidine, Arginine, and Lysine. I. R. ENGELAND and FRIEDRICH KUTSCHER (*Zeitsch. Biol.*, 1912, **59**, 415—419).—On methylation of histidine monochloride with methyl sulphate and barium hydroxide, *pentamethylhistidine* is obtained. The *aurichloride* crystallises in large, lustrous needles, the *chloride* is an oil, and the free base decomposes rapidly. Small quantities of the crystalline *aurichloride* of tetramethylhistidine are obtained at the same time.

Under similar conditions, arginine yields a *tetramethyl* derivative, the *aurichloride* forms short, stout needles, m. p. 173—175°. Three of the methyl groups are attached to nitrogen in the side-chain, one only to nitrogen in the guanidine complex.

Lysine yields a compound, probably the *ethyl* ester of *hexamethyllysine*, which gives an *aurichloride*, m. p. 208°, corresponding with the formula $C_{14}H_{34}O_3N_2,Au_2Cl_8$. E. F. A.

Strychnos Alkaloids. XVI. Dihydrobrucinoic Acid and *iso*Brucinolone. HERMANN LEUCHS and GEORGE PEIRCE (*Ber.*, 1912, **45**, 3412—3420).—Dihydrobrucinonic acid, which contains an alcoholic

hydroxyl (compare A., 1212, i, 210), forms an acetyl derivative when acted on by acetic anhydride and sodium acetate. More vigorous action produces a neutral compound containing two further acetyl residues less a molecule of water. Dihydrobrucinonic acid does not react with nascent hydrogen or with hydroxylamine. It is broken down by sodium hydroxide into glycollic acid and *iso*brucinolone, $C_{21}H_{22}O_5N_2$. The latter forms an acetyl derivative, and on treatment with concentrated hydrogen chloride gives iso*brucinolone hydrate*. At higher temperatures this is reconverted into *iso*brucinolone (compare Leuchs and Brewster, A., 1912, i, 210). With concentrated nitric acid a nitro-derivative, $C_{19}H_{15}O_7N_3$, is obtained; the change involves the formation of a quinone and the subsequent nitration of this. With sulphurous acid a paler reduction compound is obtained from the quinone.

Acetyldihydrobrucinonic acid forms colourless, four-sided prisms, m. p. 235—238°. The neutral product, $C_{27}H_{28}O_9N_2$ or $C_{29}H_{30}O_{10}N_2$, crystallises in colourless, chisel-shaped prisms, m. p. 280—282°, after becoming yellow at 260°.

By the action of acetic anhydride on brucinonic acid, a componnd,

$$(C_{13}H_{14}O_4N)_x,$$

is obtained, crystallising in long, matted, lustrous needles, m. p. 125—127°.

*Acetyl*iso*brucinolone* forms large, colourless platelets, m. p. 281—283° (decomp.).

iso*Brucinolone hydrate* separates in four-sided prisms, which froth at 205—208°, become solid again, turn brown at 290°, m. p. 310—315° (decomp.).

The *hydrochloride* forms four-sided platelets; the *sulphate* consists of massive prisms, which become brown at 235°, decomp. 238°.

*Nitrobis*apo*methyldihydro*iso*brucinolone* crystallises in flat, orange-yellow needles, which become brown at 250°, and completely charred at 340°.

*Nitrobis*apo*methyl*iso*brucinolone* gives massive, reddish-yellow prisms, which become brown at 240°.

*Nitrobis*apo*methylbrucinolone* crystallises in small, yellow octahedra, dissolving in concentrated sulphuric acid with a yellow coloration and in concentrated sodium hydroxide with a violet coloration.

E. F. A.

Strychnos Alkaloids. XVII. Isolation of the Hydrate of a Fourth Strychninesulphonic Acid. HERMANN LEUCHS and JOHANNES WUTKE (*Ber.*, 1912, **45**, 3686—3691).—Analogous to the fourth brucinesulphonic acid (Leuchs and Geiger, A., 1911, i, 1018), a fourth strychninesulphonic acid (compare Leuchs and Schneider, A., 1909, i, 671) has been obtained as a very stable hydrate, which retains the additional water very tenaciously.

The solution of the reaction product obtained as described earlier (Leuchs and Schneider, *loc. cit.*), after crystallisation of strychnine-sulphonic acids I and II, and subsequent concentration under reduced pressure, deposits a mixture of the acids I, II, and III with the above-mentioned hydrate, which last can be separated in the free

state and also as a compound with strychninesulphonic acid III; the total yield of hydrate in the two forms amounts to approximately 3%.

Strychninesulphonic acid IV *hydrate*, $C_{21}H_{24}O_6N_2S,2H_2O$, stout prisms or rhombohedra, m. p. 275° (decomp.), $[\alpha]_D^{20}$ +18·3°, could not be dehydrated beyond $C_{21}H_{24}O_6N_2S$, even at 135° in a vacuum over phosphoric oxide. The *double* compound with strychninesulphonic acid III, $C_{21}H_{22}O_5N_2S,C_{21}H_{24}O_6N_2S$, slender prisms or needles, m. p. 250° (decomp.), $[\alpha]_D^{20}$ +101°, can also be obtained by mixing solutions of the hydrate and excess of the acid III; in the absence of excess of strychninesulphonic acid III, the compound is resolved by hot water into its constituents. D. F. T.

Synthesis of Hæmopyrrole-*b*. OSKAR PILOTY and A. BLÖMER (*Ber.*, 1912, **45**, 3749—3753).—Ethyl acetylpyruvate condenses with aminobutanone or with aminoacetone to form pyrrole derivatives. In the former case, 4-acetyl-2 : 3-dimethylpyrrole-5-carboxylic acid,

$$NH<\begin{array}{l}C(CO_2H):C\cdot COMe\\ CMe{=\!=\!=}CMe\end{array},$$

is obtained, which on heating at 215° is converted into 4-*acetyl*-2 : 3-*dimethylpyrrole*, $NH<\begin{array}{l}CH{=}C\cdot COMe\\ CMe:CMe\end{array}$. When this is treated with hydrazine and sodium ethoxide, 2 : 3-dimethyl-4-ethylpyrrole (hæmopyrrole-*b*), $NH<\begin{array}{l}CH{=}CEt\\ CMe:CMe\end{array}$, is formed.

With aminoacetone the product is 4-*acetyl*-3-*methylpyrrole*-5-*carboxylic acid*, $NH<\begin{array}{l}C(CO_2H):C\cdot COMe\\ CH{=\!=\!=}CMe\end{array}$. This has m. p. 200°. During the reaction an isomeric by-product, m. p. 250° (decomp.), is also formed.

4-*Acetyl*-2 : 3-*dimethylpyrrole*-5-*carboxylic acid* crystallises in colourless, prismatic rods, m. p. 204° (decomp.).

4-*Acetyl*-2 : 3-*dimethylpyrrole* separates in short, colourless, prismatic platelets with sharp edges, m. p. 137°. The synthetic hæmopyrrole-*b* is identical with the natural compound. E. F. A.

Cyclic Imines. VII. Ahrens' So-called γ-Picoline. JULIUS VON BRAUN and A. SCHMATLOCH (*Ber.*, 1912, **45**, 3649—3652).—The method described by Ahrens for the separation of pure 4-methylpyridine (γ-picoline) by precipitation with mercuric chloride (A., 1905, i, 232) is found to yield a mixture instead of a pure product.

Successive reduction and benzoylation of 4-methylpyridine, prepared by Ahrens' method, produced a *benzoyl* derivative, $C_6H_{12}NBz$, b. p. 189—190°/17 mm., which on distillation with phosphorus pentabromide (compare von Braun and Sobecki, A., 1911, i, 413) formed a product which could be separated into two fractions by distillation. The smaller and less volatile portion, b. p. 150°/19 mm., D_4^{20} 1·9305, was probably *αβε-tribromo-β-methylpentane*, and gave an unsaturated organo-magnesium compound which absorbed carbon dioxide with the formation of *δ-methylene*-n-*hexoic acid*, $CO_2H\cdot[CH_2]_3\cdot CMe:CH_2$, b. p. 218—221°, D_4^{20} 0·9406, n_D 1·4442; the formation of this series of compounds is attributed to the presence of 3-methylpyridine in the

original base. The more volatile fraction, $C_6H_{12}Br_2$, b. p. 115—120°/19 mm., D_4^{20} 1·608, on treatment with potassium cyanide yielded a dinitrile, $C_6H_{12}(CN)_2$, b. p. 171—174°/10 mm., which was hydrolysable, apparently to a mixture of β- and γ-methylpimelic acids. Neither fraction therefore was of pure 4-methylpyridine. D. F. T.

The Action of Hydroxylamine and Phenylhydrazine on Benzoyldehydracetic Acid. A Correction. JOH. SCHÖTTLE (*Ber.*, 1912, **45**, 3779. Compare A., 1912, i, 915).—Reaction between free hydroxylamine and benzoyldehydracetic acid was effected by mixing hydroxylamine sulphate with the theoretical quantity of alcoholic potassium hydroxide, filtering the precipitated potassium sulphate, and adding the phenyl-lactam of benzoyldehydracetic acid to the filtrate. E. F. A.

Cyclic Imines. VI. Ring Homologues of Tetrahydroquinoline. JULIUS VON BRAUN and B. BARTSCH (*Ber.*, 1912, **45**, 3376—3389).—The tendency to form seven-membered rings such as hexamethyleneimine is very much increased when two of the carbon atoms are members of a benzene nucleus; thus *o*-δ-chlorobutylaniline, on elimination of hydrogen chloride, readily forms *tetrahydrohomoquinoline*, $C_6H_4{<}{\begin{matrix}CH_2\cdot CH_2\\NH-CH_2\end{matrix}}{>}CH_2$. The constitution of the quinoline is established by the fact that when the ring is opened by the action of phosphorus pentachloride, δ-chloro-*o*-benzoylaminobutylbenzene, $COPh\cdot NH\cdot C_6H_4\cdot[CH_2]_4Cl$, is formed, which is in turn convertible into the already known δ-*o*-benzoylaminophenylvaleric acid.

Homotetrahydroquinoline resembles the isomeric 2-methyltetrahydroquinoline and the lower ring homologues in its stability towards hydrolytic and reducing reagents, and also towards oxidation; it is hardly altered by distillation with silver sulphate.

The quinoline could not be prepared by other methods, such as the distillation of δ-*o*-diaminobutylbenzene hydrochloride or by the interaction of γ-phenylpropylamine with formaldehyde.

o-*Amino-δ-hydroxybutylbenzene*, $NH_2\cdot C_6H_4\cdot[CH_2]_4\cdot OH$, prepared by the reduction of the ester, $NH_2\cdot C_6H_4\cdot[CH_2]\cdot CO_2Et$, by means of sodium and alcohol, is a viscid, almost odourless oil, b. p. 180—183°/12 mm. The *dibenzoyl* compound crystallises in snow-white platelets which sinter at 127°, m. p. 130°; the *platinichloride* forms dark red platelets, which blacken at 168°, m. p. 175°; the *picrate* separates in green leaflets, m. p. 179°.

o-*Amino-δ-chlorobutylbenzene* was not obtained pure; the *platinichloride* crystallises in pale yellow platelets, m. p. 182—183°.

Tetrahydrohomoquinoline is an almost colourless oil, b. p. 131—133°/16 mm., 253—255°/760 mm., D_4^{20} 1·0325, solidifying to colourless crystals, m. p. 32°. The *hydrochloride* has m. p. 186°; the pale yellow, granular crystals of the *platinichloride* blacken at 192°, m. p. 194°; the *picrate* crystallises in yellowish-red needles, m. p. 179°; the *benzoyl* derivative has m. p. 96°, whilst the *benzenesulphonyl* compound has m. p. 109°.

The *platinichloride* of the *dimethyl* derivative, $C_{10}H_{12}NMe_2PtCl_6$, produced on long heating with methyl iodide, has m. p. 197°.

When heated with phosphorus pentachloride at 150°, tetrahydrohomoquinoline yields *δ-chloro-o-benzoylaminobutylbenzene*, which crystallises in lustrous, silvery platelets, m. p. 117°. The corresponding iodide when decomposed with potassium cyanide yields *δ-benzoylaminophenylvaleronitrile*, $C_6H_5\cdot CO\cdot NH\cdot C_6H_4\cdot[CH_2]_4\cdot CN$, m. p. 114°, from which the corresponding acid (A., 1907, i, 524) is obtained on hydrolysis.

δ-o-Diaminobutylbenzene, prepared by reducing the nitrile of *o*-benzoylaminophenylbutyric acid, forms a colourless oil of strongly basic odour, b. p. 172°/14 mm.

o-γ-Chloropropylbenzonitrile is a pale yellow oil, volatile in steam, b. p. 153°/19 mm. On hydrolysis, *o-γ-chloropropylbenzoic acid*,

$$CO_2H\cdot C_6H_4\cdot[CH_2]_3\cdot Cl,$$

is obtained, m. p. 79°.

The nitrile condenses with sodium phenoxide to *o-γ-phenoxypropylbenzonitrile*, $CN\cdot C_6H_4\cdot[CH_2]_3\cdot OPh$, a pale yellow oil, b. p. 210°/23 mm. The corresponding *o-γ-phenoxypropylbenzoic acid* has m. p. 120°. E. F. A.

Thiazoles. REINHOLD VON WALTHER and H. ROCH (*J. pr. Chem.*, 1913, [ii], 87, 27—66).—Although the condensation of thiocarbamide with ω-bromoacetophenone and other halogeno-ketones of the type CHXR·COR may give rise to either aminothiazoles (formula II below, R′ and R″ = H) or iminothiazolines (IV or V, R′,R″ = H), the work of Traumann (A., 1889, 414) and others has shown that only aminothiazoles are produced. *s*-Disubstituted thiocarbamides always yield iminothiazolines, whilst the *as*-disubstituted derivatives give rise to aminothiazoles.

With respect to the mechanism of the condensation, the authors suggest that the first stage consists in the addition of the halogenoketone to the sulphur atom of the thiocarbamide, and that the removal of hydrogen haloid and water from the intermediate compound thus produced is preceded by the formation of an internal salt, derived from the enolic form, the constitution of this salt being determined by the relative basicity of the amino-residues of the thiocarbamide; thus, in the condensation of *as*-disubstituted thiocarbamides,

$$NR'R''\cdot CS\cdot NH_2,$$

with ω-bromoacetophenone, the compound

$$NR'R''\cdot C(NH_2)\colon SBr\cdot CH_2\cdot COPh$$

is first produced, which is transformed successively into the enolic salt I and aminothiazole II if NHR′R″ is more feebly basic than NH_3:

$$\text{I.}\ \begin{array}{l} NR'R''\cdot C{-}{-}NH_3{-}O \\ \qquad\quad \| \qquad\quad\ | \\ \qquad\quad SBr\cdot CH\colon CPh \end{array} \longrightarrow \text{II.}\ \begin{array}{l} NR'R''\cdot C{=}{=}{=}N \\ \qquad\quad | \qquad\quad | \\ \qquad\quad S\cdot CH\colon CPh \end{array} + H_2O + HBr.$$

On the other hand, if NHR′R″ is a stronger base than NH_3, the compound III is formed as an intermediate product, which decomposes

into a secondary amine and thiocyanoacetophenone as shown in the following scheme:

$$\text{III.}\ \begin{array}{l}\text{NHR}'\text{R}''\text{—C}\cdot\text{NH}_2\\ \text{O}\cdot\text{CPh:CH}\cdot\text{SBr}\end{array} \longrightarrow \text{HBr} + \text{H}_2\text{O} +$$

$$\begin{array}{l}\text{NR}'\text{R}''\text{—CN}\\ \text{CPh:CH}\cdot\text{S}\end{array} \xrightarrow{\text{H}_2\text{O}} \text{NHR}'\text{R}'' + \text{OH}\cdot\text{CPh:CH}\cdot\text{SCN}.$$

An explanation is thus afforded of the behaviour of *as*-dimethylthiocarbamide, which, with ω-bromoacetophenone, does not form an aminothiazole, but undergoes decomposition into dimethylamine and thiocyanoacetophenone (Spica and Carrara, A., 1892, 215).

s-Disubstituted thiocarbamides, NHR′·CO·NHR″, in which the amino-residues are of approximately equal basicity, may give rise to two isomeric iminothiazolines:

$$\text{IV.}\ \begin{array}{l}\text{CPh}\cdot\text{NR}''\\ \text{CH——S}\end{array}\!\!>\text{C:NR}' \qquad \text{V.}\ \begin{array}{l}\text{CPh}\cdot\text{NR}'\\ \text{CH——S}\end{array}\!\!>\text{C:NR}'';$$

the formation of isomerides of this kind has been observed by Stenz (*Diss.*, Dresden, 1899) and Wünsche (*ibid.*, 1901). When the basicity of one of the amino-groups is much greater than that of the other, only one isomeride will be formed; thus, both *s*-*p*-tolylbenzylthiocarbamide and *s*-*p*-tolylmethylthiocarbamide condense with ω-bromoacetophenone to form only one iminothiazoline (formula V, where R″ = *p*-C_6H_4Me, and R′ = ·CH_2Ph or Me). The constitution of the iminothiazolines derived from *s*-disubstituted thiocarbamides is readily determined (1) by heating with carbon disulphide, which leads to the removal of the imino-group as the corresponding thiocarbimide, or (2) by hydrolysis with hydrochloric acid, the imino-group, in this case, being removed in the form of a primary amine.

With respect to the thiazoles derived from mono-substituted thiocarbamides, the authors point out that no definite proof of their constitution has hitherto been brought forward. Although the work of Traumann (*loc. cit.*) appears to indicate that the thiazole obtained from methylthiocarbamide and ω-bromoacetophenone is probably a 2-methylimino-4-phenylthiazoline, the observations described in the present paper prove conclusively that the thiazole derived from *p*-tolylthiocarbamide has the constitution of an aminothiazole.

2-p-*Toluidino-4-phenylthiazole*, $\begin{array}{l}\text{CPh}\cdot\text{N}\\ \text{CH—S}\end{array}\!\!>\text{C}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$, is obtained in the form of its *hydrobromide*, slender needles, m. p. 205° (decomp.), by heating *p*-tolylthiocarbamide with ω-bromoacetophenone in alcoholic solution, the free base being liberated from the hydrobromide by warming with pyridine. It crystallises in leaflets, m. p. 123°, and forms a *hydrochloride*, which melts and becomes green at 212°, a *sulphate*, m. p. 152°, an *acetate*, m. p. 85°, and *thiocyanate*, m. p. 125°, all of which crystallise in colourless needles; the *platinichloride* forms orange leaflets, m. p. 230°, the *picrate*, yellow needles, m. p. 185°. It reacts with phenylcarbimide in ethereal solution to form the *carbamide*, $\begin{array}{l}\text{CPh}\cdot\text{N}\\ \text{CH—S}\end{array}\!\!>\text{C}\cdot\text{N}(\text{C}_6\text{H}_4\text{Me})\cdot\text{CO}\cdot\text{NHPh}$, crystallising in lustrous leaflets,

m. p. 196·5°. Towards both oxidising and reducing agents the thiazole is remarkably stable, but is decomposed by hydrochloric acid at 225—250° into acetophenone, *p*-toluidine, and ammonia; when heated with carbon disulphide at 250°, it forms *p*-tolylthiocarbimide.

The *acetyl* derivative, $C_{18}H_{16}ON_2S$, forms colourless prisms, m. p. 124·5°; the *benzoyl* derivative, prepared by the pyridine method in benzene solution, crystallises in hard prisms, m. p. 207°.

With the object of synthesising the above acyl derivatives, the authors have endeavoured to condense ω-bromoacetophenone with *s*- and *as*-acetyl-*p*-tolylthiocarbamide and *s*-benzoyl-*p*-tolylthiocarbamide in alcoholic solution, but find that no condensation occurs. It would thus appear that acylthiocarbamides are incapable of undergoing the thiazole condensation.

2-*p*-Toluidino-4-phenylthiazole combines with 1-chloro-2 : 4 : 6-trinitrobenzene in hot alcoholic solution to form an unstable, additive *compound*, $C_{22}H_{16}O_6N_5SCl$, which crystallises in red needles, m. p. about 90°, and is resolved by acids or alkalis into its components; the additive *compound* with 1-chloro-2 : 4-dinitrobenzene forms stout, dark red crystals, m. p. about 60°.

as-p-*Tolylbenzylthiocarbamide*, $C_6H_4Me\cdot N(CH_2Ph)\cdot CS\cdot NH_2$, obtained by heating *N*-benzyl-*p*-toluidine hydrochloride with ammonium thiocyanate and water, crystallises in colourless needles, m. p. 155·5°, and is converted by the action of ω-bromoacetophenone in warm alcoholic solution into 2-p-*tolylbenzylamino*-4-*phenylthiazole*,

$$\begin{array}{l} CPh\cdot N \\ \| \\ CH{-}{-}S \end{array}\!\!>C\cdot N(C_6H_4Me)\cdot CH_2Ph,$$

which forms large prisms, m. p. 125°, and yields a *hydrochloride*, a *picrate*, m. p. 155°, and a *platinichloride*, m. p. 225° (decomp.).

2-p-*Tolylimino*-4-*phenyl*-3-*benzylthiazoline*,

$$\begin{array}{l} C_6H_4Me\cdot N{:}C{-}{-}{-}{-}N\cdot CH_2Ph \\ \qquad\qquad\quad | \qquad\quad | \\ \qquad\qquad\quad S\cdot CH{:}CPh \end{array},$$

prepared from *s*-*p*-tolylbenzylthiocarbamide and ω-bromoacetophenone, forms colourless needles, m. p. 152°; the *hydrochloride*, *platinichloride*, m. p. 233° (decomp.), and *picrate*, m. p. 155°, are described. That the compound has the above constitution, and not that of the isomeric 2-benzylimino-4-phenyl-3-*p*-tolylthiazoline, has been established by its behaviour towards carbon disulphide, which at 200° leads to the removal of the *p*-tolylimino-group as *p*-tolylthiocarbimide and the formation of 2-*thion*-4-*phenyl*-3-*benzylthiazoline*, $\begin{array}{l} S{-}{-}{-}CS \\ | \\ CH{:}CPh \end{array}\!\!>N\cdot CH_2Ph$, which crystallises in pale yellow needles, m. p. 101°.

When heated with benzyl chloride for eight hours at 175°, 2-*p*-toluidino-4-phenylthiazole yields 2-p-*tolylbenzylamino*-4-*phenyl*-5-*benzylthiazole*, $\begin{array}{l} CPh{-}{-}{-}{-}N \\ \| \\ C(CH_2Ph)\cdot S \end{array}\!\!>C\cdot N(C_6H_4Me)\cdot CH_2Ph$. This forms needles, m. p. 125°, and is accompanied by 2-p-*toluidino*-4-*phenyl*-5-*benzylthiazole*, $\begin{array}{l} CPh{-}{-}{-}{-}N \\ \| \\ C(CH_2Ph)\cdot S \end{array}\!\!>C\cdot NH\cdot C_6H_4Me$, which crystallises in needles, m. p. 174°, and yields a *platinichloride*, m. p. 203° (decomp.), and a *picrate*, m. p. 151°.

That the introduction of the benzyl group has taken place in the thiazole ring and not in the *p*-toluidino-residue has been proved in the case of the last-mentioned thiazole by the formation of an *acetyl* derivative, $C_{25}H_{22}ON_2S$, m. p. 144°, and also by the removal of the *p*-tolylimino-group as *p*-tolylthiocarbimide when the thiazole is heated with carbon disulphide.

2-p-*Tolylimino-4-phenyl-3-methylthiazoline*,

$$\begin{matrix} CPh\cdot NMe \\ \| \\ CH\text{——}S \end{matrix} \!>\! C{:}N\cdot C_6H_4Me,$$

obtained in the form of its *methiodide*, large needles, m. p. about 200° (decomp.), by heating 2-*p*-toluidino-4-phenylthiazole with methyl iodide in methyl alcoholic solution, crystallises in colourless leaflets, m. p. 118°. It has also been prepared by the condensation of *s*-*p*-tolylmethylthiocarbamide with ω-bromoacetophenone; the *hydrochloride* and *picrate*, m. p. 158°, are described. When heated with carbon disulphide, it yields *p*-tolylthiocarbimide and 2-*thion*-4-*phenyl*-3-*methylthiazoline*, $\begin{matrix} CS\cdot NMe \\ | \\ S\text{—}CH \end{matrix} \!>\! CPh$, which crystallises in pale yellow needles, m. p. 127°.

2-p-*Tolylimino*-4-*phenyl*-5-*benzyl*-3-*methylthiazoline*,

$$\begin{matrix} CPh\text{—}NMe \\ \| \\ C(CH_2Ph)\cdot S \end{matrix} \!>\! C{:}N\cdot C_6H_4Me,$$

prepared by the action of methyl iodide on 2-*p*-tolylimino-4-phenyl-5-benzylthiazole, forms colourless prisms, m. p. 151°, and yields a *hydrochloride*, and a *methiodide*, crystallising in needles, m. p. about 250° (decomp.). It is resolved by carbon disulphide into *p*-tolylthiocarbimide, and 2-*thion*-4-*phenyl*-5-*benzyl*-3-*methylthiazoline*, $\begin{matrix} NMe\cdot CPh \\ | \\ CS\text{——}S \end{matrix} \!>\! C\cdot CH_2Ph$, which forms silvery, lustrous leaflets, m. p. 116°.

5-*Bromo*-2-p-*toluidino*-4-*phenylthiazole*, obtained by brominating 2-*p*-toluidino-4-phenylthiazole in benzene solution, crystallises in colourless leaflets or needles, which melt and decompose at 134°, yielding *p*-tolylthiocarbimide; the *hydrobromide*, m. p. 179° (decomp.), and *acetyl* derivative, m. p. 142·5°, crystallise in colourless prisms. It is reduced by zinc and acetic acid to the original thiazole. Attempts to prepare the bromothiazole by the condensation of *p*-tolylthiocarbamide with di-ω-bromoacetophenone yielded a *substance*, m. p. 142° (decomp.).

When warmed with amyl nitrite in alcoholic solution, 2-*p*-toluidino-4-phenylthiazole yields the 5-*nitroso*-derivative,

$$\begin{matrix} CPh\text{—}N \\ \| \\ C(NO)\cdot S \end{matrix} \!>\! S\cdot NH\cdot C_6H_4Me.$$

This separates in yellowish-brown leaflets, m. p. 184° (decomp.), yields a *hydrochloride*, red needles, an *acetyl* derivative, lustrous, dark red leaflets, m. p. 163°, and is reduced by zinc and acetic acid in alcoholic solution to the corresponding *amino*-compound, which, however, could not be isolated in a pure condition.

On treatment with cold aqueous alkalis it becomes brown, probably owing to the formation of salts derived from the tautomeric form (see VI, next page); when boiled with aqueous alkalis it undergoes com-

plete decomposition, yielding hydrogen sulphide, *p*-tolylthiocarbimide, carbon dioxide, thiocyanic acid, benzoic acid, ammonia, and *p*-toluidine.

The *silver* salt, $C_{16}H_{12}ON_3SAg$, prepared by treating an alcoholic solution of the nitroso-compound with the equivalent amounts of ammonia and silver nitrate, separates as an indistinctly crystalline, red precipitate which readily decomposes and explodes when rapidly heated.

On treatment with benzoyl chloride, a solution of the nitroso-compound in aqueous alkalis yields benzoyl-*p*-tolylcyanamide (Heller and Bauer, A., 1902, i, 444), benzoic and thiocyanic acids. This reaction, which establishes the position of the nitroso-group in the thiazole ring, takes place according to the following scheme :

$$\text{VI.}\quad C_6H_4Me\cdot N{:}\begin{array}{l} N{:}CPh \\ \mid \\ C \text{———} S \end{array}\!\!>\!C{:}NOH \xrightarrow{H_2O+BzCl}$$

$$C_6H_4Me\cdot NBz\cdot C({:}NH)\cdot S\cdot C({:}NOH)\cdot COPh \longrightarrow$$

$$C_6H_4Me\cdot NBz\cdot C{:}N + HS\cdot C{:}N + OH\cdot COPh.$$

5-*Bromo*-2-p-*tolylnitrosoamino*-4-*phenylthiazole*,

$$\begin{array}{l} CPh\cdot N \\ \parallel \\ CBr\text{—}S \end{array}\!\!>\!C\cdot N(C_7H_7)\cdot NO,$$

prepared by warming 5-bromo-2-*p*-toluidino-4-phenylthiazole with amyl nitrite, forms colourless needles, m. p. 220°.

2-*p*-Toluidino-4-phenylthiazole combines with benzenediazonium chloride in alcoholic solution, yielding 5-*benzeneazo*-2-p-*toluidino*-4-*phenylthiazole*, $C_6H_4Me\cdot NH\cdot\begin{array}{l} N\cdot CPh \\ \parallel \\ C\text{———}S \end{array}\!\!>\!C\cdot N{:}NPh$, which crystallises in orange-red needles, m. p. 191°, and forms an *acetyl* derivative, $C_{24}H_{20}ON_4S$, red prisms, m. p. 217°, and a *hydrochloride*, crystallising in dark violet-red needles having a greenish glance, m. p. 184° (decomp.).

5-p-*Nitrobenzeneazo*-2-p-*toluidino*-4-*phenylthiazole*, obtained in a similar manner from *p*-nitrobenzenediazonium chloride, crystallises in dark red needles, m. p. 245° (decomp.); the *hydrochloride*, reddish-violet needles, and *acetyl* derivatives, red needles, both melt indefinitely at 250°.

The authors have also studied the behaviour of the remaining aminothiazoles and iminothiazolines described in this paper towards diazonium salts, and find that the iminothiazolines in no circumstances couple with the diazonium salts, whilst the aminothiazoles, in which the 5-position is unsubstituted, readily combine, yielding azo-compounds. The behaviour of 5-bromo-2-*p*-toluidino-4-phenylthiazole is, however, exceptional, the action of benzenediazonium chloride leading to the removal of the bromine atom and the formation of the above-mentioned 5-benzeneazo-2-*p*-toluidino-4-phenylthiazole. The reaction towards diazonium salts thus furnishes a ready means of distinguishing whether the product obtained by the condensation of a monosubstituted thiocarbamide with ω-bromoacetophenone and analogous halogeno-ketones is an aminothiazole or iminothiazoline.

2-p-*Toluidino*-4 : 5-*diphenylthiazole*, $\begin{array}{l} CPh\cdot N \\ \parallel \\ CPh\cdot S \end{array}\!\!>\!C\cdot NH\cdot C_6H_4Me$, pre-

pared from desyl bromide and *p*-tolylthiocarbamide, crystallises in colourless needles, m. p. 178°, and forms a *hydrochloride*.

The condensation of ω-bromoacetophenone and allylthiocarbamide yields 2-*allylamino*-4-*phenylthiazole*, $\begin{matrix} CPh{\cdot}N \\ \| \\ CH{-}S \end{matrix}\!\!>\!C{\cdot}NH{\cdot}C_3H_5$, which has m. p. 73°, and couples with diazonium salts to form red azo-compounds. F. B.

Decomposition of Alkylidenehydrazines. NICOLAI M. KISHNER (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1754—1759).—*Menthylidenehydrazine*, $CH_2\!<\!\begin{matrix} CH_2{\cdot}CHPr \\ CHMe{\cdot}CH_2 \end{matrix}\!>\!C{:}N{\cdot}NH_2$, is a colourless liquid, b. p. 144°/30 mm., 248—249°/759 mm., D_0^{20} 0·9333, n_D 1·4940, $[\alpha]_D - 52{\cdot}45°$. When distilled under reduced pressure, it leaves a viscous residue which, on treatment with 10% sulphuric acid in the cold, yields menthone and *l*-menthazine (compare A., 1908, i, 91). Pure menthylidenehydrazine yields no menthazine with cold 10% sulphuric acid, the sole product being menthone, which exhibits a low specific rotation owing to partial inversion. Distillation of the base with platinised porous tile yields hydrazine and *l*-menthazine. Menthylidenehydrazine is slightly decomposed, with evolution of nitrogen, when distilled with fused potassium hydroxide, whilst in presence of both platinised porous tile and fused alkali, it is resolved into nitrogen and menthane.

iso*Thujylidenehydrazine*, $CMe\!<\!\begin{matrix} CHPr^{\beta}{\cdot}CH_2 \\ \quad\;\; | \\ CMe{-}C{:}N{\cdot}NH_2 \end{matrix}$, prepared from *iso*thujane and hydrazine hydrate, is a faint yellow, viscous liquid, b. p. 143—144°/17 mm., 152—153°/25 mm., D_0^{20} 0·9579, n_D 1·5328. Distillation of the base in presence of potassium hydroxide, spongy platinum, or molecular silver yields (1) nitrogen, (2) hydrazine, (3) a mixture of the hydrocarbons, $C_{10}H_{18}$ and $C_{10}H_{16}$, giving a cherry-red coloration with sulphuric acid and acetic anhydride and a green one with sulphuric acid and methyl alcohol, and (4) iso*thujazine*,

$$C_{10}H_{16}{:}N_2{:}C_{10}H_{16},$$

which crystallises in golden-yellow needles, m. p. 161—162°.

When distilled with potassium hydroxide, carvylidenehydrazine yields a *hydrocarbon*, $C_{10}H_{16}$, b. p. 175—176°/749 mm. (175—176°/757 mm.), D_0^{20} 0·8361 (0·8349), n_D 1·4678 (1·4665), $[\alpha]_D - 36{\cdot}74°$ (−35·36°), which with hydrogen bromide gives the *dipentene hydrobromide*, $C_{10}H_{16},2HBr$, m. p. 63°, and with ethyl nitrite and hydrochloric acid, *l*-limonene β-nitrosochloride. T. H. P.

Hydantoins. XX. Action of Thiocyanates on α-Amino-acids. TREAT B. JOHNSON (*Amer. Chem. J.*, 1913, **49**, 68—69).—It has been shown in earlier papers that by the action of thiocyanates on acyl derivatives of α-amino-acids, acylthiohydantoins are produced. The author has now found that the salt used in certain experiments (A., 1912, i, 53, 316, 390, 807) which was supposed to be potassium thiocyanate was really the ammonium salt, and the yields recorded were therefore obtained from the latter. The two salts show a remarkable difference in their behaviour with hippuric acid; the same com-

pound is formed in each case, but with the potassium salt it is obtained as an oily product which only slowly solidifies, whilst when prepared from the ammonium salt it solidifies at once on being poured into water. E. G.

Tetraphenyldi-iminotetrahydromiazthiole (3 : 5-Diphenylimino-1 : 4-diphenyltetrahydro-1 : 2 : 4-thiodiazole). EMIL FROMM [with WILHELM BITTERICH] (*Annalen*, 1912, **394**, 284—290).—3 : 5-Diphenylimino-1 : 4-diphenyltetrahydro-1 : 2 : 4-thiodiazole is probably a direct product of the oxidation of diphenylthiocarbamide, and is not formed through the intermediate production of an unstable disulphide (compare Fromm and Heyder, A., 1909, i, 903). It is best prepared by Hugershoff's method of oxidation by alcoholic bromine, care being taken to work in the cold, otherwise triphenylguanidine is obtained. The substance is converted into triphenylguanidine by concentrated hydrochloric acid, and is decomposed by boiling glacial acetic acid into acetanilide and 1-anilinobenzothiazole. By heating with aniline at 110° for several hours, the diphenyliminodiphenyltetrahydrothiodiazole is converted into the isomeric *triphenylguanidobenzothiazole*, $NHPh\cdot C(:NPh)\cdot NPh\cdot C<^{N}_{S}>C_6H_4$, m. p. 142°, which is not desulphurised by lead oxide and an alkali, and yields by the Schotten-Baumann process 2-*benzoylphenylaminobenzothiazole*,

$$C_6H_4<^{N}_{S}>C\cdot NPh\cdot COPh,$$

m. p. 156°, which is also obtained from 2-anilinobenzothiazole, benzoyl chloride, and aqueous sodium hydroxide. C. S.

Trimethylparamide. HANS MEYER and KARL STEINER (*Ber.*, 1912, **45**, 3676—3677. Compare Mumm and Bergell, A., 1912, i, 1015).—Trimethylparamide can be prepared in a pure condition by heating methylamine mellitate for two hours in a sealed tube at 200° and recrystallising the colourless product from chlorobenzene; it is quantitatively hydrolysed to mellitic acid on prolonged boiling with potassium hydroxide solution. D. F. T.

Disulphides with Neighbouring Double Linkings. Derivatives of Dithiobiurets and of Thiurets. EMIL FROMM [and RICHARD HEYDER, ADOLF JUNG, and MARGRET STURM] (*Annalen*, 1912, **394**, 258—284).—Since only one example is known of the simultaneous production of an arylguanidoarylthiocarbamide and a diarylguanidothiocarbamide by the decomposition of an arylthiuret by an aromatic amine (A., 1908, i, 700), the action of different aromatic amines on a series of thiurets has been examined. It is found that, as a rule, the two products of the decomposition are formed when the arylthiuret and the aromatic amine contain the same aromatic group.

o-*Anisyldithiobiuret*, $C_9H_{11}ON_3S_2$, m. p. 153°, yellowish-white needles, obtained by heating equal weights of perthiocyanic acid and *o*-anisidine on the water-bath, is converted by boiling hydrochloric acid and ferric chloride into o-*anisylthiuret hydrochloride*, $C_9H_9ON_3S_2,HCl$, m. p. 220° (hydrated) or 235° (anhydrous). The latter and *o*-anisidine in

boiling alcohol yield sulphur, o-*anisylguanido*-o-*anisylthiocarbamide*, $OMe{\cdot}C_6H_4{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C(:NH){\cdot}NH{\cdot}C_6H_4{\cdot}OMe$ (the constitution of which is proved by its conversion into o-*anisylguanido*-o-*anisyl*-ψ-*benzylthiocarbamide*,

$$OMe{\cdot}C_6H_4{\cdot}N:C(S{\cdot}C_7H_7){\cdot}NH{\cdot}C(:NH){\cdot}NH{\cdot}C_6H_4{\cdot}OMe,$$

m. p. 116°, by boiling with benzyl chloride and an excess of aqueous alcoholic sodium hydroxide), and *di*-o-*anisylguanidothiocarbamide*, which is isolated as the *hydrochloride*,

$$C(NH{\cdot}C_6H_4{\cdot}OMe)_2:N{\cdot}CS{\cdot}NH_2,HCl,$$

m. p. 205°. By boiling this hydrochloride with lead oxide and alcoholic sodium hydroxide, *di*-o-*anisyldicyanodiamide*,

$$CN{\cdot}N:C(NH{\cdot}C_6H_4{\cdot}OMe)_2,$$

m. p. 168°, white needles, is obtained. In a similar manner, *p*-phenetylthiuret hydrochloride and *p*-phenetidine in boiling alcohol yield *di*-p-*phenetylguanidothiocarbamide*, m. p. 142° (*hydrochloride*, m. p. 167°), and p-*phenetylguanido*-p-*phenetylthiocarbamide*, m. p. 172°, of which the former is converted into *di*-p-*phenetyldicyanodiamide*, m. p. 176°, by lead oxide and alcoholic sodium hydroxide, and the latter into p-*phenetylguanido*-p-*phenetyl*-ψ-*benzylthiocarbamide*, m. p. 180°, by benzyl chloride and alcoholic sodium hydroxide. *p*-Phenetylthiuret hydrochloride and aniline react to form phenylguanido-*p*-phenetylthiocarbamide, m. p. 184°, not 170° (A., 1907, i, 982), and a small amount of *phenyl*-p-*phenetylguanidothiocarbamide*, $OEt{\cdot}C_6H_4{\cdot}NH{\cdot}C(NHPh):N{\cdot}CS{\cdot}NH_2$, m. p. 137°, the *hydrochloride* of which, $C_{16}H_{18}ON_4S,HCl,H_2O$, has m. p. 113—114°.

p-Phenetylguanidophenylthiocarbamide (*loc. cit.*) has m. p. 158°, not 168°, and forms a *hydrochloride*, m. p. 168°.

o-*Tolylthiuret hydrochloride*, $C_9H_9N_3S_2,HCl,2H_2O$, m. p. 175°, obtained from *o*-tolyldithiobiuret and boiling hydrochloric acid and ferric chloride, reacts with *o*-toluidine in boiling alcohol to form *tri*-o-*tolyldiguanide hydrochloride*, $C_{23}H_{25}N_5HCl$, m. p. 233°, from which *tri*-o-*tolyldiguanide*, $C(NH{\cdot}C_6H_4Me)_2:N{\cdot}C(:NH){\cdot}NH{\cdot}C_6H_4Me$, m. p. 179°, is liberated by ammonia. The by-product of the preceding reaction is *di*-o-*tolylguanidothiocarbamide*, m. p. 172°, or o-*tolylguanido*-o-*tolylthiocarbamide*, $C_{16}H_{18}N_4S,EtOH$, m. p. 178°, according to the dilution of the solution. *o*-Tolylthiuret and aniline in boiling alcohol yield only *phenylguanido*-o-*tolylthiocarbamide*, m. p. 135° (*hydrochloride*, m. p. 183°), and phenylthiuret and *o*-toluidine under similar conditions yield only *phenyl*-o-*tolylguanidothiocarbamide*, m. p. 111° (*hydrochloride*, m. p. 89°). *Phenylguanido*-o-*tolyl*-ψ-*benzylthiocarbamide*, $C_{22}H_{22}N_4S$, m. p. 124°, crystallises in yellow octahedra.

The following substances have been obtained by the interaction of arylthiuret hydrochlorides and phenylhydrazine in boiling alcohol (A., 1907, i, 982; 1908, i, 700), and are converted into triazole derivatives by boiling aqueous alcoholic alkalis; thus *o*-tolylthiuret hydrochloride and phenylhydrazine yield *anilguanido*-o-*tolylthiocarbamide* or *anil*-o-*tolylguanidothiocarbamide*,

$$NHPh{\cdot}NH{\cdot}C(:NH){\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_4Me \text{ or}$$

$NHPh{\cdot}NH{\cdot}C(NH{\cdot}C_6H_4Me):N{\cdot}CS{\cdot}NH_2$, m. p. 157° [3:5(or 5:3-)-*amino*-o-*toluidino*-1-*phenyltriazole*, $NPh{<}{\genfrac{}{}{0pt}{}{N=\!=\!=\!=\!=\!=C{\cdot}NH_2}{C(NH{\cdot}C_6H_4Me):N}}$ or

$NPh<\begin{matrix}N=\!=\!=C:NH\cdot C_6H_4Me \\ C(NH_2):N\end{matrix}$, has m. p. 143°]; *o*-anisylthiuret and phenylhydrazine yield two substances which could not be obtained pure, but have been converted into 5-*amino*-3-o-*anisidino*-1-*phenyltriazole*, $OMe\cdot C_6H_4\cdot NH\cdot C<\begin{matrix}N\cdot NPh \\ N:C\cdot NH_2\end{matrix}$, and 3-*amino*-5-o-*anisidino*-1-*phenyltriazole*, one of which forms a sparingly soluble *hydrochloride*,

$$C_{15}H_{15}ON_5,HCl,H_2O,$$

m. p. 228°, and a *picrate*, m. p. 250°, red needles, and the other an easily soluble *hydrochloride*, and a *picrate*, m. p. 169°; *p*-phenetylthiuret hydrochloride and phenylhydrazine (Fromm and Vetter, A., 1907, i, 982) yield anilguanido-*p*-phenetylthiocarbamide or anil-*p*-phenetylguanidothiocarbamide, m. p. 170°, not 168°, and aminophenylguanido-*p*-phenetylthiocarbamide or aminophenyl-*p*-phenetylguanidothiocarbamide, m. p. 168°, white needles (not m. p. 236°, white leaflets), the latter forming a *benzylidene* derivative, m. p. 183°.

The formation of 3-amino-5-thiol-1-phenyltriazole, m. p. 234°, and dianildithiobiuret, m. p. 178°, from phenylhydrazine and phenylmethylthiuret has already been recorded (A., 1908, i, 700). The former reacts with benzyl chloride and aqueous sodium hydroxide to form 3-*amino*-5-*benzylthiol*-1-*phenyltriazole*, m. p. 116°, and with benzoyl chloride and aqueous sodium hydroxide to form 3-*benzoylamino*-5-*thiol*-1-*phenyltriazole*, m. p. 267°, from which 3-*benzoylamino*-5-*benzylthiol*-1-*phenyltriazole*, m. p. 161°, is obtained by means of benzyl chloride and aqueous sodium hydroxide. The action of benzoyl chloride and sodium carbonate on dianildithiobiuret or on 3-thiol-5-phenylhydrazino-1-phenyltriazole yields 3-*thiol*-5-*benzoylphenylhydrazino*-1-*phenyltriazole*, $NHPh\cdot NBz\cdot C<\begin{matrix}NPh\cdot N \\ N-\!-C\cdot SH\end{matrix}$, m. p. 218°, which yields the 3-*benzylthiol* derivative, m. p. 171°, by boiling with benzyl chloride and the calculated quantity of aqueous alcoholic sodium hydroxide, and 3-*benzylthiol*-5-*phenylhydrazino*-1-*phenyltriazole*, m. p. 118°, red needles, when an excess of the alkali is employed. The substance, m. p. 218°, obtained by the action of acetic anhydride on dianildithiobiuret (*loc. cit.*) is 3-*thiol*-5-*acetylphenylhydrazino*-1-*phenyltriazole*; by treatment with benzyl chloride and an alkali, it yields 3-*benzylthiol*-5-*acetylphenylhydrazino*-1-*phenyltriazole*, m. p. 102°, yellow leaflets. The constitution of the oxidation product, m. p. 218°, of 3-thiol-5-phenylhydrazino-1-phenyltriazole as a benzeneazotriazole (*loc. cit.*) is proved as follows. In the presence of an alkali, the substance is converted into 5-*benzeneazo*-3-*thion*-2-*benzoyl*-1-*phenyltriazole*, $PhN_2\cdot C<\begin{matrix}NPh\cdot NBz \\ N-\!-CS\end{matrix}$, m. p. 167°, red needles, by benzoyl chloride, and into 5-*benzeneazo*-3-*benzylthiol*-1-*phenyltriazole*,

$$PhN_2\cdot C<\begin{matrix}NPh\cdot N \\ N-\!-C\cdot SC_7H_7\end{matrix},$$

m. p. 116°, reddish-yellow leaflets, by benzyl chloride. The latter is also produced when the former is treated with benzyl chloride and an alkali. The oxidation product can be acylated or alkylated, but not

both simultaneously, thus proving that the same hydrogen atom is concerned in each process and that the substance is tautomeric.

The base $C_{14}H_{13}N_5S$, m. p. 181°, which is obtained together with the preceding azo-compound by the action of boiling hydrochloric acid on dianildithiobiuret (*loc. cit.*), forms, in addition to the diacetyl and the dibenzylidene derivatives already described, a *dibenzoyl* derivative, m. p. 216°, does not react with benzyl chloride in the presence of an alkali, and requires 2 mols. of sodium nitrite for its diazotisation. These facts are contrary to the formula previously ascribed to the base, and are more in harmony with the constitution :

$$NH_2\cdot C_6H_4\cdot N:C<\genfrac{}{}{0pt}{}{-S-}{NH}>C:N\cdot C_6H_4\cdot NH_2.$$

Under the influence of hydrogen chloride, substituted dithiobiurets react with aldehydes or ketones to form aldurets or keturets (A, 1893, i, 575 ; 1906, i, 656), which can be alkylated in consequence of the presence of the thiol groups; thus *o*-tolyldithiobiuret and acetone yield o-*tolyldimethyl-ψ-dithioketuret*, $C_6H_4Me\cdot N:C(SH)\cdot N<\genfrac{}{}{0pt}{}{C(SH)}{CMe_2-}>N$, m. p. 236°, which forms a *benzyl* derivative, m. p. 192°, and a *dibenzyl* derivative, m. p. 83°; *o*-tolyldithiobiuret and benzaldehyde yield *phenyl*-o-*tolyl-ψ-dithioalduret*, $C_6H_4Me\cdot N:C(SH)\cdot N<\genfrac{}{}{0pt}{}{C(SH)}{CHPh}>N$, m. p. 207°, yellow leaflets (*dibenzyl* derivative, m. p. 118°) ; *o*-tolyldithiobiuret and 40% formaldehyde yield o-*tolyl-ψ-dithioalduret*,

$$C_6H_4Me\cdot N:C(SH)\cdot N<\genfrac{}{}{0pt}{}{C(SH}{CH_2-}>N,$$

m. p. 197°, yellow leaflets (*dibenzyl* derivative, m. p. 80°). o-Tolyldithiobiuret does not react with acetophenone or benzophenone.

C. S.

Crystallographic Study of the Sodium Salt of *iso*Hydroxytetrazole. ARISTIDE ROSATI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 645—648).—The author has studied the salt $CHON_4Na,3H_2O$, which was obtained by Palazzo (A., 1910, i, 342). The salt loses its water at 120—130°, and explodes at 240°. It occurs in two crystalline forms: (1) pale straw-yellow tablets belonging to the pinacoidal class of the triclinic system; $a:b:c = 1{\cdot}2494:1:0{\cdot}8521$, α 130°6′, β 114°47′, γ 79°34·5′ ; (2) colourless tablets, also belonging to the pinacoidal class of the triclinic system ;

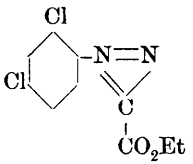
$$a:b:c = 0{\cdot}6798:1:1{\cdot}0834,\ \alpha\ 54°53',\ \beta\ 124°32{\cdot}5',\ \gamma\ 121°43'.$$

R. V. S.

Action of Chlorine on Ethyl Phenylazoacetoacetate. A New Way to Prepare Derivatives of Formimido-chloride. CARL BÜLOW and PETER NEBER (*Ber.*, 1912, **45**, 3732—3744).—Elimination of the carbethoxyl group takes place when ethyl phenylazoacetoacetate is hydrolysed by sodium hydroxide (Richter and Münzer, A., 1884, 1342) or brominated (Hecking, *Diss.*, 1910). The action of chlorine, however, results in the removal of the acetyl group and the formation of the dichlorophenylhydrazone of ethyl monochloroglyoxylate. When this substance is completely reduced,

2 : 4-dichloroaniline is formed, and the compound may also be synthesised from this base. The remaining chlorine atom must necessarily be attached to the α-carbon atom of the side-chain, and it is very reactive. It may be replaced by an amino-group, more prolonged action of ammonia replacing, in addition, the ester group.

A method is given for the preparation of ethyl phenylazoacetoacetate. Chlorination may be effected in glacial acetic acid by chlorine or sulphuryl chloride, but the best results are obtained by chlorine in chloroform. The 2 : 4-*dichlorophenylhydrazone* of *ethyl α-chloroglyoxylate*, $C_6H_3Cl_2\cdot NH\cdot N\dot{:}CCl\cdot CO_2Et$, crystallises in brilliant needles, m. p. 98°. When treated with alcoholic potash, hydrogen chloride is eliminated, and a *product*, $C_{10}H_8O_2N_2Cl_2$, is obtained in beautiful yellow needles, m. p. 196°. Its constitution is probably represented by the annexed formula.



The 2 : 4-*dichlorophenylhydrazone* of *ethyl α-aminoglyoxylate*, $C_{10}H_{11}O_2N_3Cl_2$, which is immediately formed when alcoholic ammonia is added to the imido-chloride, crystallises in long, flat needles from dilute ethyl acetate, m. p. 99°, and is readily soluble in mineral acids, but does not form a diazonium salt. More prolonged action of ammonia results in the formation of the *amide*, $C_6H_3Cl_2\cdot NH\cdot N\dot{:}C(NH_2)\cdot CO\cdot NH_2$, in long, grey needles, m. p. 170°.

Ethyl 2 : 4-*dichlorobenzeneazoacetoacetate*, $C_6H_3Cl_2\cdot N_2\cdot CHAc\cdot CO_2Et$, may be prepared in a similar manner by condensing the diazotised dichloroaniline with ethyl acetoacetate. It crystallises in yellow needles, m. p. 127°, and gives the above α-chloro-compound with chlorine. When condensed with hydrazine hydrate, it gives 4-o-p-*dichlorobenzeneazo-5-hydroxy-3-methylpyrazole*, $C_{10}H_8O_2N_2Cl_2$, in orange-yellow needles, m. p. 207°, which cannot be precipitated by water from piperidine, in which the substance is very soluble.

Similarly, phenylhydrazine yields 4-o-p-*dichlorobenzeneazo-5-hydroxy-1-phenyl-3-methylpyrazole*, $C_{16}H_{12}ON_4Cl_2$, in brick-red needles, m. p. 195°, which concentrated nitric acid converts into 2 : 4-dichlorophenyldiazonium chloride and 4-nitro-1-benzene-3-methylpyrazolone (compare A., 1910, i, 902). J. C. W.

The Racemisation of Proteins and their Derivatives Resulting from Tautomeric Change. I. HENRY D. DAKIN (*J. Biol. Chem.*, 1912, 13, 357—362).—There is an analogy between the hydantoin, $NH{<}\begin{matrix}CO\text{—}NH\\ CRH\cdot CO\end{matrix}$, and peptide,

$$RCH{<}\begin{matrix}NH\cdot CO\text{–}\\ CO\cdot NH\cdot CHR\cdot CO_2H\end{matrix}$$

groupings, in both of which the –CH·CO– group can exhibit keto-enolic tautomerism and hence racemisation (compare Dakin, A., 1910, i, 590). In the peptide complex the terminal amino-acid containing a free carboxyl group cannot, however, undergo this change. Such tautomeric change apparently takes place when a protein is digested at low temperatures with dilute alkali (compare Kossel and Weiss, A., 1909, i, 542; 1910, i, 791).

The optical rotatory power of gelatin falls to a minimum when it is digested with dilute alkali. On subsequent hydrolysis with acids, inactive leucine, aspartic acid, arginine, histidine, and phenylalanine are obtained, whereas proline, glutamic acid, and lysine are obtained in the optically active forms together with part of the alanine. The conclusion is drawn that none of the carboxyl groups in the substances which were obtained inactive are free in gelatin. On the other hand, glutamic acid, lysine, and alanine may have some of their carboxyl groups free, that is, they may occupy terminal positions in the peptide chains. An alternative is that these amino-acids are rapidly liberated in the free state by the hydrolytic action of the alkali and so escape racemisation. E. F. A.

The Refractive Indices of Solutions of Certain Proteins. VIII. Globin. T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1913, **13**, 455—462).—Globin was prepared from ox-corpuscles by three different modifications of Schulz's method. The value of a for the purest preparation dissolved in decinormal potassium hydroxide or hydrochloric acid is 0·00169 ± 0·00005. W. D. H.

The Preparation and Properties of a Compound Protein; Globin Caseinate. T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1913, **13**, 499—506).—Globin caseinate may be prepared by mixing two parts of globin with one of casein, each in a faintly alkaline solution. It displays properties intermediate between those of the two component proteins, the acid function of globin being enhanced by union with casein and the basic function of casein by union with globin.

The compound is not decomposed by dilute acetic acid in the cold, but it is by boiling dilute acetic acid, or by pepsin and acetic acid. The change in the refractive index of decinormal potassium hydroxide due to the introduction of 1% of globin caseinate is 0·00162 ± 0·00005. The refractivity of a compound protein is an additive function of the refractivities of its components. W. D. H.

Constitution of the Blood and Bile Pigments. I. HANS FISCHER and ERICH BARTHOLOMÄUS (*Zeitsch. physiol. Chem.*, 1913, **83**, 50—71).—The formation of tri- and tetra-substituted pyrroles on the decomposition of hæmin is explained on the hypothesis that the pyrrole nuclei are united by a CH_2 radicle in the 2-positions. Such 2- and 3-methylene derivatives have been synthesised by Colacicchi (A., 1912, i, 491).

Bis-(5-acetyl-2 : 4-dimethylpyrryl)methane, in which the methylene group is in the 3-position, resists the reducing action of hydrogen iodide and acetic acid during two hours. To some extent the α-acetyl residue is eliminated and *bis-(2 : 4-dimethylpyrryl-3 : 3′)methane*, $NH\Big\langle\begin{matrix}CMe\colon C-CH_2-C\colon CMe\\ CH{=}CMe \quad MeC{=}CH\end{matrix}\Big\rangle NH$, is formed. This compound has many of the properties of hemibilirubin; it gives the aldehyde reaction, is unstable, shows the urobilin bands, and the fluorescence reaction with zinc acetate. It forms a *picrate* and an α-azo-dye

When the action of the reducing agent is prolonged for fourteen to sixteen hours, 2 : 3 : 4-trimethylpyrrole admixed with some 2 : 4-dimethylpyrrole is obtained.

Bis-(3-acetyl-2 : 4-dimethylpyrryl)methane (Colacicchi, *loc. cit.*) is readily reduced to pyrrole derivatives by acetic acid and hydrogen iodide. The mixture of pyrrole picrates was not separated.

Trialkylated pyrroles condense with formaldehyde in presence of alkali. The products are regarded as methylene derivatives, although the possibility of an alcohol structure, $NH<\begin{matrix}CMe{:}C\cdot CH_2\cdot OH\\ CMe{:}CMe\end{matrix}$, is not overlooked.

Tetramethylpyrrole was obtained on reducing the condensation product from 2 : 4 : 5-trimethylpyrrole; phyllopyrrole from the condensation product of cryptopyrrole.

2 : 3 : 5-*Trimethylpyrrole*-4-*propionic acid*,

$$NH<\begin{matrix}CMe{:}C\cdot CH_2\cdot CH_2\cdot CO_2H\\ CMe{:}CMe\end{matrix},$$

was not obtained on reducing the amorphous condensation product of formaldehyde with phonopyrrolecarboxylic acid, but it is readily formed on methylation of phonopyrrolecarboxylic acid. Tetramethylpyrrole is obtained at the same time.

The pyrrole, $CO_2Et\cdot C\lessgtr\begin{matrix}CMe{:}C-CH_2-C{=}CMe\\ CMe\cdot NH \qquad NH\cdot CMe\end{matrix}\gtrless C\cdot CO_2Et$, obtained by the action of formaldehyde on 3-carbethoxy-2 : 4-dimethylpyrrole, when boiled with acetic acid gives an intense green solution showing a characteristic band in the red similar to that of the copper salt of hemibilirubin.

Bis-5-acetyl-2 : 4-dimethylpyrrylethane,

$$NH<\begin{matrix}CMe{=}C-CHMe-C{=}CMe\\ C(COMe){:}CMe \qquad MeC\cdot C(COMe)\end{matrix}>NH,$$

produced from 5-acetyl-2 : 4-dimethylpyrrole by the action of acetaldehyde, is decomposed by acetic acid and hydrogen iodide into 2 : 4-dimethylpyrrole. The formation of cryptopyrrole could not be determined.

All the foregoing pyrrole derivatives are decomposed by sodium methoxide, forming tetramethylpyrrole.

Tripyrrole is absolutely stable towards acetic acid and hydrogen iodide in the sense that no volatile bases are formed.

Bis-(2 : 4-*dimethylpyrryl*-3 : 3')*methane* crystallises in tiny pyramids and prisms, m. p. 139—140°; the *picrate* forms yellowish-brown needles, m. p. 125—126°.

2 : 3 : 5-*Trimethylpyrrole*-4-*propionic acid* forms a picrate, m. p. 126—127°. E. F. A.

Bilirubin and Hæmin. WILLIAM KÜSTER [and P. DEIHLE] (*Zeitsch. physiol. Chem.*, 1912, 82, 463—483).—Sodium amalgam does not necessarily reduce vinyl groups, which remain unattacked during the conversion of hæmin into the leuco-compound or of bilirubin into hemibilirubin. The complex giving rise to methylethylmaleinimide on oxidation is contained already in bilirubin. One of the two complexes

in hæmin which gives hæmatic acid on oxidation loses carbon dioxide during conversion into bilirubin, and so gives rise to the imide when oxidised. On esterification with methyl alcohol and hydrochloric acid, bilirubin behaves differently from hæmin. A dimethyl derivative is obtained, in which one methyl replaces hydrogen, and the other is due to the addition of methyl alcohol.

The formulæ given by Piloty (A., 1912, i, 923) and by H. Fischer and Röse (A., 1912, i, 575) for bilirubic acid, etc., are discussed, and a complete structural formula for hæmin is suggested.

Pure mesoporphyrin yields methylethylmaleinimide on oxidation.

Bilirubin forms a silver salt containing 4 atoms of silver when fresh preparations are used; older preparations react with 2 atoms only of silver. The salts have a metallic lustre, and the silver is not replaceable by barium. Bilirubin regenerated from the zinc salt dissolves in sodium hydrogen carbonate. This *aci*-form is more soluble in chloroform than the normal. *Dimethylbilirubin*, $C_{34}H_{40}O_7N_4$, is a blackish-green powder. E. F. A.

The Action of Yeast on Yeast-nucleic Acid. SAMUEL AMBERG and WALTER JONES (*J. Biol. Chem.*, 1913, **13**, 441—446).—Yeast has no action on thymus-nucleic acid, but it causes the disappearance of yeast-nucleic acid. If compressed yeast is used, adenine and guanine appear; if yeast powder is employed, adenine and guanosine are found. W. D. H.

Nucleases. III. PHŒBUS A. LEVENE and F. B. LA FORGE (*J. Biol. Chem.*, 1913, **13**, 507—510).—The pyrimidine ribosides are more resistant towards the hydrolytic action of mineral acids than are the purine ribosides. Their behaviour to enzymes runs parallel to this. The differences towards acids can be removed by reducing the pyrimidine base in the riboside to the corresponding dihydropyrimidine. No tissue enzyme has, however, yet been discovered which hydrolyses either the original or the dihydro-derivative.

W. D. H.

Influence of the Reaction of the Medium on the Action of Ptyalin. WILHELM E. RINGER and H. VAN TRIGT (*Zeitsch. physiol. Chem.*, 1912, **82**, 484—501).—The action of ptyalin on starch is studied in presence of varying amounts of sodium hydroxide and phosphoric acid, and the amount of reducing sugar formed contrasted with the hydrogen-ion concentration of the liquids as determined by the conductivity method. At 37° the optimum activity is observed in a solution having $p_H = 6{\cdot}0$. When citrate is substituted for phosphate, the position of the optimum varies with the concentration of the citrate; it is observed in more nearly neutral solutions with citrate than is the case with phosphate. In presence of sodium acetate and acetic acid the optimum is at $p_H = 6{\cdot}0$. The presence of both phosphate and acetate reduces the amount of starch hydrolysis; citrate has still more influence. The enzyme itself is not damaged during the duration of the experiment. When these are prolonged for five times as long, the position of the optimum is not materially altered. E. F. A.

Temperatures of Destruction of Emulsin in Ethyl Alcohol of Various Strengths. ÉMILE BOURQUELOT and MARC BRIDEL (*J. Pharm. Chim.*, 1913, [vii], 7, 27—31).—A solution of emulsin in water was diluted with alcohol or alcohol and water to produce alcoholic liquids of various strengths containing the same quantity of emulsin. Portions of these liquids were then heated to various temperatures, and afterwards tested for activity on salicin. It was found that the temperature at which emulsin begins to become inactive under these conditions varies from 60° to 40° for liquids containing from 10 to 50% of alcohol, and remains constant at 45° to 40° for liquids containing 60 to 95% of alcohol. Total destruction of activity occurs at temperatures ranging from 70° to 55°. Different figures are obtained when the preparations are made by macerating emulsin in the alcoholic liquids. T. A. H.

Rennin. I. Properties of the Ferment when Prepared by Different Methods. II. Acceleration of the Action of Rennin by Phosphoric Acid. III. The Variation in the Length of Time Required to Curdle Different Specimens of Milk. A. ZIMMERMANN (*J. Ind. Eng. Chem.*, 1912, 4, 506—508).—The distinctive properties of rennin when prepared by the following different methods are described: (1) precipitated by sodium chloride, (2) precipitated by sodium sulphate, (3) rennin in scales (granular rennin), and (4) commercial rennin.

Phosphoric acid (0 075%) when added to milk increases the activity of the rennin, a property possessed in a less degree by lactic, hydrochloric, and oxalic acids.

The length of time required to curdle by the same specimen of rennin appears to be influenced by the length of time the milk has been kept; the staler the milk, the more rapid the action of the rennin; this would appear to be a bacterial effect, yet it is found that a mixture of rennin and milk kept several hours at 40° will not curdle, whereas if the milk alone be subjected to this treatment, the addition of the same rennin causes rapid curdling.

The preparation of standardised rennin, the permanency of rennin solutions and of pepsin are also discussed. F. M. G. M.

Antagonism between Citrates and Calcium Salts in Milk Curdling by Rennet. J. R. KATZ (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 434—445).—Whilst $N/125$- and $N/25$-solutions of citric acid delay the curdling of milk more than two hours, the action is much weakened when substitution occurs at one of the active groups of the citric acid, and stops altogether when two or three of the groups are made inactive.

When substitution occurs at the alcohol group, the curdling is delayed three and a-half and nine and a-half hours respectively by $N/125$- and $N/25$-solutions. Similar results were obtained by tribasic acids not containing an alcohol group.

When substitution occurs at one carboxyl group in citric acid, a delay in curdling milk of one and a-quarter hours with $N/125$- and of six and a-half hours with $N/25$-solutions takes place. Results similar

to these were again obtained by employing dibasic acids with one or more alcohol groups.

The results show that when one active group is taken from citric acid, the characteristic action of the acid is reduced to about 6% of its original value, and that when two groups are substituted to about 1%.

N. H. J. M.

Synthesising Action between Galactose and Ethyl Alcohol under the Influence of Kephir. ÉMILE BOURQUELOT and HENRI HÉRISSEY *Compt. rend.*, 1912, **155**, 1552—1554).—β-Ethyl galactoside is slowly synthesised, in small quantities in the presence of kephir, from an alcoholic solution of galactose. The authors suggest that the synthesising agent in this case and also in that of emulsin obtained from almonds (compare A., 1912, i, 946) is really the lactase present in these two substances.

W. G.

Physiological Chemistry

Variations in the Irritability of the Reflex Arc. I. Variations under Asphyxial Conditions, with Blood-gas Estimations. E. L. PORTER (*Amer. J. Physiol.*, 1913, **31**, 223—244).—The experiments were made on the spinal cat, subjected to asphyxial conditions. The records obtained offer no conclusive evidence of increased reflex irritability under asphyxia, but as the oxygen in the blood lessens and the carbon dioxide accumulates, the flexion reflex disappears. This is the general result, but the details differ according as the admixture of the two gases supplied varies. W. D. H.

The Chemistry of Portal Blood. I. A Portal Fistula. EFIM S. LONDON and N. A. DOBROVOLSKAJA (*Zeitsch. physiol. Chem.*, 1912, **82**, 415—416).—A description of the operative procedure in making a fistula for the obtaining of blood from the portal vein. Results will follow later. W. D. H.

Glycolysis. III. PETER RONA and F. ARNHEIM (*Biochem. Zeitsch.* 1913, **48**, 35—49. Compare A., 1911, ii, 619).—The authors confirm the previous statement that sugar is not destroyed by lysed corpuscles. They now show that if the corpuscles are previously lysed, they can still destroy sugar provided that phosphate or carbonate ions are present in sufficient concentration. They further show that the glycolysis is much diminished if intact corpuscles are diluted with physiological saline alone; if, however, carbonates or phosphates are added in sufficient concentration in a Ringer's fluid, when such a liquid is used to dilute the corpuscles, the glycolysis is not less than that produced by the undiluted corpuscles. The comparative glycolytic

properties of white and red corpuscles was also investigated. The red corpuscles diluted with saline to the volume of the original blood exerted nearly as great a glycolytic effect as the original blood, whereas the white corpuscles diluted to the same extent were almost inactive. Nevertheless, if the white corpuscles are diluted with a liquid containing phosphates, they exert a very marked glycolytic action. In the experiments carried out, no glycolytic power markedly superior to that of the red corpuscles could be demonstrated.

S. B. S.

The Alkalinity of Pancreatic and Intestinal Juice in Living Dogs. FRIEDRICH AUERBACH and HANS PICK (*Arb. K. Gesundheitsamte*, 1912, **43**, 155—186).—Both these juices are strongly alkaline in spite of the blood being nearly neutral in reaction; the alkalinity was determined in the juices obtained from fistulæ in dogs by electrometric, colorimetric, and titrimetric methods. It corresponds with that of a sodium hydrogen carbonate solution, rather than with one of sodium carbonate. It is probable that the juices contain free carbon dioxide. The H-ion concentration averages $0·5.10^{-8}$ mol./litre; the OH-ion concentration at 18° is about 10^{-6}, and at 37°, 5.10^{-6} mol./litre.

In intestinal juice, sodium chloride is more abundant than sodium hydrogen carbonate; in pancreatic juice the reverse obtains. The alkalinity of the duodenal contents corresponds with that which is the optimum for peptolytic (not tryptic) activity. W. D. H.

Effects of Nutrition with Maize. IV. Action of the Succus entericus of the Dog on Zein, Gliadin, Zeoses, and Gliadoses. SILVESTRO BAGLIONI [with G. AMANTEA and L. MANINI] (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 655—660. Compare A., 1911, ii, 999).—The *Succus entericus* of the dog has a weak digestive action on gliadin and an even weaker action on zein, but it has an almost equal digestive action on zeoses and gliadoses of peptic and tryptic origin. R. V. S.

Are the Endogenous Purine Substances the Products of the Activity of the Digestive Organs? FRANZ MAREŠ (*Pflüger's Archiv*, 1912, **149**, 275—286).—Polemical against Sivén (A., 1912, ii, 780; compare following abstract). W. D. H.

The Source of Uric Acid in Man. II. FRANZ SMETÁNKA (*Pflüger's Archiv*, 1912, **149**, 287—317).—This also is a reply to Sivén's criticism on the work of Mareš (A., 1910, ii, 973) and Smetánka (A., 1911, ii, 218). The article is mainly polemical, but does contain some fresh experimental work, and the main conclusions drawn are as follows. Intake of a purine-free diet causes an increase of purine excretion. This is due to nuclear catabolism occurring in and associated with the activity of the digestive glands. The increase lasts five to six hours after a meal; but when much protein is taken with the evening meal it may go on all night. The question whether variations in the protein intake produce variations in the purine

output is not definitely answered. Diets rich in starch act similarly, but less markedly. The original views of Mareš on the question are considered to remain unshaken. W. D. H.

Animal Calorimetry. VII. The Metabolism of a Dwarf. FRANCIS H. McCRUDDEN and GRAHAM LUSK (*J. Biol. Chem.*, 1913, **13**, 447—454).—A dwarf, suffering from infantilism, seventeen years old, and weighing 21 kilos., had a basal metabolism of 775 calories per square metre of body surface in twenty-four hours; this is about the same as in a dog. The metabolism was increased by 6·6% after food, and this again by 14·7% by reading illustrated periodicals in bed. The protein metabolism yielded the normal proportion of 15% of the total calories of heat-production. Nothing abnormal in metabolic processes was detected. W. D. H.

The Part Played by Acid in Carbohydrate Metabolism. Acid Diabetes. HERBERT ELIAS (*Biochem. Zeitsch.*, 1913, **45**, 120—143).—Relatively small amounts of acids, administered to rabbits, can cause glycogen in large quantities to disappear from the liver; this disappearance results in hyperglycæmia and glycosuria in the animals The fact was established by the distinct positive results obtained in a series of researches in animals with livers rich in glycogen, whereas negative results were obtained from animals in which the livers were glycogen-free. The suprarenals take no part in this action, as positive results were obtained when dyspnœa was avoided, during chloral hydrate narcosis, and after cutting the splanchnics. In all cases, furthermore, the histological structure of the suprarenals remained intact. It was shown also, by perfusion experiments through the isolated liver, that adrenaline plays no part in the disappearance of the glycogen. The acid appears to act, therefore, directly on the liver itself. Perfusion experiments on the isolated liver of tortoises indicated that the glycogen separates from the liver cells for the most part unchanged when acid is added to the perfusion fluid.

S. B. S.

Has Heated Milk the Same Feeding Value as Raw Milk? EICHLOV (*Bied. Zentr.*, 1913, **42**, 56—58; from *Mitt. deut. milchwirt. Ver.*, 1912).—Milk when heated loses the property of being coagulated by rennet, and the soluble calcium salts become insoluble; both changes presumably decrease the feeding value of milk.

Experiments in which dogs (ten days old) were fed for several months with fresh milk and boiled milk respectively gave the following results. The bones of the dogs fed with boiled milk, with one exception, contained less ash than when fed with fresh milk; the blood also contained less ash and only about half as much fibrin as the blood of the dogs which had fresh milk. When milk is heated for ninety minutes in boiling water, ammonia and hydrogen sulphide are produced in small amounts; the vapour from the heated milk also contained phosphorus. N. H. J. M.

The Influence of Standing or Lying on the Metabolism of Cattle. HENRY PRENTISS ARMSBY and J. AUGUST FRIES (*Amer. J. Physiol.*, 1913, **31**, 245—253).—Details are given of the increase of metabolism in cattle when they are in a standing as compared with the lying position. The increased emission of heat during the standing periods is accompanied with a correspondingly increased elimination of both carbon dioxide and water. W. D. H.

Nitrogen Retention on Feeding with Urea. EDUARD GRAFE and K. TURBAN (*Zeitsch. physiol. Chem.*, 1913, **83**, 25—44).—A full account is given of metabolic experiments in dogs and pigs which show that retention of nitrogen occurs when urea is added to a carbohydrate rich diet. Sometimes equilibrium was attained; a small part of the nitrogen was excreted in the after period. W. D. H.

Histochemistry of Spermatozoa. III. HERMANN STEUDEL (*Zeitsch. physiol. Chem.*, 1913, **83**, 72—78).—Dried defatted spermatozoa from herrings consists as to three-quarters of nucleic acid and one-quarter of clupeine. The two compounds are united through the free amino-groups of the arginyl groups of the protamine. E. F. A.

The Biochemistry of the Female Genitalia. I. The Lipins (Lipoids) of the Ovary and Corpus Luteum of the Pregnant and Non-pregnant Cow. JACOB ROSENBLOOM (*J. Biol. Chem.*, 1913, **13**, 511—512).—Data are presented showing the percentages of fat, fatty acids, cholesterol, and lipoids in the ovary and corpus luteum of the cow. No increase in these occurs during pregnancy. W. D. H.

The Sulphatide of the Brain. PHŒBUS A. LEVENE (*J. Biol. Chem.*, 1913, **13**, 463—464).—The lipoid of the brain (ox), which contains sulphur, was isolated from the phosphatides; the method is not described. Elementary analyses are given which differ considerably from those of both Thudichum and W. Koch. W. D. H.

The Influence of Quantity and Concentration of Poisons of the Digitalis Group on the Frog's Heart. ARNOLD HOLSTE (*Arch. expt. Path. Pharm.*, 1912, **70**, 435—438).—The experiments recorded show the importance of concentration as a factor.

W. D. H.

Systole and Diastole of the Heart Under the Influence of Digitalin. ARNOLD HOLSTE (*Arch. expt. Path. Pharm.*, 1912, **70**, 439—446).—It is stated that digitalin applied internally to the heart produces systolic standstill, and to the exterior, diastolic standstill. This has been explained by supposing that the outer layers of the cardiac muscle respond differently to the drug from the internal layers. The present experiments show that the medium used is a factor. Fluids which contain blood, or Albanese's solution, always produce stoppage in systole, whereas if Ringer's solution is employed as the medium, the stoppage is diastolic. W. D. H.

Replacement of Urea in Artificial Solutions for the Isolated Heart of Selachians. R. BOMPIANI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 667—672).—Solutions containing urea, when administered by perfusion or otherwise, increase the time of survival of isolated hearts. The author's experiments on isolated hearts of *Torpedo ocellata* and *Scyllium* show that no substance will quite replace urea in this respect, but the derivatives of urea favour the survival more than other substances (methylcarbamide, survival 480 minutes; urea, survival 600 minutes), but the action is less marked the more distantly the substances are related to urea. Neither glycerol, acetone and urethane (although they are soluble in lipoids), nor the amino-acids, glycine, asparagine, aspartic acid and its salts keep the isolated hearts alive. R. V. S.

Toxicological Investigations on Bio-electric Currents. III. Comparative Toxicological Specificity of the Chemical Alteration Current, and Comparative Physiology and Toxicology of the Heart of Helix pomatia. C. LOVATT EVANS (*Zeitsch. Biol.*, 1912, 59, 397—414).—Henze and Hermann have shown that skeletal and heart muscle of the frog responds specifically to poisons, and that the electrical changes run parallel to such action. This thesis is supported by the present investigations on the snail's heart, which is recommended as a convenient object for such work. Its electrogram is very simple, showing a pure diphasic effect, which corresponds with the single peristaltic wave which travels over it. Carbon dioxide acts tonically on it. The heart of the snail is sensitive to potassium, and very resistant to calcium; muscarine has the usual effect, but this is not antagonised by atropine. Antiarin has no action, but strophanthin and saponin are active. W. D. H.

Tolerance for Sugar in the Pig. ANTON J. CARLSON and F. M. DRENNAN (*J. Biol. Chem.*, 1913, 13, 465—468).—Minkowski stated that the removal of the pancreas in the pig did not result in as severe diabetes as in other animals. In the present experiments, fatal diabetes did occur, but it was of slow onset. The pig has a lower tolerance for dextrose than any species so far studied; that is, it becomes glycosuric when quite small amounts of sugar are given by the mouth.

Occurrence of Metals in the Human Liver. LEOPOLD VAN ITALLIE and J. J. VAN ECK (*Pharm. Weekblad*, 1912, 49, 1157—1163.* Compare Lehmann, A., 1896, ii, 486).—An investigation of the corpses of persons of various ages indicates that arsenic is not a normal constituent of the human liver, but that copper and zinc are always present, the proportion of copper being greater during the fœtal period than in later life. Otherwise, age, sex, occupation, and place of residence appear to have no influence on the proportion of copper and zinc. The values given by Lehmann for the amount of copper present are appreciably too low. A. J. W.

* and *Arch. Pharm.*, 1913, 251, 50—55.

The Influence of Iodine on Autolysis. M. KASCHIWABARA (*Zeitsch. physiol. Chem.*, 1912, **82**, 425—438).—Contrary to the statements of Kepinov (A., 1912, ii, 69), autolysis does not occur in a medium containing 0·5% of sodium hydroxide; what does occur there is hydrolysis produced by the alkali; this is only slightly increased by the presence of iodine. In alkali-free mixtures, iodine increases autolysis only in a slight degree. In rabbits which had received an intravenous injection of Lugol's solution, autolysis of the liver is also slightly accelerated, but even the fresh liver of such animals show an increase in non-coagulable nitrogen. W. D. H.

The Catalytic Action of Iron Salts on the Autolysis of the Liver. LUIGI POLLINI (*Biochem. Zeitsch.*, 1912, **47**, 396—404).—Small and large quantities of ferric sulphate and ferric chloride increase the total nitrogen and the nitrogen of the monoamino-acids, proteoses and purine substances in the autolysis products when calves' liver is allowed to autolyse in the presence of these salts. Small quantities of iron citrate exert a weak inhibitory action, whereas larger quantities exert an accelerating action; still larger quantities inhibit the autolysis as regards total nitrogen and the nitrogen of amino-acids. The proteose nitrogen, on the other hand, continually increases with increasing amounts of the iron salt. Very small quantities of iron lactate accelerate the autolysis, but progressingly larger quantities exert a progressive amount of inhibition. S. B. S.

The Physiology of the Thyroid Glands. The Content of Phosphorus, Nitrogen, and Lipoids in the Organs of Thyroidectomised Animals. A. S. JUSCHTSCHENKO (*Biochem. Zeitsch.*, 1913, **48**, 64—85).—The experiments were carried out with young dogs, of which a certain number were submitted to thyroidectomy, and an equal number from the same litter were used as controls. It was found that the organic and total phosphorus was diminished in the thyroidectomised animals in the brain, heart, and spleen, whereas the inorganic phosphorus is increased. In the liver, the changes were similar, but in the muscles the results were indefinite. In the kidneys the amount of phosphorus in all forms, and especially the inorganic, was increased. The nitrogen in the majority of the organs of thyroidectomised animals was increased; this statement does not apply, however, to the kidneys and the serum. In animals with hyperthyroidism the total and organic phosphorus in brain, muscles, and heart are diminished; in the liver, kidneys, spleen, and serum, on the other hand, they are increased. In most organs, the nitrogen content is diminished. In thyroidectomised animals, the lipoids, and all the fractions of the same, are diminished in quantity in the brain, liver, and muscles, whereas they are in increased amount in the serum. In other organs, the lipoid quantity is also less than in the normal. In hyperthyroidism, the content of lipoid in the serum is diminished, whereas no very definite results were obtained by the examination of other organs. The ratios of the nitrogen to phosphorus in various fractions of the lipoids in thyroidectomised animals, and in cases of hyperthyroidism, were also investigated. Thyroidectomy also

causes increase in the content of the purine substances of the organs. Complete thyroidectomy causes at first an increase in the phosphorus : nitrogen ratio in the urine, followed by a diminution of this ratio; the quantity of urea diminishes. The quantity of ammonia at first falls, and then rises; there is apparently an increase in amino-acids and purine bases; the creatinine, on the other hand, diminishes.

S. B. S.

Seasonal Variation in the Iodine Content of the Thyroid Gland. ATHERTON SEIDELL and FREDERIC FENGER (*J. Biol. Chem.*, 1913, **13**, 517—526).—In sheep, ox, and pig there is about three times as much iodine in the thyroid between June and November as between December and May. In the sheep and ox (but not in the pig) the gland is larger during the latter months. W. D. H.

Enzyme Synthesis. IV. Lactase of the Mammary Gland. HAROLD C. BRADLEY (*J. Biol. Chem.*, 1913, **13**, 431—440).—These experiments give no support at all to the theory of enzyme syntheses in tissues, for lactase was never found in the mammary gland, or in the milk. W. D. H.

Muscle Chemistry. IV. The Extractive Nitrogen and the Free Amino-nitrogen, Titratable by Formaldehyde in the Musculature of Different Animals. GIUSEPPE BUGLIA and A. COSTANTINO (*Zeitsch. physiol. Chem.*, 1912, **82**, 439—462. Compare A., 1912, ii, 1077, 1078).—A large number of details of the distribution of nitrogen in muscle in many animals are given, and great variations are met with in both vertebrate and invertebrate animals; but no constant and characteristic features distinguish the musculature of the various animal groups. W. D. H.

Muscle Chemistry. V. Purine Bases of the Smooth Muscle of the Higher Animals. GIUSEPPE BUGLIA and A. COSTANTINO (*Zeitsch. physiol. Chem.*, 1913, **83**, 45—49).—The purine bases of the smooth muscle of the ox (retractor penis) consist of oxypurines; xanthine, probably preformed, exceeds hypoxanthine in amount, which is the opposite to that found in striated muscle. W. D. H.

The Formation of Lactic Acid in the Antiseptic Autolysis of Organs. NICOLAUS SOBOLEV (*Biochem. Zeitsch.*, 1912, **47**, 367—373).—In estimating the lactic acid produced by autolysis of the organs, account was taken of the amount of acid carried down by the coagulum when the autolysis product was heated, the amount withdrawn from the solution in this process being estimated by Mondschein's method. At the ordinary temperature, less lactic acid is formed on autolysis than at 40°. Most organs show a maximum production at this temperature after about thirty-three days, after which the amount diminishes. The maximum production took place in the liver, followed by the spleen, heart, muscles, and kidneys in diminishing order.

S. B. S.

Enzyme Synthesis. II. Diastase and Glycogen of Animal Tissues. HAROLD C. BRADLEY and E. KELLERSBERGER (*J. Biol. Chem.*, 1913, **13**, 419—424).—Tissues rich in diastase may or may not

contain glycogen, and what is more significant from the point of view of the enzyme-synthesis theory, tissues rich in glycogen may or may not contain diastase. W. D. H.

Enzyme Synthesis. I. Lipase and Fat of Animal Tissues. HAROLD C. BRADLEY (*J. Biol. Chem.*, 1913, **13**, 407—418).—No broad correlation exists between the amounts of fat and lipase in tissues. Some of the tissues which actively produce fat may, in fact, contain relatively little lipase, and tissues which are poor in fat may contain a good deal. The experiments afford no support to the theory of enzyme synthesis. W. D. H.

The Influence of the Lipoids on the Action of Oxydases. HORACE M. VERNON (*Biochem. Zeitsch.*, 1912, **47**, 374—395).—If minced tissue is left for half an hour in varying strengths of solutions of a narcotic up to a certain concentration, the narcotic is then washed out and the oxidising power of the tissue tested by *a*-naphthol and *p*-phenylenediamine, it will be found that the oxidising power is either uninfluenced or increased. In higher concentrations the oxydase is injured. Concentrations, twice or three times as large as those necessary to produce initial action, destroy the oxydase completely; thus, for example, acetone first in 4*M*-solution attacks the oxydase, which is destroyed completely in 7*M*-solution. These limits were investigated in several cases. The concentrations of monohydroxy-alcohols, which degrade the oxidative capacity 50%, are about twenty times stronger than those necessary to narcotise tadpoles, whereas in the case of fatty esters and methylurethane, they are twelve times stronger. In poisons other than lipoid-soluble substances, such as formaldehyde, the range of action is larger; thus, 1330 times as much formaldehyde is necessary completely to destroy the oxydase as is necessary to produce the initial action. In the case of the typical narcotic, paracetaldehyde, the relationship of these quantities is only 1·8 : 1. The range of action of ammonia is even greater than that of formaldehyde. Concentrations of narcotics which cause the initial effects are only a little greater than those necessary to hæmolyse red blood-corpuscles. The author draws the conclusion that the action of the indophenol oxydase is dependent on the lipoid, or perhaps the lipoid membrane, which, he considers, holds together the tissue oxydase and the peroxydase, which are thereby enabled to exert their joint action. S. B. S.

The Ferments of the Purine Group. ARTHUR SCHULZ (*Biochem. Zeitsch.*, 1913, **48**, 86—119).—In estimating uric acid in organs, formaldehyde up to 2% was added to the solution, after coagulating the proteins in the presence of sodium chloride and acetic acid. The effect of this addition is to render the uric acid more soluble. It was then estimated in the filtrate in the ordinary way by the Schmid-Krüger method. For investigating the uricolytic ferment, dried organ powders were generally employed. It was found that radium emanations of an activity of 5—10 Mache units per c.c were without any recognisable influence on the uricolytic action of

dogs' liver or ox-kidneys. Radium emanations increase the activity of the uricolytic ferments of ox-spleen, both as regards the formation of uric acid from added purine bases and from those produced by autolysis. The increased amount of uric acid formed varied, under the conditions of the experiments, from 10 to 20%. There was an increase, in the case of autolysis, in the activity of the proteolytic ferments, as shown by the increase in the nitrogen of the uncoagulable substances. This amount was, however, relatively less than the increased amount of uric acid formed. The uricolytic ferments of ox-kidneys are totally inhibited in action by fresh pulp of ox-spleen. Ox-kidney powder can inhibit the purine deamidases and the oxydases of the ox-spleen, but not the autolytic uric acid formation by the same organ. The author did not succeed in producing anti-uricolytic ferments by immunisation of rabbits by organs containing uricolytic ferments. S. B. S.

Creatine, Creatinine, and Monoamino-acids in Certain Fishes, Mollusca, and Crustacea. Y. OKUDA (*J. Coll. Agric. Imp. Univ. Tokyo*, 1912, 5, 25—31).—Seven varieties of fishes were found to contain from 0·421 to 0·754% of creatine and 0·070 to 0·660% of creatinine. Mollusca contained only traces of these compounds, and crustacea only traces, if any at all.

All the marine animals examined contained much more nitrogen as organic bases than in the form of monoamino-acids, the amount of which is usually very small in fish, but somewhat higher in lobsters and cuttle-fish.

Most of the proteins are soluble in dilute alkali solution, and a good deal is soluble in 10% sodium chloride. N. H. J. M.

The Occurrence of Glycogen in Sea-Molluscs (Especially Cephalopods and Aplysiæ). EMIL STARKENSTEIN and MARTIN HENZE (*Zeitsch. physiol. Chem.*, 1912, 82, 417—424).—*Cephalopods* and *Aplysiae* have been stated to be free from glycogen. This is not so; they contain abundance of it. Glycogen is the same substance whether it is derived from vertebrates or invertebrates. W. D. H.

Carbon Metabolism. The Labile and Stable Carbon of the Urine. ENRICO REALE (*Biochem. Zeitsch.*, 1912, 47, 355—366).—The carbon of the urine was estimated by a wet-oxidation process, by oxidation with chromic acid and sulphuric acid, for which a modification of the apparatus of Desgrez (which is figured in the text) was employed. It was found that only about half the carbon in the urine exists in the form of urea. It was also found that a part of the carbon is readily oxidised to carbon dioxide in the presence of hydrogen peroxide when manganese peroxide is used as a catalyst. This is designated by the author "labile carbon," whereas the carbon which is not so oxidised is called "stable carbon." Full experimental details for the estimation of carbon in these two forms are given. S. B. S.

The Intensity of Urinary Acidity in Normal and Pathological Conditions. LAWRENCE J. HENDERSON and WALTER W. PALMER (*J. Biol. Chem.*, 1913, 13, 393—405).—Normal urine ranges

from a concentration of ionised hydrogen of about 4·82 to 7·45; the mean value is 6·00. Pathological conditions occasionally cause a greater acidity, but never unusual alkalinity. No attempt is made at present to generalise, except in cases of cardio-renal disease, where the high mean acidity may indicate a form of acidosis. W. D. H.

The Origin and Destiny of Cholesterol in the Animal Organism. X. The Excretion of Cholesterol in Man when Fed on Various Diets. GEORGE W. ELLIS and JOHN A. GARDNER (*Proc. Roy. Soc.*, 1912, *B*, 86, 13—18. See A., 1912, ii, 275, 958).—In man as in other animals, the excretion of cholesterol in the fæces can be accounted for by that taken in with the food, provided the body-weight remains constant. If, however, a rapid loss of weight takes place, as in illness, the output of cholesterol exceeds the intake.

Further work will be necessary before this view can be regarded as established. W. D. H.

Influence of Alkaline Salts in the Elimination of Urinary Ammonia by Normal Dogs. HENRI LABBÉ (*Compt. rend.*, 1912, 155, 1620—1622. Compare A., 1911, ii, 220).—With dogs in a state of nitrogenous equilibrium on a meat diet, the simultaneous ingestion of ammonium salts and excess of sodium carbonate produces a slightly less elevated elimination of volatile basic nitrogen than when the ammonium salts are ingested alone. The difference is more marked with ammonium carbonate than with ammonium chloride. A large excess of sodium carbonate (about 2 grams per kilo. of body-weight), which provoked great thirst and marked polyuria, did not cause all the basic volatile nitrogen to disappear. W. G.

The Relationship between the Nitrogen of the Amino-acids and Total Nitrogen in Urine under Various Normal and Pathological Conditions. ERNESTO SIGNORELLI (*Biochem. Zeitsch.*, 1912, 42, 482—506).—The experiments were carried out on dogs. The percentage of the amino-acid nitrogen (of the total nitrogen) varied in starvation between 1·09 and 1·30. It showed no very marked increase when oxidation was increased by the animals breathing pure oxygen. The value showed no marked differences when the proteins ingested by the animals were varied (caseinogen, gelatin, gluten, and zein). The percentage was only slightly increased (1·57—2·51) when the hydrolysis products of these proteins were administered subcutaneously. When azoturia was produced by fever, etc., the percentage still remained normal. In phosphorus poisoning, when the functions of the liver were disturbed, it rose to 3·66. Two hypotheses are advanced to account for the approximate constancy of the percentage: (*a*) that in all proteins there is a part which is not readily oxidised, and (*b*) that in the enzyme reaction producing deamidisation there is an equilibrium point at which part of the substance remains unacted on. S. B. S.

The Fat Content of Normal and Pathological Urine. KOZO SAKAGUCHI (*Biochem. Zeitsch.*, 1913, 48, 1—34).—The method

employed for estimating fat was that of Kakiuchi (A., 1910, ii, 549). The amount excreted in a normal adult urine is 0·0085 gram in twenty-four hours, which can be increased to 0·0341 gram after diets containing very large amounts of fat. Out of three cases of nephritis investigated, in only one was the fat excretion regularly above normal. In diabetes, tuberculosis of the lungs, jaundice, and cirrhosis of the liver, the excretion was normal. No extra excretion could be detected in cases of fractures of bones or re-section, and in this respect the results of the author differ from those obtained by earlier investigators. S. B. S.

Urobilin. III. and IV. G. FROMHOLDT and N. NERSESSOV (*Chem. Zentr.*, 1912, ii, 1678; from *Zeitsch., expt. Path. Ther.*, 1912, **11**, 400—407).—The administration of fresh bile leads to the appearance of urobilin in the urine, but this does not occur when pure bilirubin or bile extracted with ether is given. A method of extracting urobilin from blood is described. After preliminary extraction with alcohol and filtration, it is acidified and extracted with amyl alcohol, in which solvent the pigment is detected spectroscopically. If urobilin is absent from the urine, it is also absent from the blood, but when present in the urine it is usually present in the blood as well. W. D. H.

Blood Destruction, Bile and Urobilin. The Formation of Bile Pigment in Blood. III. THEODOR BRUGSCH and KARL RETZLAFF (*Chem. Zentr.*, 1912, ii, 1678—1679; from *Zeitsch. expt. Path. Ther.*, 1912, **11**, 508—525).—Estimations of urobilin in urine and fæces in various cases of liver disease lead to the conclusion that urobilinuria is the clinical expression for a series of substances related to blood and bile pigment. Hæmatogenous or extra-hepatic urobilinuria occurs after extravasation of blood in the tissues; its other cause is usually hepatic insufficiency. If the bile enters the intestine, its pigment is converted into urobilin and re-absorbed; the liver then manifests its insufficiency by being incapable of re-synthesising bile-pigment from the urobilin, which therefore passes into the blood and urine. Urobilin in urine and fæces was estimated by making alkaline with ammonium carbonate and letting the mixture remain at 37° for two days. It was then extracted with light petroleum until Ehrlich's reaction was negative, then acidified with tartaric acid, and extracted with ether. A measured quantity of the ethereal solution was mixed with an ethereal solution of *p*-dimethylaminobenzaldehyde and a few drops of hydrochloric acid in absolute alcohol, and examined chromophotometrically. W. D. H.

The Protective and Curative Properties of Certain Foodstuffs against Polyneuritis Induced in Birds by a Diet of Polished Rice. EVELYN A. COOPER (*J. Hygiene*, 1913, **12**, 436—462).—In pigeons weighing 350 grams, as much as 20 grams of raw beef are necessary daily to prevent polyneuritis; the anti-neuritic value of beef is therefore low. Heart muscle is better, and sheep's brain about twice as efficient as beef. Brain is specially efficient in preventing loss of body-weight which ensues when polished

rice is given. Fish is very inefficient in both directions. Egg-yolk, even if boiled, is the most efficient of all the animal foods examined: 3 grams daily is enough. Dried lentils and unhusked barley are about equal to egg-yolk. Yeast is the most efficient of all foods. The antineuritic and weight-maintaining action of the various foods differs. The weight-maintaining constituents are not protein, fatty or lipoidal. W. D. H.

Congenital Family Steatorrhœa ARCHIBALD E. GARROD and W. H. HURTLEY (*Quart. J. Med.*, 1913, **6**, 242—258).—The details of a curious case of an inborn metabolic error are recorded. The boy (aet. 8) has been subject since infancy to the passage of liquid fat from the bowel; one cooling it solidifies; another brother who died in infancy had the same defect. Health was apparently unaffected; the stools contained 25% of the fat in the food; with an intake of 177 grams of fat only 4% was split; this figure rises when the intake is less, but even then it is not absorbed. Sodium glycocholate and various pancreatic preparations increased fat-splitting, but not the absorption; indeed, the latter aggravated the condition.
W. D. H.

The Mechanism of the Action of Silver Haloids. OSKAR GROS (*Arch. expt. Path. Pharm*, 1912, **70**, 375—406).—Colloidal silver chloride and iodide intravenously injected in rabbits are strongly toxic, and the chloride is more so, even though the concentration of silver ions is the same in both cases. This is considered to be due to the formation of a complex of the silver salt and the chlorides of the blood plasma which is more readily carried to the tissue cells. Sodium iodide, which is non-toxic if given simultaneously, increases the poisonous action of silver iodide. This is explained on similar lines. In vitro, both salts are hæmolytic, and again the chloride is more effective, but here sodium iodide does not increase the action of silver iodide. W. D. H.

A Physiological Series of Cations. N. K. KOLTZOV (*Pflüger's Archiv*, 1912, **149**, 327—363).—The observations were made on the effect of salt solutions on the vitality and contractility of a marine infusorian (*Zoothamnium alternans*). They follow in the main the work of Overton and others who have bestowed attention to osmotic phenomena and the rôle of the plasmatic membrane of cells. If chlorides are employed throughout, the cations are arranged in the following order: K, Rb, Na, Cs, NH_4, Li, Sr, Mg, and Ca. Each member of the series lowers the surface tension of plasma-water less than the succeeding one, and toxicity runs parallel with the adsorption of the cations. W. D. H.

Temporary Fixation and Mode of Elimination of Manganese in the Rabbit. GABRIEL BERTRAND and FLORENTIN MEDIGRECEANU (*Compt. rend.*, 1912, **155**, 1556—1559).—Four rabbits received repeated subcutaneous injections of manganous sulphate in varying doses, and the effect on their weight and length of life was noted.

Even with minute doses there was a marked loss in weight, and three injections of 5 mg. of manganese per kilo. of body-weight, at intervals of twenty-four hours, caused the death of the rabbit. The amount of manganese in the various organs of the four rabbits and of an uninjected rabbit was determined, and the results show that manganese, when subcutaneously injected, is rapidly diffused throughout the body, and all the tissues, including the nervous tissue, become temporarily impregnated. It is readily eliminated through the liver, bile, and mucus of the alimentary canal, and a small quantity is excreted in the urine. W. G.

The Action of Certain Substances of the Chloroform Group on the Vestibular Eye-Reflex. J. ROTHFELD (*Pflüger's Archiv*, 1913, **149**, 435—446).—Nystagmus (vestibular eye-reflex) disappears under the influence of narcotics; first vertical, then rotatory, and finally horizontal nystagmus. As anæsthesia passes off, they reappear in the reverse order. The substances employed in the research were chloroform, ether, chloral hydrate, and paracetaldehyde. The differences in detail between these four substances are treated at length. W. D. H.

The Fixation of Digitoxin (Merck) in the Organism of the Rabbit after Intravenous Injection. Comparative Experiments with Strophantin-*g*. CAMILL LHOTÁK VON LHOTA (*Biochem. Zeitsch.*, 1913, **48**, 144—154).—If digitoxin is injected intravenously into rabbits, it disappears almost immediately from the blood (as ascertained by tests on the frog's heart), even when ten times the lethal dose is employed and the conditions of the animal are favourable. These conditions are, that the heart should be active, and the functions of the blood-vessels intact. If these are interfered with in any way (by narcosis, etc.), digitoxin can be detected in the blood when only twice the lethal dose has been employed. After injection of ten lethal doses, the digitoxin can be detected in all organs, especially the heart and liver. The greater the length of the circulatory system the drug must travel from the point of injection to reach the heart, the greater is the dose necessary to produce the specific action, This fact indicates that the drug is fixed by the vessels as well as the heart, and was demonstrated by experiments on animals with crossed circulatory systems. The drug can also be detected chemically at the point of application. Intravenously injected strophantin-*g* only disappears immediately from the blood in small quantities. S. B. S.

The Fate of Proline in the Animal Body. HENRY D. DAKIN (*J. Biol. Chem.*, 1913, **13**, 513—516).—When proline is added to blood, and the mixture perfused through the surviving liver of a dog, there is no increase in the formation of acetoacetic acid; but in the glycosuric animal it causes a marked increase in the sugar output. The formation of dextrose from proline involves the disruption of the ring. Glutamic acid also yields sugar (Lusk); so also do arginine and ornithine. The close structural relationship of glutamic acid, ornithine, and proline is shown graphically. W. D. H.

The Results of Poisoning with Adrenaline, Histamine, Pituitrin and Peptone in Relation to Anaphylaxis and the Vegetative Nervous System. ALFRED FRÖHLICH and ERNST P. PICK (*Arch. expt. Path. Pharm.*, 1912, **71**, 23—61).—The substances mentioned in the title greatly lessen or abolish the excitability of the autonomic nervous system, both to faradic stimuli and to drugs. The same occurs in "peptone immunity" and in anti-anaphylaxis. As both these phenomena soon disappear, they are separable and reversible. The effect of the poisons is a selective one on the nerve endings. A considerable amount of the work recorded was performed on the uterus, and it was then found that after the use of histamine, adrenaline and pilocarpine had no effect, and pituitrin very little. After treatment with tyramine, pituitrin, histamine and adrenaline act normally; after treatment with pituitrin, adrenaline acts normally; after peptone, pituitrin, tyramine and adrenaline have no action. Barium chloride locally applied to the uterus causes contraction of the uterus after it has been rendered inexcitable by histamine, tyramine, or peptone. W. D. H.

The Pharmacological Action of *p*-Hydroxyphenylethylamine. A. BICKEL and MICH. PAVLOV (*Biochem. Zeitsch.*, 1912, **47**, 345—354).—This substance, which can be isolated from ergot, shows the following actions. When 1—2 c.c. of a 0·5% solution are injected into rabbits or dogs of medium size, the arterial blood-pressure, after a short-lasting fall, rises, remains high for two or three minutes, and then sinks to normal. This is due to a contraction of the capillaries, with a consequent diminution of the amount of blood in the veins, which was detected by the measurement of the blood-flow in the venous system. As a further consequence there is a diminution of volume of organs which have a well-developed venous supply. This fact was demonstrated directly by the measurement of changes produced in the kidneys after the injection of the drug, and indirectly by the changes in the intestinal volume after injection of extracts of *Secale cornutum*. S. B. S.

Action of Scopolamine (Hyoscine). ARTHUR R. CUSHNY (*Arch. expt. Path. Pharm.*, 1912, **70**, 433—434).—A criticism on the work of Hug (A., 1912, ii, 790), who finds, like the author, that *l*- and *i*-hyoscine differ in their action on nerves. The quantitative differences between the two workers are explained as due to differences in the methods used. W. D. H.

The Method of Action of Quinine. J. MOLDOVAN (*Biochem. Zeitsch.*, 1912, **47**, 421—446).—The action on *Colipidia* is to cause a change in the state of the colloids of the protoplasm, leading to a separation of droplets of lipoid character, and producing a change in the osmotic relationship of the protoplasm to its surroundings; afterwards the nucleus and motility of the cell are injured, and finally death results. The cause of death is the stoppage of oxygen respiration. In the case of trypanosomes, the action is similar, but the separation of droplets is less marked, owing to the smaller content of lipoids. Similar actions were also observed on plant cells. There is a con-

siderable difference of behaviour in the individual cells as regards the resistance to the action of quinine, which depends on the energy of the oxygen respirations; older cells appear to be more resistant than young cells. The combined effect of two toxins on the cells is not the sum of the effect of each individual toxin, but depends, amongst other factors, on the relative concentrations of the two. In rabbits and guinea-pigs, the action of quinine is to diminish the oxidative processes, especially in the brain. This fact was demonstrated by various methods of intra vitam staining (according to the method of Ehrlich, etc.). The quinine in influencing the oxidative process does not effect the oxygen taken up, but acts as an anticatalyst. In view of the first action of quinine on cells, in causing the separation of the lipoids, it can act as a narcotic or local anæsthetic. To produce general narcosis, however, the required dose is so high that it acts deleteriously on the respiration, and it cannot therefore be used in practice for this purpose. S. B. S.

Influence of the Constitution of Purine Derivatives on their Action with Respect to Arterial Pressure. ALEXANDRE DESGREZ and DORLÉANS (*Compt. rend.*, 1913, **156**, 93—94).—Whilst guanine on intravenous injection into a rabbit causes a diminution in the arterial blood pressure (compare A., 1912, ii, 585), hypoxanthine, xanthine, and uric acid exert a hypertensive action. The increase in pressure, whilst slight for hypoxanthine, is greater for xanthine and still greater for uric acid. From this it appears that the guanine owes its hypotensive action to the presence of the amino-group in its molecule. The action of these substances, especially of uric acid, is of interest in the pathogenesis of arthritic diseases, in which Bouchard has shown that there is marked arterial hypertension. W. G.

The Biological Action of Certain Protein Products Introduced Parenterally. ALFRED SCHITTENHELM and WOLFGANG WEICHARDT (*Chem. Zentr.*, 1912, ii, 1680; from *Zeitsch. Immunitäts-forsch. exper. Ther.*, 1912, **14**, 609—630).—The simple and conjugated proteins introduced into the blood stream are relatively innocuous; but the protein constituents of conjugated proteins (globin, histone, protamine) cause great depression of blood pressure, affect breathing and temperature, and lead in quite small doses to death. This has been attributed to the high percentage of diamino-acids they contain, but this cannot be the case because histone is poor in such acids, and certain kyrines rich in them are not toxic. Such proteins when united to nucleic acid or to hæmochromogen in the case of globin lose their toxicity. Toxic symptoms which occur when hæmolysis takes place in the blood stream may be due to the liberation of the poisonous globin (proteinogenous cachexia). W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

The Relation of Concentration of Food-supply to the Generation Time of Bacteria. W. J. PENFOLD and (Mrs.) DOROTHY NORRIS (*J. Hygiene*, 1913, **12**, 527—531).—The generation time of *B. typhosus* in 1% peptone at 37° is forty minutes. If the peptone solution is less than 0·2% in strength the generation time is inversely proportional to the concentration. The addition of 0·17% of dextrose to a medium containing only 0·1% of peptone lowers the generation time by 50%; with 1% peptone this effect is less marked.

W. D. H.

The Bactericidal Properties of Blood Serum. I. The Reaction Velocity of the Germicidal Action of Normal Rabbit Serum on the Bacillus coli commune, and the Influence of Temperature Thereon. (Miss) HARRIETTE CHICK (*J. Hygiene*, 1913, **12**, 414—535).—The action *in vitro* of rabbit serum on *B. coli* consists of several phases, the duration of which is inversely proportional to temperature. Its germicidal action follows the logarithmic law, and so falls into line with other cases of disinfection. Its temperature-coefficient is low (2·84 to 1·93). W. D. H.

Chemical Action of Bacillus cloacæ (Jordan) on Citric and Malic Acids. JAMES THOMPSON (*Proc. Roy. Soc.*, 1912, *B*, **86**, 1—12).—The respiratory coefficient for malic and citric acids was determined and found to be 1·63 and 2·35—3·2 respectively.

In the presence of oxygen, *B. cloacæ* decomposes malic acid with the production of carbon dioxide, acetic acid, succinic acid, a small quantity of fatty substance, and traces of alcohol. It is suggested that the action probably goes on in two ways: an oxidation of acid to carbon dioxide and acetic acid by atmospheric oxygen, and an oxidation accompanied by reduction of a portion of the acid to succinic acid. The organism does not attack malic acid in the absence of oxygen.

The products resulting from the decomposition of citric acid are the same as from malic acid. Under aerobic conditions the amount of acetic acid is greater, whilst anaerobic conditions lead to an increase in the production of acetic and formic acids. Acetylmethylcarbinol is not formed by the action of *B. cloacæ* on malic or citric acids.

H. B. H.

The Degradation of Polypeptides by Bacteria. II. The Action of the Non-liquefying Organisms TAKAOKI SASAKI (*Biochem. Zeitsch.*, 1912, **42**, 462—471. Compare A., 1912, ii, 669).—Organisms which are incapable of liquefying gelatin contain nevertheless an erepsin-like ferment capable of hydrolysing glycyl-glycine and glycyl-*l*-tyrosine. Relatively large quantities of tyrosine could be isolated as a result of the action. This action was demonstrated

by typhus and various strains of paratyphus bacilli, various bacilli of dysentery, bacilli of mouse typhus, chicken cholera, and *Micrococcus tetragenus*. S. B. S.

The Degradation of Polypeptides by Bacteria. III. The Action of Liquefying Organisms. TAKAOKI SASAKI (*Biochem. Zeitsch.*, 1912, **47**, 472—481).—Glycyl-glycine and glycyl-*l*-tyrosine were hydrolysed (in Fränkel's solution) by the following strains. Bacilli of splenic fever, *Staphylococcus pyogenes aureus*, *citreus*, and *albus*, *B. subtilis*, *B. proteus vulgaris*, *B. pyocyaneus*, *B. prodigiosus*, cholera vibrio, and the vibrios of Metchnikov and Dunbar and the water vibrio. S. B. S.

Production of Citric Acid from Glycerol by Fungi. CARL WEHMER (*Chem. Zeit.*, 1913, **37**, 38—39. Compare A., 1893, ii, 591; 1909, ii, 602; 1910, ii, 60, 61).—When two species of *Citromyces* were grown in nutrient solution containing ammonium nitrate, potassium phosphate, magnesium sulphate, calcium carbonate, and glycerol (3—20%), large quantities of citric acid were produced. In the absence of calcium carbonate no such accumulation occurs, and it is assumed that, in the absence of any neutralisable base, any citric acid formed is destroyed immediately by the fungi. Similar growth takes place when the glycerol is replaced by sucrose, lactose, mannitol, xylose or arabinose. Sucrose is inverted, and reducing substances are formed in cultures supplied with glycerol. The author discusses the mechanism of citric acid formation from glycerol, and contests the view advanced by Mazé, that acid is only produced when there is a deficiency of nitrogen, or that it is in any way due to a lack of iron or zinc. H. B. H.

Action of Hydrogen Ions, Boric Acid, Copper, Manganese, Zinc, and Rubidium on the Metabolism of Aspergillus niger. H. J. WATERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 753—764).—In investigating the culture conditions of *Aspergillus niger* it is not sufficient to merely ascertain the dry weight produced, as was done by Raulin and others. Spore formation, for instance, produces differences in composition. It is, therefore, desirable to determine the changes of the plastic equivalent, or of the assimilation quotient, several times during development.

Addition of 2·35 c.c. of *N*-sulphuric acid to 100 c.c. of culture solution and of 0·5% of boric acid has very slight effect on the plastic equivalent of the carbon.

A high weight of mycelium is not always a favourable indication. It was found that certain concentrations of copper sulphate, zinc chloride and sulphate considerably increase the plastic equivalent of the carbon, whilst the increase in the weight of mould is proportional to the retarded spore production. Very dilute zinc solutions have no effect; copper salts, in all dilutions, counteract spore formation. Minimal quantities of manganese do not alter the plastic equivalent of the carbon, but only affect the rate of metabolism. The amounts of dry matter found by Bertrand should be considered as values indicating the velocity of the process.

When potassium is replaced by rubidium, spore formation is checked, the weight of mould increased, whilst the metabolism of the carbon remains the same. N. H. J. M.

Influence of Zinc, Magnesium, Calcium, Potassium. and Sodium Salts on the Growth of Aspergillus niger. J. BUROMSKI (*Centr. Bakt. Par.*, 1912, ii, **36**, 54—66. Compare A., 1908, ii, 124; 1911, ii, 222, 421, 664; 1912, ii, 377, 861).—The fungus was grown in a medium consisting of ammonium sulphate or nitrate 1%, sucrose 5%, magnesium sulphate 0·25%, monopotassium phosphate 0·5%, traces of ferrous sulphate, and distilled water. The addition of zinc sulphate in the proportion of 0·001—0·1% led to an increase in the respiratory coefficient (carbon dioxide crop): that of the control and treated cultures respectively being 1·8 and 2·4 at 30°, and 2·8 and 3·5 at 20°. The addition of calcium sulphate to magnesium-free medium decreased the growth of the organism; 0·25% magnesium sulphate to magnesium-free medium increased the crop very greatly, whilst calcium and magnesium sulphates increased the growth still more. The presence of calcium salts prevents the accumulation of oxalates in the cultures. Magnesium sulphate may be beneficially increased to 0·5%, although fructification begins to be affected at this concentration. Sodium salts proved to be without value, but increasing amounts of potassium salts caused corresponding increases of growth. Magnesium and potassium salts therefore, not only serve as nutrients, but also exercise a stimulative action. H. B. H.

Enzymatic Nature of Uric Acid and Hippuric Acid Fermentation. ALEXANDER KOSSOWICZ (*Chem. Zentr.*, 1912, ii, 1300, 1482; from *Zeitsch. Gährungsphysiol*, **1**, 121—123, 317—319. Compare this vol., i, 146).—Filtered solutions from cultures of *Aspergillus niger*, *Mucor Boidin*, *Phytophthora infestans*, *Isaria farinosa*, and *Botrytis bassiana*, in which urea was present as only source of nitrogen, liberated ammonia from uric and hippuric acid, and from the latter, benzoic acid as well. A filtrate from *Cladosporium herbarum* only showed distinct production of ammonia in the case of uric acid. Similar results were obtained by means of the alcohol precipitates obtained from the filtrates from *Aspergillus* and *Cladosporium*.

Referring to Shibata's negative results with *Aspergillus niger* and uric acid, it was found in similar experiments that *Aspergillus niger*, *Mucor Boidin*, *Phytophthora infestans*, *Isaria farinosa*, *Botrytis bassiana*, and *Cladosporium herbarum* all produce ammonia from uric acid, and that all, except *Cladosporium*, decompose hippuric acid with production of ammonia and benzoic acid. N. H. J. M.

The Rate of Fermentation as Measured by Difference of Potential. M. C. POTTER (*Proc. Univ. Durham Phil. Soc.*, 1912, **4**, 230—231. Compare *ibid.*, 1910, **3**).—It has been shown previously that during the fermentation of sugar by yeast an *E.M.F.* is developed. The author now finds that the measurement of the rate of fermentation by the development of the *E.M.F.* and by the evolution of carbon dioxide as in Slator's method are in close agreement, so that the electrical method provides a ready means of determining the rate of fermentation

Experiments are also quoted, showing that the carbon dioxide given off during fermentation carries an electric charge, and that the rate of fermentation is uninfluenced by the potential of the fermenting liquid.
F. B.

Fermentations with Yeast in the Absence of Sugar. IX. Fermentation of Keto-acids by Wine Yeasts. CARL NEUBERG and J. KERB (*Biochem. Zeitsch.*, 1912, **47**, 405—412).—Wine yeasts, of which a large number of German varieties were investigated, exert the same action on pyruvic acid as the beer yeasts, giving rise to acetaldehyde (which was isolated as its *p*-nitrophenylhydrazone) and carbon dioxide. These yeasts also attack oxalacetic acid and α-keto-*n*-butyric acid.
S. B. S.

Fermentations with Yeast in the Absence of Sugar. X. The Fermentation of α-Ketobutyric Acid CARL NEUBERG and J. KERB (*Biochem. Zeitsch.*, 1912, **47**, 413—420).—This acid is very readily attacked by various yeasts and yeast preparations. The actual course of fermentation is not yet ascertained, in that propaldehyde could only be isolated in small quantity (about 4%). α-Ketoglutaric acid is also very readily attacked; phenylpyruvic acid is also fermented, but not $\alpha\gamma$-diketovaleric acid.
S. B. S.

The Acidification of Musts by Yeasts during Alcoholic Fermentation. AUGUSTE FERNBACH (*Compt. rend.*, 1913, **156**, 77—79). A study of the influence of the original acidity of the medium on the production of acids during the fermentation by yeasts of a saccharine liquid. Even in varying conditions the results show that the acidification produced by the yeasts, independently of their individual character, is subject to the acidity of the medium in which they function, low acidity in the medium favouring high acid production.
W. G.

Fixation of Elementary Nitrogen by Yeasts, Monilia candida, and Oidium lactis. ALEXANDER KOSSOWICZ (*Bied. Zentr.*, 1913, **42**, 68—69; from *Zeitsch. Gährungsphysiol*, **1**).—The results of experiments with (1) *Saccharomyces Pastorianus III Hausen*; (2) *Monilia candida*; (3) *Saccharomyces membranaefaciens*; (4) *Saccharomyces anomalus*; (5) *Oidium lactis*, cultivated in solutions containing sucrose (5%), glucose (0·2%), and mannitol (0·2%), in addition to minerals, showed in three months the following gains of nitrogen: (1) 4·8 and 5·2; (2) 6·2 and 6·8; (3) 6·9; (4) 7·4, and (5) 4·8 and 5·8 mg.

The air in the flasks was freed from combined nitrogen.
N. H. J. M.

Mode of Action of Dilute Solutions of Electrolytes on Germination. HENRI MICHEELS (*Bull. Acad. roy. Belg.*, 1912, 753—765. Compare A., 1910, ii, 883).—Germination experiments with wheat in electrolysed and non-electrolysed N/100-potassium chloride solutions through which chlorine was passed showed that chlorine was rendered more favourable by the cathode liquid and was poisonous in the non-electrolysed solution.

In the case of potassium hydroxide (25 c.c. of a 0·1% solution added to 500 c.c. of *N*/100-potassium chloride), a very injurious effect was observed in the non-electrolysed solution; its toxicity was diminished in the anodic liquid, but only in a slight degree.

Copper sulphate (*N*/200) in anodic solution, which is acid, is more toxic than the cathodic solution, which is only slightly acid. The solution is toxic when not electrolysed.

Comparing *N*/100-potassium chloride with electrolysed solutions in which the cathodic and anodic liquids received hydrochloric acid and potassium hydroxide respectively, the best results were obtained in the non-electrolysed solution and in the cathodic liquid notwithstanding the acidity, whilst the disappearance of the acidity of the anodic liquid only slightly diminished its toxicity.

The conclusion is drawn that anodic and cathodic liquids owe their characters in part to the liberated cations and anions, not passed to the chemical state. In solutions of electrolytes, the action of cations would not be exclusive, but only preponderating. N. H. J. M.

Effects of Manurial Salts on the Germination of Different Plants. ALBERT RUSCHE (*J. Landw.*, 1912, 60, 305—365; from *Diss.*, Göttingen, 1912).—Potassium chloride does not act unfavourably on the germination of cereals, peas, rape, and beet, but is unfavourable in the case of clovers, serradella, lucerne, and lupins, especially white clover and serradella. Sodium chloride is more unfavourable than potassium chloride, except with barley, lupins, serradella, and rape. Magnesium and calcium chlorides generally have the same effect as potassium chloride, but not in every case; whilst ammonium chloride is injurious, especially with clovers. Nitrates are generally more favourable than chlorides; ammonium nitrate, however, resembles the chloride. Potassium sulphate is generally favourable, except with serradella; sodium sulphate is similar in its effects, whilst magnesium and calcium sulphates are also favourable. Of all the salts employed, sodium and potassium carbonates are the most favourable.

As regards the length of roots, nitrates produced the shortest roots with cereals. The longest roots were obtained with sulphates and phosphates.

In the case of peas the longest roots were obtained when no manure was employed. With red clover the longest roots were produced under the influence of sulphates and carbonates, the shortest with carbonates and chlorides.

The full results relating to germination, length and weight of roots, and the development of the above-ground parts of the different plants are given in numerous tables. N. H. J. M.

Influence of Previous Conditions on the Value of the Respiratory Quotient of Green Leaves. LÉON MAQUENNE and EM. DEMOUSSY (*Compt. rend.*, 1912, 156, 28—34).—The authors have studied a number of abnormal cases where the respiratory quotient of leaves gathered in full sunlight was considerably lower than that of leaves which had been kept in the dark for several hours. They worked with leaves of sorrel, stonecrop, geranium, rhubarb, and *Sedum*

acre, and from their results they consider that the respiration of a plant is effected in two successive phases; the first leading to a production of fixed acids, the result of an oxidation rendered incomplete owing to the slowness of penetration of the oxygen; the second to a combustion of these acids. It is necessary also to take into account the solution of the carbon dioxide in the cell-sap and the temperature, which has an influence both on the acidification and the absorption of carbon dioxide by the leaf.

Working with an *Aspidistra* leaf and observing the variation of pressure, using their manometric measuring apparatus (compare A., 1912, ii, 1201), they find that with leaves taken straight from the sunlight the pressure at first diminishes and then rises, whilst with leaves kept in the dark for some hours before measuring, the pressure rises immediately and continuously. W. G.

Hydrolysis and Displacement by Water by Nitrogenous and Mineral Substances Contained in Leaves. GUSTAVE ANDRÉ (*Compt. rend.*, 1912, **155**, 1528—1531. Compare A., 1912, ii, 198).—Chestnut leaves show much the same loss of nitrogen, phosphoric acid, and potassium, by exosmosis, when steeped in water, as do grains of wheat and haricot beans (compare A., 1912, ii, 591). After 255 days steeping, the leaves had lost 6·27% of their nitrogen, 74·14% of phosphoric acid, and 94·58% of potassium. Most of the loss occurred in the first few days, and it was found to be more rapid the younger were the leaves. W. G.

Does Potassium Participate in the Building Up and Degradation of Carbohydrates in Higher Plants? JULIUS STOKLASA and E. SENFT (*Zeitsch. landw. vers. Oesterr.*, 1912, **15**, 711—736).—It is found that by the action of ultraviolet rays on nascent carbon dioxide and hydrogen in the presence of potassium hydroxide a photosynthesis occurs with the formation of formaldehyde, and that the latter subsequently condenses to furnish sugars; the reduction of carbon dioxide in the cell does not take place in the absence of potassium hydrogen carbonate, even in the presence of nascent hydrogen; and formic acid (which is subsequently reduced) is also found to be one of the products of this reaction. F. M. G. M.

Enzyme Synthesis. III. Diastase and Starch of Plant Tissues. HAROLD C. BRADLEY and E. KELLERSBERGER (*J. Biol. Chem.*, 1913, **13**, 425—430).—With some exceptions the results in this series are more favourable to the view of enzyme synthesis in the tissues, for no tissues which contain starch are destitute of diastase, although many tissues which contain diastase are free from starch.

W. D. H.

Occurrence of Arsenic in the Vegetable Kingdom. F. JADIN and A. ASTRUC (*J. Pharm. Chim.*, 1912, [vii], **6**, 529—535).—The occurrence of arsenic in the vegetable kingdom appears to be general, as the authors have detected its presence in some sixty-seven different kinds of vegetables, fruits, cereals, plants, parasitic plants, fungi, etc.

The quantity of arsenic found per 100 grams of substance varied from 0·008 mg. in dates to 0·266 mg. in radishes. Parasitic plants contained arsenic, even although they were not in direct contact with the soil, but there was no relation between the amounts of arsenic in the parasite and its support. Plants belonging to the same family do not invariably contain similar quantities of arsenic, but in the case of one and the same plant the portions containing chlorophyll contained more arsenic than the parts not exposed to light. It is pointed out that one of the sources of the arsenic found in animal organs lies in the vegetable substances consumed as food. W. P. S.

Stimulative Action of Manganese and Copper Sulphates on Plants. L. MONTEMARTINI (*Bied. Zentr.*, 1913, **42**, 65; from *Staz. sper. agrar. ital.*, 1911, **41**, 564).—Manganese and copper sulphates absorbed from aqueous solutions stimulate respiration, the effect varying with different plants. Vine plants are stimulated by 0·001% manganese sulphate, whilst greater concentrations are injurious, and are injured by 0·01% of copper sulphate. Garden beans, and still more potatoes leaves, are more resistant and more stimulated.

N. H. J. M.

Demonstration of Carotinoids in Plants. Separation in Crystalline Form. C. VAN WISSELINGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 511—526).—The various methods employed in detecting the presence of carotinoids are described. Indications were obtained that several distinct carotinoids frequently occur in plants.

N. H. J. M.

Demonstration of Carotinoids in Plants. Behaviour of Carotinoids towards Reagents and Solvents. C. VAN WISSELINGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 686—692).—In presence of carotinoids a blue coloration is produced by strong sulphuric, sulphurous, and nitric acids, bromine water, and strong hydrochloric acid with a little phenol or thymol; iodine dissolved in potassium iodide solution or chloral hydrate gives a green coloration. Two new reagents were also employed: concentrated solutions of antimony trichloride and of zinc chloride, both in 25% hydrochloric acid, which colour crystals of caratinoids dark blue.

Lists of flowers and other parts of plants which were tested with the different reagents are given. N. H. J. N.

Demonstration of Carotinoids in Plants. Leaf of Urtica dioica, the Flower of Dendrobium thyrsiflorum and Hæmatococcus pluvialis. C. VON WISSELINGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 693—700).—The flower of *Dendrobium thyrsiflorum* contains two carotinoids, one of which, of a reddish-orange colour, is not common in plants, and perhaps belongs to the xanthophylls. The examination of *Haematococcus pluvialis* indicated the presence of a greater number of carotinoids than have hitherto been detected (compare Zopf, *Biol. Centr.*, 1895, **15**, 417; H. C. Jacobson, *Folia Microbiol*, 1912, **1**, 24). N. H. J. M.

Mannitol in the Sap of Asparagus. E. Busolt (*J. Landw.*, 1912, **60**, 393—396).—The mannitol in the sap of asparagus is produced by fermentation, and is not originally present.

N. H. J. M.

Presence of Stachyose in the Haricot and in the Seeds of Some Other Leguminoseæ. Georges Tanret (*Compt. rend.*, 1912, **155**, 1526—1528).—The author has isolated stachyose in a crystalline form, by means of its strontium compound, from the haricot bean and the seeds of certain other leguminoseæ, namely, lentils, clover, galega, lupin, and the soja bean. In all cases sucrose was present as well. The lupeose, obtained as an uncrystallisable syrup from haricots and lupins by Schulze, was, therefore, stachyose in an impure state. No stachyose could be isolated from pea-seeds.

W. G.

Presence of Adenine and Aspartic Acid in Mulberry Leaves. Z. Mimuroto (*J. Coll. Agric. Imp. Univ. Tokyo*, 1912, **5**, 63—65).—From 500 grams of air-dried mulberry leaves, 1·2 gram of adenine (as picrate) and 0·3 gram of aspartic acid were obtained.

N. H. J. M.

Action of Stimulants on Rice. Manuel Rocas (*Bied. Zentr.*, 1913, **42**, 41—42; from *Philippine Agric. Forester*, 1912, **1**, 89).—Previous investigations indicate that there are no poisons which cannot act as stimulants on plants; that compounds of gold, silver, platinum, mercury, tungsten, palladium, copper, nickel, cobalt, boron, tin, cadmium, tellurium, arsenic, iodine and fluorine are poisonous, whilst chromium, manganese, bismuth, sulphur and magnesium are only poisonous under certain conditions.

The following concentrations of the various compounds were found to be favourable: sodium borate, 1/1000; manganese sulphate, 1/1000; ferrous sulphate, 1/1000; ferric chloride, 1/5000; copper sulphate, 1/2000; nickel sulphate, 1/5000; cobalt nitrate, 1/10,000, and zinc sulphate, 1/1000 mol. solutions.

Mercuric chloride in 1/50,000 mol. solutions inhibited growth, whilst ferric chloride and copper sulphate (1/1000) are injurious, and sodium borate (1/100) somewhat injurious.

The optimum results for rice are generally much higher than previous experiments have shown for other plants. The experiments were, however, not made with water-cultures, but in soil. N. H. J. M.

Presence of Nicotinic Acid in Rice Bran. Umetaro Suzuki and S. Matsunaga (*J. Coll. Agric. Imp. Univ. Tokyo*, 1912, **5**, 59—61).—Nicotinic acid was obtained from rice bran, freed from fat, by extracting with 80—85% alcohol. The acid had not previously been found in any vegetable substance. The yield of picrate amounted to about 1 gram from 1 kilo. of bran. N. H. J. M.

The Substitution of Different Chemical Elements for Zinc in the Culture of Sterigmatocystis nigra. Maurice Javillier (*Compt. rend.*, 1912, **155**, 1551—1552).—The author has

replaced the zinc in the culture medium of *Sterigmatocystis nigra* by a wide range of other elements, and, with the exception of one, namely, cadmium, they were all without influence on the crop. While the addition of zinc to the extent of 1 in 10,000,000 produces a crop 6·2 times as great as in its absence, the same concentration of cadmium produces a crop only 2·6 times as great, and cadmium has a marked injurious effect on the sporulation. W. G.

Volatile Aliphatic Acids of Corn Silage. ARTHUR W. DOX and RAY E. NEIDIG (*J. Amer. Chem. Soc.*, 1913, **35**, 90—93).—With reference to the work of Hart and Willaman (Abstr., 1912, ii, 1205) on the volatile fatty acids and alcohols in maize silage, the authors draw attention to their own paper on the subject (*Iowa Agric. Exp. Sta., Research Bull.*, 1912, 7, 32). The results are in fair agreement, except with regard to formic acid and methyl alcohol; in the latter investigation, only traces of formic acid were found and methyl alcohol was absent, whereas Hart and Willaman found 17% of formic acid in the volatile acids and 21% of methyl alcohol in the alcohols. Certain sources of error are pointed out in the methods employed by Hart and Willaman, and it is considered that these may account for the discrepancies. E. G.

Action of Long-continued Exclusive Manuring on Plants and Soils. S. GRAF ROSTWOROWSKI (*J. Landw.*, 1912, **60**, 371—392). —The results of experiments with potatoes showed that, when there is a tendency to leaf curl, it is desirable to employ potassium salts in moderation.

As regards the effect of manures on the composition of potato ash it was found that the ashes of potatoes from plots manured with potassium and with potassium + phosphorus + nitrogen were almost identical in composition, and there was also no difference between the ashes of potatoes from plots manured with nitrogen and the unmanured plot.

The composition of the ash of potato leaves varied considerably with different manures; potash varied from 5% (unmanured) to 33% (potassium manure), and lime varied from 21% (potassium alone, or with phosphorus and nitrogen) to 41% (unmanured). Application of sodium nitrate resulted in a high percentage of sodium in the leaf ash.

Notwithstanding the long-continued application of potassium manures, the potash in the ash of the tubers never reached 60%.

Experiments were also made to ascertain the effect of the long-continued manuring on the soil. N. H. J. M.

Chemical and Physical Nature of "Roterden." EDWIN BLANCK (*J. Landw.*, 1912, **60**, 397—400).—A reply to Hissink (A., 1912, ii, 981; compare van der Leeden and Schneider, *Internat. Mitt. Bodenkunde*, 1912, **2**, 81). N. H. J. M.

Analysis of a Florida Clay. ARCHIBALD A. HALL (*Proc. Univ. Durham Phil. Soc.*, 1912, **4**, 228—229).—The author gives an analysis of a clay subsoil underlying peat, from Duval in the great swamp of Florida, and points out that the composition of this clay, on which

vegetation is now growing under conditions which approximate to those of the coal age, is very similar to that of a typical underclay, underlying coal. F. B.

Osmosis in Soils. Soils Act as Semipermeable Membranes. I. C. J. LYNDE (*J. Physical Chem.*, 1912, **16**, 759—765).—The movements of water in soil have been attributed to gravitation, capillary action, and heat. To these must now be added osmotic pressure.

Osmotic cells of the Pfeffer type were prepared as follows: Glass tubes 150 mm. × 11 mm. diameter were closed at one end with cotton cloth and wire gauze. A layer of sterilised heavy clay subsoil was deposited in each tube, and consolidated against the cloth by centrifugal action. The tubes were filled up with 10% sugar solution, or 10% potassium sulphate solution, and immersed in distilled water. In each case water diffused into the cells osmotically through the clay. The rate of diffusion inwards was considerably greater at 24·5° than at 22·5°. It is probable that the solution leak outwards through the clay was considerable. R. J. C.

Osmosis in Soils. Soils Act as Semipermeable Membranes. II. C. J. LYNDE and F. W. BATES (*J. Physical Chem.*, 1912, **16**, 766—781. Compare preceding abstract).—Three pairs of osmotic cells were prepared with clay subsoil as already described, the layers of sterilised clay being 54 mm., 36 mm., and 18 mm. thick respectively. The solution filling the cell was the aqueous extract of the clay forming the membrane in each case. The cells were closed by rubber stoppers carrying capillary tubes. The predetermined capillary rise of each solution was deducted from the total rise, the remainder being the osmotic rise.

The osmotic pressures obtained with the thickest layers of clay were the highest, but the concentrations of the soil solutions were also highest in these cases. On the assumption that the osmotic pressures should be equal to these given by solutions of potassium chloride of equal electrical conductivity, the osmotic efficiency of the membranes was calculated to be only 2·5% (54 mm. membrane), 1·4% (36 mm.), and 1·0% (18 mm.), the efficiency being roughly proportional to the thickness of the membrane. An experiment with a membrane of clay 108 mm. thick gave still higher pressures. It is calculated that about 2 metres thickness of clay would be a perfect semipermeable membrane. In all cases the osmotic rise at 36·5° was somewhat higher than at 16·7°.

The soil used in the above experiments had the physical composition: sand 10·5%, silt 50·4%, clay 36·3%, organic matter 2·8%. A number of soils containing 44—61% of sand and only 12—16% of clay failed to show any decided osmotic properties.

It is suggested that osmotic effects play an important part in agricultural operations, particularly on heavy clay subsoils. Tillage, drainage, manuring, and mulching by favouring bacterial action increase the proportion of soluble matter in the soil, and therefore the amount of moisture which is raised osmotically through the subsoil. The same

effect may be brought about by the addition of mineral fertilisers and such substances as gypsum and salt which are not directly plant foods. There may be other substances which are not plant foods, but might be beneficial as fertilisers from the osmotic point of view. R. J. C.

Importance of the Error of Analysis in Questions Relating to the Nitrogen Economy of Arable Soils. THEODOR PFEIFFER and EDWIN BLANCK (*Landw. Versuchs-Stat.*, 1912, **78**, 367—374).—A final attempt was made to obtain a satisfactory nitrogen balance with the experimental soils at Breslau. Six plots (9 sq. metres each) were selected, which had given similar amounts of crops during two years, and from each plot five samples of soil were taken. Ten or twelve nitrogen estimations were made with each sample. The experimental error was found to be ± 0.00086, which would correspond with 25·8 kilos. of nitrogen per hectare to a depth of 25 cm. if the weight of the soil is taken as 3,000,000 kilos., or 32·2 kilos. if the total weight of soil is taken as 3,750,000 kilos. As this number has to be multiplied by three it would only be possible to show a difference exceeding 77·4 or 96·6 kilos. of nitrogen per hectare. With fewer samples or analyses the error would, of course, be greater. It must also be borne in mind that the nitrogen of crops is not all derived from the surface soil, but from the subsoil as well. N. H. J. M.

Estimation of the Value of Plant Foods in Soils and Manures so far as Dependent on Solubility. J. G. MASCHHAUPT and L. R. SINNIGE (*Bied. Zentr.*, 1913, **42**, 16—20; from *Verslag. Landbouwkund. onderzoek. Rijkslandbouwproefstat.*, 1912, No. 11).—Single extractions of different phosphates with a definite volume of water containing carbon dioxide will not show the relative values of the manures. Better results will be obtained when successive extracts are made, and it is probable that a method of continuous extraction in which the dissolved substances are at once removed will give better results than intermittent extraction.

Repeated extraction with fresh amounts of citric acid solution will probably indicate the relative values of phosphates. As, however, carbon dioxide is the chief solvent at the disposal of soil and roots, it is to be preferred to citric acid. N. H. J. M.

Antagonism between Anions as Affecting Ammonification in Soils. CHARLES B. LIPMAN (*Centr. Bakt. Par.*, 1913, ii, **36**, 382—394).—Experiments in soils on the lowering of the toxicity of salts by the addition of other salts, as measured by the amount of ammonia produced. The first series, which deals with the antagonism between the salts of "white alkali," sodium chloride and sulphate, showed that addition of sodium chloride (0·2%) to the soil reduced the amount of ammonia from 54·46 to 30·73 mg., whilst the further addition of sodium sulphate (0·3%) increased the amount to 37·1 mg., less effect being produced by smaller or larger amounts of sulphate. In an experiment with sodium chloride and carbonate, the ammonia was reduced from 41·75 to 22·05 mg. by 0·2% of sodium chloride; sodium carbonate in amounts of 0·2% and more increased the ammonia

production, the greatest amount being 70·7 mg. with 0·7% of sodium carbonate in addition to 0·2% of chloride.

Further experiments are described in which sodium sulphate and carbonate were employed.

The results show that antagonism is shown most strongly between sodium carbonate and sodium chloride; next between sodium carbonate and sodium sulphate, and least between sodium chloride and sodium sulphate.

When 0·3 or 0·4% of sodium carbonate is added to soil containing 0·9% of sodium sulphate there is an increased toxic effect; when, however, the amount of carbonate is increased to 0·5%, the toxic effect of the sulphate is reduced, and with 0·6% of carbonate it is still further reduced. N. H. J. M.

Influence of Organic Substances on the Decomposition and [Manurial] Action of Nitrogenous Compounds. MAX GERLACH and ALFRED DENSCH (*Bied. Zentr.*, 1913, **42**, 21—30; from *Mitt. Inst. Landw. Bromberg*, 1912, **4**, 259).—Pot experiments in which slightly humus, loamy sand manured with sodium nitrate both alone and with dextrose and straw respectively; with an ammonium salt, alone and with dextrose; and with dextrose and straw respectively, was kept for two months, after which the amounts of total nitrogen and the nitrates and soluble organic nitrogen were estimated. The results showed that the total nitrogen changed very little, and indicated that the nitrogen added as ammonium salt and as nitrate was converted into insoluble proteins.

The same soil was then utilised for a series of vegetation experiments from April, 1909, to August, 1911, during which time, oats, mustard, rye, mustard and wheat were grown.

Dextrose and straw was always unfavourable to oats, but were beneficial to next plants (mustard). The final results relating to nitrogen did not show any greater increase when dextrose was added than without. Nitrogen applied as nitrate showed no loss, whilst application as ammonium sulphate resulted both in loss and gain. Straw alone and in conjunction with nitrate had only a slight effect on the total nitrogen.

The results indicate that ammonium salts and nitrates are converted into insoluble proteins in presence of undecomposed organic substances, and that the insoluble nitrogen compounds readily decompose into substances which plants can utilise. N. H. J. M.

Relation of Active Potash to Pot Experiments. GEORGE S. FRAPS (*J. Ind. Eng. Chem.*, 1912, **4**, 525—526).—An account of pot experiments with representative Texas soils, from which the conclusions are drawn that (1) the percentage of crops deficient in potash decrease with the increase of active potash in the soil; (2) the percentage of crops injured by potash increase with the active potash in the soil; (3) the effect of fertiliser potash on the weight of the crop decreases as the active potash content of the soil increases; (4) the percentage of potash in the crop increases as the active potash in the soil increases; (5) the total potash removed by the crop from

the soil increases as the active potash content of the soil increases. The term "active potash" is applied to that which is soluble in $N/5$-nitric acid. F. M. G. M.

Effect of Sugar on the Fertility of Soils. THEODOR PFEIFFER and EDWIN BLANCK (*Landw. Versuchs-Stat.*, 1912, 78, 375—388).—The results of plot experiments in which oats, beet, and oats were grown successively both without and with sugar and phosphoric acid, and with both sugar and phosphoric acid, showed that the application of sugar was slightly injurious the first year, and resulted in a slight increase the second year. In the third year there was no appreciable difference due to sugar. No evidence of increased fixation of nitrogen was obtained. N. H. J. M.

Calcium Cyanamide. C. J. MILO (*Chem. Zentr.*, 1912, ii, 1054—1055; from *Med. Proefstat. Java-Suikerind.*, 1912, 427—527). —When calcium cyanamide is used as a manure, the lime is readily taken up and held by the soil, but the nitrogen is not held so well as in the case of ammonium sulphate. In spite of this no nitrogen is lost if the cyanamide is applied in the dry season and the soil is not heavily watered immediately afterwards, and none is lost by volatilisation if the manure is properly applied. The nitrogen is utilised mainly by bacterial agency, but is also absorbed in other ways. Comparison of calcium cyanamide with ammonium sulphate as a manure has not yet given definite results. Dicyanodiamide is not poisonous to sugar-cane, and although calcium cyanamide shows some toxic effects, it appears to be rapidly converted into harmless cyanamide in the soil.

T. A. H.

Behaviour of Calcium Cyanamide when Stored, and under the Influence of Soil and Colloids. G. HENSCHEL (*Bied. Zentr.*, 1913, 42, 33—34; from *Cent. Bakt. Par.*, 1912, ii, 34, 279).—Dry sterilised soil or colloids decompose cyanamide more quickly than when not sterilised. Under sterilised conditions, urea and dicyanodiamide are formed, but no ammonia. Experiments with different soils showed almost complete agreement between the intensity of the decomposition when sterilised and the production of ammonia when not sterilised; an exception, however, occurred in the case of a sandy soil containing much humus, which showed a strong colloid, but feeble bacterial, action.

When cyanamide is stored, a good deal of urea may be produced under some conditions; different preparations show, however, considerable differences, both in this and other respects. No loss of nitrogen was ever observed, the lower percentages of nitrogen after storing being due to absorption of water and carbon dioxide. N. H. J. M.

Organic Chemistry.

Some Reactions of Sodamide in the Presence of Liquid Ammonia. Formation of Ethylene Hydrocarbons. E. CHABLAY (*Compt. rend.*, 1913, **156**, 327—330).—By the addition of alkyl iodides or chlorides to sodamide in liquid ammonia, primary amines are not the only products as has been supposed (compare Lebeau, A., 1905, i, 401, 512), but at the same time, except in the case of the methyl haloids, the corresponding olefine is formed in varying amounts. Starting from the ethyl haloids, the yield of olefine increases on passing up the series, and is always greater when using the chlorides than if the iodides are employed; thus *iso*butyl iodide gives a yield of 62·4% of *iso*butylene, whilst the chloride gives a yield of 83·6%. In this reaction sodamide resembles alcoholic potassium hydroxide in its behaviour (compare Meunier and Desparmet, A., 1907, i, 186).

W. G.

The Adsorption of Acetylene by Palladium Black. CARL PAAL and CHRISTIAN HOHENEGGER (*Ber.*, 1913, **46**, 128—132).—In the previous investigation on the same subject (A., 1910, i, 807), the palladium black was suspended in aqueous solutions of various substances. The authors have now investigated the adsorption of acetylene, using either suspensions of palladium black in pure water, or else dry palladium black. The experiments in which 60% alcohol was used in place of pure water were also repeated.

In all cases the adsorption of the acetylene takes places slowly, and the results given do not point to any fixed ratio between the weight of palladium and the amount of gas adsorbed. It is probable that the acetylene is not completely adsorbed as such, but undergoes partial polymerisation.

When the dry palladium black is not completely free from oxygen, formation of feeble sparks occurs immediately it is brought into contact with the acetylene.

T. S. P.

Acetylene or Acetylidene Compounds. The "Oxidation Rearrangement." HEINRICH BILTZ (*Ber.*, 1913, **46**, 143—149).—Nef and his school assign to the halogen substitution products of acetylene an acetylidene formula, as, for example, $CI_2\text{:}C$, di-iodo-acetylidene. No definite proof of this constitution has been afforded, and the facts observed are more in favour of the acetylene structure, CI⋮CI. Di-iodoacetylene is very readily formed from acetylene by the action of hypoiodites and iodine, the process involving simple substitution of iodine for hydrogen.

The reasons for the representation of dibromoacetylene as CBr⋮CBr are discussed.

E. F. A.

Sodium Silver Thiosulphate and Acetylene-Silver Acetylide. KSHITIBHUSHAN BHADURI (*Zeitsch. anorg. Chem.*, 1913, **79**, 355—356).—Sodium thiosulphate is added to an ammoniacal solution

of silver nitrate, and acetylene is passed through the clear solution. The yellow precipitate is collected, washed with water and alcohol, and dried in air. It is stable in dry air, but is decomposed by water, yielding a brick-red product. The final products of decomposition are silver sulphide and sodium sulphate.

The yellow compound is soluble in ammonia, and is re-precipitated by acids, again dissolving in an excess to form unstable solutions, which evolve sulphur dioxide and acetylene. Analysis leads to the formulæ $2Na_2S_2O_3,7Ag_2S_2O_3,18Ag_2C_2,32C_2H_2$ for the yellow compound, and $4Ag_2S_2O_3,7Na_2S_2O_3,86Ag_2C_2,13C_2H_2$ for the red compound.

C. H. D.

The Production of Chlorine Substitution Products of Methane from Natural Gas. CHARLES BASKERVILLE and H. S. RIEDERER (*J. Ind. Eng. Chem.*, 1913, **5**, 5—8).—The authors have investigated the conditions necessary for the chlorination of the methane present in natural gas, especially those which would lead to the formation of carbon tetrachloride, from which chloroform could be obtained by reduction. The apparatus used was so designed that the gases could be constantly circulated through it, the circuit always containing a heater for heating the gases, and a condenser for condensing out the products formed. In the first trials the circuit also contained an arc, either between carbon or iron terminals, but this was omitted later, as it was found that chlorination was not effected by the combustion taking place in the arc. It was ultimately found that the primarily important condition for the chlorination is a source of light rich in the rays of the visible blue spectrum, that is, the spectrum from the bluish-green through the visible violet. The ultraviolet part of the spectrum plays little part in the reaction. Apparently the necessary source of light may be obtained by an arc, between iron electrodes, in the circuit, and in some experiments a 20—25% yield of a mixture of carbon tetrachloride and chloroform was obtained.

T. S. P.

Primary Dinitro-, Nitro-nitrite and Dialdoxime Compounds of the Aliphatic Series. II. Derivatives of the Heptane Series and Synthesis of Pimelaldehyde. JULIUS VON BRAUN and E. DANZIGER (*Ber.*, 1913, **46**, 103—110).—As has already been shown (von Braun and Sobecki, A., 1911, i, 830), the action of silver nitrite on aliphatic compounds of the type $I\cdot[CH_2]_n\cdot I$ gives a mixture of dinitro, nitro-nitrite, and dinitrite derivatives, the first two of these being reducible to dialdoximes and amino-alcohols respectively. These changes have already been performed with n equal to 4, 5 and 10, and are now extended to the heptamethylene chain.

$\alpha\eta$-Di-iodoheptane was prepared from $\alpha\epsilon$-dibromopentane by conversion of the latter into an organo-magnesium compound, causing this to react with monochloromethyl ether (compare Dionneau, A., 1906, i, 134) and hydrolysing the product with hydriodic acid. It was also obtained by the stages: dibromopentane, diaminopentane, dichloroheptane, and diphenoxyheptane, the last of which again is converted into di-iodoheptane by hydriodic acid. In the conversion of dichloro-

heptane into diphenoxyheptane by sodium ethoxide, a small quantity of α-phenoxy-ζ-methylene-n-hexane, b. p. 145°/12 mm., was obtained as by-product.

$\alpha\eta$-Di-iodoheptane reacts vigorously with silver nitrite, producing a mixture which can be separated at 10 mm. into three fractions, b. p. 108—140° (mainly *heptamethylene nitrite*, $NO_2\cdot[CH_2]_7\cdot NO_2$), 140—160° (mainly *$\eta$-nitroheptyl nitrite*), and 160—205°, the last on refractionating yielding pale yellow *$\alpha\eta$-dinitroheptane*, b. p. 198—200°/10 mm. The second fraction when reduced with tin and hydrochloric acid yields *η-hydroxyheptylamine*, a strong base, b. p. 150—152°/10 mm.; *benzoyl*, *nitrobenzoyl*, and *picrate* derivatives are oily; *platinichloride*, solid, m. p. 157°.

$\alpha\eta$-Dinitroheptane when treated with sodium ethoxide in alcoholic solution gives an immediate precipitation of the white *sodium* salt, the aqueous solution of which can be used for the preparation of the salts of the heavier metals, for example, the *copper* (green), *barium* and *calcium* salts; with bromine, it forms an oily *bromide* (compare von Braun and Sobecki, *loc. cit.*), and with a diazobenzene solution there is obtained yellowish-red *$\alpha\eta$-bisphenylazo-$\alpha\eta$-dinitroheptane*,

$$N_2Ph\cdot CH(NO_2)\cdot[CH_2]_5\cdot CH(NO_2)\cdot N_2Ph,$$

m. p. 139°.

The reduction of a solution of the sodium salt of dinitroheptane by gradual addition to a solution of stannous chloride in hydrochloric acid gives *pimelaldoxime*, $OH\cdot N:CH\cdot[CH_2]_5\cdot CH:N\cdot OH$, a pale yellow, crystalline powder, m. p. 150—151°, from which, on boiling with dilute sulphuric acid, pimelaldehyde is not obtained, as it partly polymerises to a viscous oil, and partly becomes dehydrated to tetrahydrobenzaldehyde, semicarbazone, m. p. 211—212° (Wallach, A., 1906, i, 563). *Pimelaldehyde*, a pungent, colourless oil of b. p. 110—112°/13 mm., D_4^{20} 0·9895, is obtainable by the action of nitrous fumes on a suspension of the dioxime in cooled water until no more nitrous oxide is liberated; it readily reduces Fehling's solution, and an ammoniacal silver solution, and gives a *semicarbazone*, m. p. 183°; the *phenylhydrazone* and p-*nitrophenylhydrazone* are oily, whilst the *diphenylmethanedimethyldihydrazone*, $CH_2<\begin{matrix}C_6H_4\cdot NMe\cdot N:CH\\ C_6H_4\cdot NMe\cdot N:CH\end{matrix}>[CH_2]_5$ (structure not proved), is a yellow solid, m. p. 96—97°. The aldehyde resembles adipaldehyde in showing much less tendency to polymerise than do the other dialdehydes of this series.

A preliminary investigation has shown that glutaraldoxime when heated with mineral acids gives pyridine, probably by reason of the condensation of glutaraldehyde and hydroxylamine which are first formed. D. F. T.

Synthesis of an Unsaturated Hydrocarbon. CORNELIS J. ENKLAAR (*Chem. Weekblad*, 1913, **10**, 60—63).—A note on the preparation of unsaturated alcohols by the interaction of unsaturated aldehydes and unsaturated haloids in presence of zinc and ether, and the conversion of such alcohols into unsaturated hydrocarbons by heating with potassium hydrogen sulphate. On treatment with zinc filings or shavings and ether, crotonaldehyde and allyl iodide give a

good yield of *αε-heptadiene-δ-ol*, $CHMe{:}CH{\cdot}CH(OH){\cdot}CH_2{\cdot}CH{:}CH_2$. Its properties are still uninvestigated, but heating with potassium hydrogen sulphate converts it into a liquid. Repeated fractionation, finally over sodium, at 758 mm. gives three fractions, b. p. 105—110°, 110—112°, and 112°. On cooling to −76°, these three fractions solidify. The first has m. p. −35° to −32°, the second −23° to −21°, and the third −15° to −14·5°. One of these substances is believed to be an *αγε-heptatriene*, and their constitutions are to be determined. It is anticipated that the method will prove of general application.

A. J. W.

History of Distillation and of Alcohol. EDMUND O. VON LIPPMANN (*Zeitsch. angew. Chem.*, 1913, **26**, 46—47).—Polemical against Schelenz (this vol., i, 2).

T. S P.

Action of Magnesium on a Mixture of Ethyl *iso*Valerate and Allyl Bromide. G. MOSKALENKO (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1862—1865).—Decomposition by means of water of the product of the reaction of magnesium, ethyl *iso*valerate, and allyl bromide yields *diallyl*iso*butylcarbinol*, $CHMe_2{\cdot}CH_2{\cdot}C(OH)(CH_2{\cdot}CH{:}CH_2)_2$, which forms a colourless, mobile liquid, b. p. 92°/37 mm., D_4^{23} 0·8616, n_D^{23} 1·45682, and exhibits the normal molecular weight in freezing benzene or boiling ether.

T. H. P.

Adipiopinacone. LOUIS MICHIELS (*Bull. Soc. chim. Belg.*, 1913, **27**, 25—26).—*Adipopinacone*, $OH{\cdot}CMe_2{\cdot}[CH_2]_4{\cdot}CMe_2{\cdot}OH$, m. p. 88—89°, is obtained in the form of its *hydrate*, containing $2H_2O$, by the action of magnesium methyl bromide on ethyl adipate. The hydrate is obtained in large, white crystals, m. p. 56·5°, which effloresce in air, and completely lose their water of hydration when left in a vacuum desiccator. By the action of warm dilute sulphuric acid, the pinacone is readily converted into *tetramethylhexamethylene oxide*, $O{<}\begin{matrix}CMe_2{\cdot}CH_2{\cdot}CH_2\\ CMe_2{\cdot}CH_2{\cdot}CH_2\end{matrix}$, a liquid with an ethereal odour, b. p. 156—157°/756 mm.

W. G.

Action of Magnesium on a Mixture of Allyl Bromide and Ethyl Levulinate. E. SCHTSCHERICA (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1853—1858).—The interaction of magnesium, allyl bromide (1 mol.), and ethyl lævulate (1 mol.), and subsequent decomposition of the product with water, should yield the ester,

$$C_3H_5{\cdot}CMe(OH){\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et,$$

but this reaction could not be realised. No matter whether 1 mol. or 3 mols. of allyl bromide were employed, the resultant compound was always the *γ-glycol*, $C_3H_5{\cdot}CMe(OH){\cdot}CH_2{\cdot}CH_2{\cdot}C(C_3H_5)_2{\cdot}OH$, which is a faintly yellow, syrupy, slightly mobile liquid with a characteristic odour, b. p. 157—159°/10 mm., D_4^{25} 0·9545, n_D^{25} 1·48712. When boiled with 20% sulphuric acid solution, the glycol is converted into the corresponding *oxide*, $\begin{matrix}CH_2{\cdot}CMe(C_3H_5)\\ CH_2{\cdot}C(C_3H_5)_2\end{matrix}{>}O$, which is an almost colour-

less liquid with a peculiar pleasant odour, b. p. 104·5—105·5°/10 mm., D_4^{25} 0·8905, n_D^{25} 1·46915, and has the normal molecular weight in boiling ether. T. H. P.

Synthesis of Lecithin. Adolf Grün (*Ber.*, 1913, **46**, 125—127).—Polemical. A reply to Langheld (this vol., i, 155; compare Grün and Kade, this vol., i, 158). E. F. A.

Thionium Dibromides of Sulphides. Vladimir V. Tschelincev (*J. Russ. Phys. Chem. Soc.*, 1902, **44**, 1885—1894).—The action of bromine on ethyl sulphide in carbon tetrachloride solution yields the thionium dibromide, SEt_2Br_2, which forms yellow crystals and resembles oxonium compounds in its general characters, and also as regards the nature of the solvents in which it dissolves readily or with difficulty. With acetic acid, it forms solid solutions, but in freezing benzene it exhibits the molecular weight, 199—211, the theoretical value being 250.

By excess of water, the dibromide is rapidly decolorised with development of a considerable quantity of heat and the formation of a white emulsion. Concentrated ammonia solution decomposes the thionium dibromide much less energetically than the corresponding oxonium compound, heat being developed and an oily layer of the sulphide formed at the surface of the liquid. Sodium hydrogen sulphite solution effects the decomposition rather more rapidly, and concentrated potassium hydroxide solution much more rapidly, than does water. Moist silver oxide converts these dibromides into the corresponding oxides, for example, $SMe_2\colon O$, which are appreciably more stable than the analogous oxonium compounds.

The heat of formation of the diethyl dibromide from the alkyl sulphide and bromine is 14·15 Cal. per gram-mol., that of the diamyl dibromide being 12·91 Cal. Measurement of the amounts of heat evolved when the reaction proceeds in carbon tetrachloride solutions of various concentrations shows that the solvent is virtually without influence in this respect.

As the heats of formation of the oxonium compounds corresponding with the above thionium compounds are 9·13 Cal. for $OEt_2\colon Br_2$ and 8·72 Cal. for $O(C_5H_{11})_2\colon Br_2$, it is to be expected that alkyl sulphides would displace the ethers from oxonium compounds. Calorimetric investigations show that when the oxonium compound is prepared in absence of solvent, such displacement does occur, but does not proceed to completion, at any rate within the limits of time available for calorimetric measurements; it appears probable that the bromine finally becomes distributed between the sulphide and the ether. When, however, a carbon tetrachloride solution of ethyl sulphide (1 mol.) is added to a solution of ether (1 mol.) and bromine (1 mol.) in the same solvent, 13·76 Cal. are developed; as this amount is somewhat less than the theoretical quantity, 14·15 Cal., for complete displacement of the ether from the oxonium compound by ethyl sulphide, it may be that here, too, the bromine is distributed between the sulphide and the ether.

T. H. P.

Catalytic Acceleration of the Esterification of Organic Acid by means of Glucinum Compounds. OTTO HAUSER and A. KLOTZ (*Chem. Zeit.*, 1913, **37**, 146).—Experiments on the solubility of glucinum acetate in various organic solvents have led the authors to the discovery that the rate of esterification of organic acids and alcohols can be considerably increased by the addition of glucinum acetate or hydroxide to the boiling mixture. The catalytic action of glucinum compounds is still more pronounced when the mixed vapours of the acid and alcohol are passed over the oxide heated at 310°. The authors claim that better yields are obtained by this process than by that of Sabatier (actually 70% and over), that there is no loss of catalyst, since the glucinum oxide after use can be regenerated by simple ignition, and that tertiary alcohols and acids of high molecular weight can be esterified in this manner. The following new esters have been prepared: tert.-*butyl* n-*octoate*, b. p. 241°; tert.-*amyl* n-*heptoate*, b. p. 137°, and tert.-*amyl* n-*octoate*, b. p. 229°. H. W.

Mechanism of the Action of Bromine on Chlorides of Fatty Acids. ARTHUR MICHAEL and ERWIN SCHARF (*Ber.*, 1913, **46**, 135—138).—When butyryl chloride, saturated with hydrogen bromide at 0°, is heated in sealed tubes at 100°, double decomposition takes place with the formation of butyryl bromide and hydrogen chloride. It is probable therefore that the formation of hydrogen chloride by the action of bromine on acyl chlorides is not due to the decomposition of a bromine additive product, formed from the enolic modification of the chloride, but is brought about by the direct action of the chloride with hydrogen bromide produced during the reaction. This is not in agreement with Lapworth's (T., 1904, **85**, 30) interpretation of the change.

Proof is further given that by the action of bromine on butyryl chloride in sunlight some quantity of the β-derivative as well as the α-derivative is formed. Hydrogen chloride and bromide in equal proportions are liberated on opening the tube. When the contents were converted into the ethyl ester, and hydrolysed with barium hydroxide, considerable quantities of crotonic acid derived from the β-ester were obtained. E. F. A.

Aliphatic Nitro-compounds. XIII. Preparation of α-Nitro-α-methylbutyric Acid. WILHELM STEINKOPF (*Ber.*, 1913, **46**, 98—100).—An unfinished attempt to prepare a tertiary nitrocarboxylic acid containing an asymmetric carbon atom.

[With HARRY GRÜNUPP and LEO HUG.]—A mixture of butanoneoxime with anhydrous hydrogen cyanide is kept in a closed flask for four to eight days at the ordinary temperature, and the excess of acid then removed in a vacuum; crystals of *a-hydroxylamino-a-methylbutyronitrile*, OH·NH·CMeEt·CN, m. p. 61·5°, are obtained. When this substance is oxidised by the cautious addition of an acidified solution of potassium permanganate, a blue *oil* (probably α-nitroso-α-methylbutyronitrile) is first formed, but disappears later with the production of *a-nitro-a-methylbutyronitrile*, NO_2·CMeEt·CN, an almost colourless oil, b. p. 87—88°/17 mm. Attempts to hydrolyse this to the corre-

sponding acid, or to convert it into an imino-ester hydrochloride were unsuccessful. D. F. T.

Action of Alkali Sulphites on the Ethylenic Acids. J. BOUGAULT and MOUCHEL-LA-FOSSE (*Compt. rend.*, 1913, **156**, 396—398).—It being known that, on adding benzoylacrylic acid to a solution of normal or sodium hydrogen sulphite, combination instantly takes place, giving the sodium salt of a saturated sulphonic acid (compare Bougault, *Ann. Chim. Phys.*, 1908, [viii], **15**, 299), the authors have compared the activity of different types of ethylenic acids in this reaction. A large number of ethylenic acids combine in this way with sodium hydrogen sulphite, giving acids of the type $CH_2R\cdot CH(SO_3Na)R'$, which are very soluble in water, and, on heating with aqueous sodium hydroxide to 160°, regenerate the original unsaturated acid. The more energetic is the acid and the more electronegative groups it contains, the more rapid is the fixation of the sodium hydrogen sulphite. Acids such as *cyclo*geranic, undecenoic, and oleic acids, and in general those with long, straight chains, do not combine with the sodium hydrogen sulphite even after prolonged heating. The reaction can be employed to estimate the amount of unsaturated acid in a mixture of saturated and unsaturated acids, and also permits of the separation of the saturated acid in a pure state. W. G.

The Salts of Rare Earths with Hydroxycarboxylic Acids. I. The Glycollates of the Rare Earths. GUSTAV JANTSCH and A. GRÜNKRAUT (*Zeitsch. anorg. Chem.*, 1913, **79**, 305—321).—The internally complex salts of rare earths with hydroxycarboxylic acids might be expected to differ more widely in solubility than the normal salts, and therefore to be suitable for the purpose of separation. It is found that the glycollates of the cerium group are anhydrous, and crystallise in crusts, whilst those of the yttrium group crystallise in needles with $2H_2O$. The yttrium salt is the least soluble, then follow the lanthanum, cerium, and praseodymium salts, which are almost equal, and then, in order, the neodymium, samarium, and gadolinium salts. The solutions exhibit the normal reactions, but conductivity determinations show that complexes are present.

Lanthanum hydroxide dissolves in a warm solution of glycollic acid, the solution at first remaining clear, but at a definite temperature, depending only on the concentration, the complex salt separates as a precipitate, $La(C_2H_3O_3)_3$. The praseodymium, neodymium, and samarium salts behave in the same manner.

Gadolinium glycollate, $Gd(C_2H_3O_3)_3,2H_2O$, crystallises without first forming an unstable solution, whilst the yttrium salt behaves like those mentioned above.

The fractionation of the earths from xenotime, previously freed from cerium, has been carried out by adding a solution of sodium glycollate to the hot solution of the mixed nitrates. After each addition, in order to overcome the unstable condition, the mixture is stirred vigorously for two hours at 80—90°. It is then filtered, and the filtrate is treated in similar manner. Successive fractions show a

progressive increase in the atomic weight, whilst the spectra show a concentration of neodymium and praseodymium in the last fractions.

C. H. D.

Succinic Semialdehyde [β-Aldehydopropionic Acid]. EDMOND E. BLAISE and E. CARRIÈRE (*Compt. rend.*, 1913, **156**, 239—241).—A reply to Harries (A., 1912, i, 827), in which the authors uphold the views already expressed by Carrière (A., 1912, i, 410) that β-aldehydopropionic acid changes spontaneously into a polymeride which is termolecular, and that the bimolecular compound, m. p. 147°, of Harries (*loc. cit.*) is the compound obtained by the elimination of $1H_2O$ from two molecules of the aldehyde.

W. G.

General Method for the Preparation of the Ammonium Salts of Organic Acids. EDWARD H. KEISER and L. MCMASTER (*Amer. Chem. J.*, 1913, **49**, 84—86).—On account of the hydrolytic action of water on the ammonium salts of organic acids, comparatively few of them have hitherto been prepared, and in the case of most dibasic acids only the ammonium hydrogen salts have been obtained. It has now been found that normal salts can be readily prepared by passing dry ammonia into a solution of the organic acid in ether or alcohol, or a mixture of the two. The salts are insoluble, and separate in the form of white precipitates. *Ammonium maleate, fumarate, mesaconate, citraconate, malonate*, and *phthalate* are described.

E. G.

Sebacates and Cacodylates of the Rare Earths. C. F. WHITTEMORE and CHARLES JAMES (*J. Amer. Chem. Soc.*, 1913, **35**, 127—132; *Chem. News*, 1913, **107**, 75—77).—In an earlier paper (A., 1912, ii, 690) it was shown that yttrium can be separated quantitatively from the alkali metals by precipitation with ammonium sebacate. It has now been found that lanthanum and cerium can also be separated from the alkali metals in this way. The following salts are described: *lanthanum sebacate*, $[C_8H_{16}(CO_2)_2]_3La_2,2H_2O$; *praseodymium sebacate*, $[C_8H_{16}(CO_2)_2]_3Pr_2,2H_2O$; *neodymium sebacate*, $[C_8H_{16}(CO_2)_2]_3Nd_2,3H_2O$; *samarium sebacate*, $[C_8H_{16}(CO_2)_2]_3Sa_2,4H_2O$; *yttrium sebacate*, $[C_8H_{16}(CO_2)_2]_3Yr_2,4H_2O$.

On fractionally precipitating a solution containing chiefly the chlorides of yttrium, dysprosium, and holmium with sodium cacodylate, it was found that yttrium tended to accumulate in the early fractions, and holmium and dysprosium in the later fractions. On boiling a mixture of hydroxides, consisting mainly of those of neodymium, samarium, and gadolinium, with cacodylic acid and fractionally crystallising the cacodylates from hot water, neodymium collected in the more soluble fractions, whilst nearly all the terbium and dysprosium remained in the least soluble portions. The following salts have been prepared: *praseodymium cacodylate*, $(AsMe_2O_2)_6Pr_2,16H_2O$; *yttrium cacodylate*, $(AsMe_2O_2)_6Yr_2,18H_2O$; *thulium cacodylate*, $(AsMe_2O_2)_6Tm_2,16H_2O$.

Neodymium and samarium cacodylates have been described previously (A., 1912, i, 233).

The rare earth cacodylates readily form double salts with other salts, such as the chlorides, nitrates, and sulphates. The following are described: *lanthanum chloride cacodylate*,

$$2La(AsMe_2O_2)_3,LaCl_3,18H_2O;$$

cerium chloride cacodylate, $2Ce(AsMe_2O_2)_3,CeCl_3,18H_2O$; *cerium sulphate cacodylate*; and *neodymium chloride cacodylate*,

$$2Nd(AsMe_2O_2)_3,NdCl_3,18H_2O.$$

E. G.

The Action of *p*-Bromophenylhydrazine on Glycuronolactone. GUIDO GOLDSCHMIEDT and ERNST ZERNER (*Ber.*, 1913, **46**, 113—115).—In reply to Jolles (this vol., i, 9), the authors maintain their previous statement (this vol., i, 9), that even with purified *p*-bromophenylhydrazine the test for glycuronic acid is so uncertain as to be of little practical value. D. F. T.

Behaviour of Chloraloxime Towards Water and Alkalis. F. CARLO PALAZZO and V. EGIDI (*Gazzetta*, 1913, **43**, i, 57—69. Compare Palazzo, A., 1912, i, 946; Palazzo and Fazio, 1911, i, 421).—When Meyer's chloraloxime is kept for some days with ten times its weight of water, an acid solution is obtained, from which can be isolated a product having the composition of oximinoacetic acid; it has, however, an indefinite m. p., and is to be regarded as a mixture of two stereoisomerides. It differs from the oximinoacetic acid, m. p. 138°, already known, in yielding a red coloration with ferric chloride. When Meyer's chloraloxime is distilled, several liquid fractions, b. p. 65—85°/20—25 mm., are obtained, and also a portion, b. p. 85°/20 mm., which solidifies and has m. p. 56°. Even if carefully freed from the liquid form, the solid substance yields, when treated with water, a product similar to that given by the original mixture.

By the action of hydroxylamine hydrochloride on bromal hydrate, *bromaloxime* is obtained in acicular crystals, m. p. 115°; it has the composition and molecular weight required by the formula

$$CBr_3\cdot CH:NOH.$$

Oximinoacetic acid forms two *copper* salts, namely, a blue salt,

$$[OH\cdot N:CH\cdot CO_2]_2Cu,2H_2O,$$

and a dark green salt of the probable composition $\begin{matrix} CH:NO \\ | \\ CO_2 \end{matrix} \!\!>\! Cu.$

R. V. S.

Inosite-phosphoric Acid. ANTON RICHARD ROSE (*Biochem. Bull.*, 1912, **2**, 21—49).—A useful review with bibliography on the subject. W. D. H.

Syntheses of Alkylgalactosides by means of Emulsin, β-Propylgalactoside and β-Benzyl Galactoside. ÉMILE BOURQUELOT, HENRI HÉRISSEY, and MARC BRIDEL (*Compt. rend.*, 1913, **156**, 330—332).—The two galactosides have been prepared from galactose and the corresponding alcohols under the influence of emulsin by the method previously described (A., 1912, i, 946).

β-Propylgalactoside, m. p. 105—106° (corr.), $[\alpha]_D$ - 8·86°, crystallises in long, white needles, having a slightly bitter taste. It is not hygroscopic, but is very soluble in alcohol and water, and gives a slight reduction with Fehling's solution.

β-Benzylgalactoside, m. p. 100—101°, $[\alpha]_D$ - 25·05°, crystallises in long, white needles, having a disagreeable bitter taste. It is not hygroscopic, and gives but traces of reduction with Fehling's solution. Both of these galactosides are readily hydrolysed by emulsin in aqueous solution. W. G.

Photochemical Synthesis of Carbohydrates. WALTHER LÖB (*Biochem. Zeitsch.*, 1913, **48**, 257—258).—A reply to Stoklasa, Šebor, and Zdobnický (this vol., i, 18). S. B. S.

Cellulose. C. PIEST (*Zeitsch. angew. Chem.*, 1913, **26**, 24—30).—The viscosity of a solution of a cellulose nitrate decreases with time and, generally, a deposit settles on the bottom of the vessel containing the solution. Experiments have been made which show that the decrease in the viscosity is not due to the separation of this deposit from the solution.

It has been stated previously that, a diminution in the viscosity of a solution of cellulose nitrate is probably due to the presence of nitrates of oxycelluloses. It is shown now that if a viscous solution of a cellulose nitrate be mixed with a less viscous solution of a nitrate of a highly bleached cotton wool the viscosity of the mixture is considerably less than the calculated value, although if two solutions of the same cellulose nitrate, but of different concentrations (and, therefore, different viscosities), be mixed, the mixture has a viscosity which is very close to the calculated value.

Cellulose, when treated with oxidising agents, is known to yield oxycelluloses, the part soluble in sodium hydroxide solution being termed β-oxycellulose, whilst the insoluble portion is called α-oxycellulose. The results of numerous trials, based on determinations of the "copper value" and viscosity of a standard solution in a cuprammonium solution by Ost's method (compare A., 1911, i, 838), show that α-oxycellulose, when carefully freed from the degradation products grouped under the name β-oxycellulose, is chemically identical with normal cellulose, and differs from it only in that the fibres are much shorter and finer, owing to the attack of the oxidising agent.

It is also shown that the products of the action of acids on cellulose ("hydrocellulose"), or of a hot 30% solution of sodium hydroxide ("alkalised cellulose"; compare Ost and Katayama, A., 1912, i, 680), contain a portion insoluble in sodium hydroxide solutions which is unattacked cellulose. W. H. G.

Preparation of Higher Aliphatic Chlorinated Amines. JULIUS VON BRAUN and H. DEUTSCH (*Ber.*, 1913, **46**, 228—231. Compare von Braun and Müller, A., 1907, i, 28).—The bis-imidochlorides of the type $CPhCl:N\cdot[CH_2]_n\cdot N:CPhCl$, obtained by the action of phosphorus pentachloride on the corresponding dibenzoylated diamine, when distilled undergo decomposition mainly into benzonitrile and the

dichloride, but to a slight extent a product $Cl\cdot[CH_2]_n\cdot N:CPhCl$, in which only one of the phenyl radicles has been eliminated, is obtained (compare von Braun and Danziger, A., 1912, i, 597). As the latter class of substance on hydrolysis would give rise to chloroamines, the method might prove valuable if the yield of the second class of product could be increased.

It is now found that at very low pressures the desired decomposition at one end of the chain is greatly favoured.

$\alpha\zeta$-Di-iodohexane reacts with potassium cyanide, giving suberonitrile, $CN\cdot[CH_2]_6\cdot CN$, b. p. 176—178°/11 mm., which by successive reduction (by sodium and alcohol) and benzoylation is converted into *$\alpha\theta$-dibenzoyldiamino-octane*, $NHBz\cdot[CH_2]_8\cdot NHBz$. When the last substance is carefully fused with a bimolecular proportion of phosphorus pentachloride and the resultant mixture warmed under a pressure of 0·1 mm., there distils into the receiver, which is cooled by liquid air, a mixture of benzonitrile, $\alpha\theta$-dichloro-octane, and *θ-chlorobenzo-octylamide*, $COPh\cdot NH\cdot[CH_2]_8\cdot Cl$, colourless leaflets, m. p. 65°, the last of which is most conveniently purified by means of its *compound* with calcium chloride. θ-Chlorobenzo-octylamide is hydrolysed by hydrochloric acid at 150°, with the formation of *θ-chloro-octylamine*; *hydrochloride*, hygroscopic; *platinichloride*, m. p. 193—194° (decomp.), sparingly soluble. The base on treating its hydrochloride with alkali easily undergoes intramolecular change to a *base*, $C_8H_{17}N$, with an odour resembling pyridine; yellow *platinichloride*, m. p. 197°.

In an analogous manner by the distillation of dibenzoyldiaminoheptane and of dibenzoyldiaminododecane with phosphorus pentachloride under a pressure of 0·1 mm., *η-chlorobenzoheptylamide*, $Cl\cdot[CH_2]_7\cdot NHBz$, and *$\mu$-chlorobenzododecylamide*, $Cl\cdot[CH_2]_{12}\cdot NHBz$, m. p. 65°, can be obtained in fair quantity.

The yields were 40%, 30%, and 30% of the theoretical in the heptane, octane, and dodecane series respectively. D. F. T.

Dibromides of Tertiary Amines. VLADIMIR V. TSCHELINCEV (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1894—1905).—With a view to the comparison of dibromides obtained from tertiary amines with oxonium and thionium dibromides (compare this vol., i, 245), the author has investigated their solubilities in various solvents, their molecular weights, and their chemical and thermochemical relations.

A general parallelism exists between the solubility of trimethylamine dibromide and those of oxonium and thionium dibromides. Also in freezing acetic acid, trimethylamine dibromide has the molecular weight corresponding with the simple formula NMe_3Br_2, and is hence completely analogous to oxonium and thionium compounds in this respect (compare Hantzsch and Graf, A., 1905, i, 575).

Amine dibromides are somewhat more stable than the oxonium compounds towards moisture and are decomposed by ethyl alcohol, yielding hydrogen and ethyl bromides. When treated with excess of bromine, dibromides of amines are converted into new compounds, which possess peculiar properties distinguishing them from dibromides and represent a different class of perbromides,

The heat of formation of tripropylamine dibromide from its constituents is 39·72 Cal. per gram-mol., and that of tri*iso*amylamine dibromide, 38·76 Cal.; the carbon tetrachloride employed as solvent is without influence on the amount of heat developed (see this vol., i, 245).

Thermochemical investigation of the interaction of diethyloxonium dibromide or diethylthionium dibromide and tripropylamine in carbon tetrachloride solution shows that the tertiary amine displaces the ether or ethyl sulphide completely from oxonium or thionium compounds.

Ether has no action on diethyloxonium dibromide, and ethyl sulphide none on diethylsulphonium dibromide, but tertiary amine dibromides react energetically with tertiary amines, forming compounds separating from carbon tetrachloride in a felted mass of slender, pale yellow needles. The following thermochemical data were obtained:

$$2NPr_3Br_2 + NPr_3 = 23{\cdot}6 \text{ Cal.}$$

and $2N(C_5H_{11})_3Br_2 + N(C_5H_{11})_3 = 22{\cdot}9$ Cal. The compounds formed in this way are being investigated further.

Neither the structure suggested by Hantzsch (A., 1905, i, 576) nor that given by Cain (A., 1905, i, 747) for these amine dibromides seems to explain the reactions better than the simple formula.

T. H. P.

Preparation of Oxan and the Properties of Salts of α- and β-Oxan. ALEXANDER P. LIDOV (*J. Amer. Chem. Soc.*, 1913, **35**, 132—134. Compare Abstr., 1912, i, 541).—Oxan is obtained most readily by the action of nitric oxide or nitrous oxide on charcoal at 150—300°. α-Oxan, O·C⋮N, is a stable gas and is not affected by hot platinised asbestos, whilst β-oxan, O·N⋮C, is rapidly decomposed under these conditions. The sodium salt of α-oxan is stable when heated, whilst that of β-oxan decomposes explosively. The silver salt of β-oxan is pale yellow and darkens rapidly on exposure to light; that of α-oxan is white and is less susceptible to the action of light. The iron and calcium salts are also described. The sodium salt of α-oxan gives a white precipitate with manganous chloride or aluminium chloride, whilst that of β-oxan does not yield a precipitate. The salts of α- and β-oxan gradually cease to evolve gas, and this is probably due to polymerisation taking place. E. G.

Action of Sulphuric Acid on Dicyanodiamide. HJ. LIDHOLM (*Ber.*, 1913, **46**, 156—160).—The interaction of dicyanodiamide with acids to form guanylcarbamide has been studied quantitatively and shown to be a bimolecular reaction. Guanylcarbamide is a sufficiently strong base to be titrated with sulphuric acid and methyl-orange.

Concentrated sulphuric acid acts on dicyanodiamide, liberating carbon dioxide and ammonia and forming guanidine. Guanylcarbamide is decomposed in a similar manner. These observations confirm the structure of dicyanodiamide as guanidinoformonitrile,

NH:C(NH₂)·NH·CN. E. F. A.

The Tautomerism of Fulminic Acid. F. CARLO PALAZZO (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 713—719. Compare A., 1907, i, 298, 489; 1909, i, 776).—The author's work on this subject has led him to conclusions similar to those of Ley and Kissel (A., 1899, ii, 485), according to which fulminic acid is to be regarded as a tautomeric substance related to the pseudo-acids. In the aqueous solution of fulminic acid, there is equilibrium between various saturated and unsaturated desmotropic forms. In the present paper this opinion is developed, and a new argument in its favour is drawn from the behaviour of sodium fulminate with azoimide, for in this reaction the fulminic acid reacts sometimes as carbyloxime and sometimes in the desmotropic form of formonitryl oxide, HC⋮N⁚O. The products of the reaction are hydroxytetrazole (I), m. p. 145°, and *iso*oxytetrazole (II),

$$\text{(I.)}\quad \begin{array}{l}\text{HC——N}\cdot\text{OH}\\ \dot{\text{N}}\cdot\text{N}\!:\!\dot{\text{N}}\end{array} \qquad\qquad \text{(II.)}\quad \begin{array}{l}\text{N———CH}\\ \dot{\text{N}}\cdot\text{NH}\cdot\dot{\text{N}}\!:\!\text{O}\end{array}$$

m. p. 156°, and the relative proportions in which these two substances are formed depend on the temperature at which the reaction proceeds.

R. V. S.

Catalysis. XIV. Reversible Addition of Alcohols to Nitriles Catalysed by Ethoxides. I. ELI K. MARSHALL, jun., and SOLOMON F. ACREE [and, in part, C. N. MYERS] (*Amer. Chem. J.*, 1913, **49**, 127—158).—A study has been made of the addition of alcohols to nitriles in presence of ethoxides as catalysts. It has been found that nitriles unite with ethyl alcohol in presence of sodium, potassium or lithium ethoxide, and that in every case the reaction is reversible. The percentage of imino-ester present when equilibrium is attained is the same whether the reaction is started with the nitrile or the imino-ester. The equilibrium point varies widely with the different compounds, the percentages of imino-ester formed with certain nitriles being as follows: butyronitrile, 0·90; propionitrile, 1·75; acetonitrile, 2·50; *p*-toluonitrile, 6·8; benzonitrile, 14·0; *p*-bromobenzonitrile, 27·2; *m*-bromobenzonitrile, 38·0; *p*-nitrobenzonitrile, 62·0; *m*-nitrobenzonitrile, 78·0; di*iso*amylcyanoamide, 98·0. In some cases, the equilibrium point varies considerably with changes in the concentration of the nitrile and the ethoxide, but in other cases shows but little fluctuation. Different ethoxides catalyse the reaction with different velocities, and the equilibrium points also often vary in such cases. The velocity of the reaction varies greatly with the different nitriles, *p*-nitrobenzonitrile reacting very rapidly, whilst *o*-toluonitrile scarcely unites with alcohol at all.

Certain experiments are described which show that the velocity of reaction can be expressed as a function of both the ethoxide ions and the non-ionised ethoxide.

E. G.

Nitrile of Fumaric Acid and the Preparation of Methyl Maleate. EDWARD H. KEISER and L. MCMASTER (*Amer. Chem. J.*, 1913, **49**, 81—84).—Keiser and Kessler (A., 1911, i, 949) have shown that fumaronitrile can be prepared by heating fumaramide with phosphoric oxide. It has now been found that the nitrile can be

converted into fumaramide by treating it with an alkaline solution of hydrogen peroxide.

Methyl maleate, which has only been obtained previously by the action of methyl iodide on silver maleate, has now been prepared by heating a mixture of maleic acid, methyl alcohol, and sulphuric acid under a reflux condenser. When the ester is left with solution of ammonia for several days, it gradually dissolves, and on evaporation a yellow viscous mass is obtained which is probably maleamide.

E. G.

The Action of Light on Pigments. II. The Composition of Turnbull's Blue. ALEXANDER EIBNER and L. GERSTACKER (*Chem. Zeit.*, 1913, **37**, 137—139, 178—179, 195—197).—As a result of their experiments, the authors come to the conclusion that freshly prepared Turnbull's blue is not identical with Paris blue, but is a derivative of ferricyanic acid. It is not the most labile of the ferricyanides of the heavy metals, those of ferric iron, zinc, cadmium, lead, and copper being less stable. On long-continued washing or heating, a change takes place between the constituents of Turnbull's blue, resulting in the reduction of the ferricyanogen and oxidation of the ferrous radicle. The final result of such treatment is identical with Paris blue, the velocity of change depending on the conditions.

T. S. P.

Spirocyclane, its Synthesis and Behaviour on Catalytic Reduction. NICOLAI D. ZELINSKI (*Ber.*, 1913, **46**, 160—172; *J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1873—1884).—The hydrocarbon formed by the action of zinc dust and alcohol on the tetrabromide of pentaerythritol has been regarded by Gustavson (A., 1896, i, 669) as vinyltrimethylene. Reasons are now given for formulating the compound as spirocyclane, $\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>C<\!\!\begin{matrix}CH_2\\|\\CH_2\end{matrix}$. The only other possible constitution is that of methylene*cyclo*butane.

The hydrocarbon is very readily and completely reduced in contact with nickelised asbestos and hydrogen at about 100°. No condensation product is formed, the gaseous mixture consisting entirely of saturated hydrocarbons. This behaviour eliminates any other constitution than that of the spirocyclane.

[With V. KRAVEC.]—This is confirmed by effecting the synthesis of spirocyclane by closing the two trimethylene rings one after the other.

By the action at 0° of hydrogen bromide on pentaerythritol, the *dibromohydrin*, $C(CH_2Br)_2(CH_2{\cdot}OH)_2$, is obtained. This crystallises in well formed needles, m. p. 112°; the *diacetyl* derivative has b. p. 185°/13 mm.

When reduced with zinc dust, the *diacetate* of *dimethylol*cyclo*propane* is obtained, b. p. 115°/15 mm. The *glycol*,

$$\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>C(CH_2{\cdot}OH)_2,$$

has b. p. 126—127°/16 mm., D_4^{20} 1·0794, $n^{20\cdot5}$ 1·4705. When oxidised with permanganate, it yields *cyclo*propane-1 : 1-dicarboxylic acid.

Phosphorus tribromide converts the glycol into *dibromodimethyl-cyclopropane*, $\genfrac{}{}{0pt}{}{CH_2}{CH_2}>C\cdot(CH_2Br)_2$, b. p. 72—74°/13 mm., D_4^{20} 1·8022, $n = 1{\cdot}534$. In addition, a tribromide resulting from the opening of the *cyclo*propane ring is formed.

On reduction of the dibromide, spirocyclane is obtained, b. p. 40—41·5°, D_4^{20} 0·7266, $n = 1{\cdot}4120$, in agreement with earlier values.

[With B. SCHTSCHERBAK.]—When a mixture of spirocyclane and hydrogen is passed over platinum black at 70°, a mixture of ethyl*cyclo*propane and pentane is formed. Using palladium black in the cold, it is possible to restrict the reduction entirely to one ring and obtain ethyl*cyclo*propane alone. In order to reduce the second ring, nickel must be used as catalyst—a temperature of 200° is necessary before *iso*pentane is obtained. The reduction of spirocyclane thus takes place in two stages and selective catalysts are required. Nickel in the cold reduces it only to ethyl*cyclo*propane. E. F. A.

Preparation of the Three Cymenes (Methyl*iso*propylbenzenes) and Three Menthanes (Methyl*iso*propyl*cyclo*hexanes). PAUL SABATIER and MARCEL MURAT (*Compt. rend.*, 1913, **156**, 184—187. Compare Sabatier and Senderens, A., 1901, i, 459).—Starting from the three tolyldimethylcarbinols, $C_6H_4Me\cdot CMe_2\cdot OH$, the authors have prepared the three corresponding cymenes and menthanes, and examined their physical properties. The three carbinols were prepared either (1) by the action of magnesium methyl iodide on the ethyl *o*-, *m*-, and *p*-toluates, or on the three tolyl methyl ketones, or (2) by the action of acetone on the three magnesium tolyl bromides. The vapours of the three carbinols were completely dehydrated under the influence of thorium oxide at 350°, giving respectively *o*-, *m*-, and *p*-β-allyltoluene, $C_6H_4Me\cdot CMe{:}CH_2$, which by the action of slightly activated nickel at 200—220° yielded the corresponding cymenes. These substances underwent further hydrogenation when passed in the form of vapour over activated nickel at 170—180°, and the corresponding menthanes were obtained, all of which have been previously described. In certain cases the values of the physical constants now obtained differ from those previously given by other authors, namely, *o*-β-allyltoluene has b. p. 175°, D_0^{15} 0·9181, n_D^{15} 1·521 (compare Tiffeneau, A., 1907, i, 305).

o-Cymene has b. p. 175° (corr.), D_0^0 0·8902, n_D^{22} 1·501 (compare Sprinkmeyer, 1901, i, 519).

o-Menthane, b. p. 171° (corr.), D_0^0 0·8326, D_0^{21} 0·8135, n_D^{21} 1·447 (compare Kay and Perkin, T., 1905, **87**, 1066).

r-*m*-Menthane, b. p. 166—167° (corr.), D_0^{24} 0·7968, n_D^{24} 1·440.

d-*m*-Menthane was obtained by the hydrogenation of natural *d*-sylvestrene at 200° by activated nickel, and has b. p. 167—168°, D_0^0 0·8235, D_0^{23} 0·8116, n_D^{23} 1·446, $[\alpha]_D^{23}$ +1·60° (compare Knoevenagel, A., 1897, i, 610).

The para-isomeride has b. p. 167—168° (corr.), D_0^0 0·8134, D_0^{25} 0·8028, n_D^{25} 1·440 (compare Sabatier and Senderens, *loc. cit.*). W. G.

Systems Formed by Chloro- and Nitro-toluenes with Antimony Trihaloids. BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1939—1963).—*o*-, *m*-, and *p*-Chlorotoluenes melt at −36·2°

(Haase, A., 1892, ii, 357, gave $-34°$), $-47·8°$, and $6·2°$ (Haase, *loc. cit.*, gave $7·4°$) respectively.

With antimony trichloride, *o*-chlorotoluene forms the compound, $SbCl_3,C_6H_4MeCl$, crystallising in long plates or needles, m. p. 3°, and the eutectic points and compositions are (1) 37·5° and

$$SbCl_3,24·1C_6H_4MeCl,$$

and (2) $-0·5°$ and $SbCl_3,1·95C_6H_4MeCl$. *m*-Chlorotoluene gives the compound, $SbCl_3,C_6H_4MeCl$, which is much less stable than that formed by the ortho-derivative and decomposes before melting; the eutectic points are (1) $-14°$, $SbCl_3,2·7C_6H_4MeCl$, and (2) $-49°$, $SbCl_3,24·1C_6H_4MeCl$. *p*-Chlorotoluene and antimony trichloride form no compound, the diagram showing only one eutectic point at $-7·5°$, corresponding with $SbCl_3,2·3C_6H_4MeCl$.

With antimony tribromide, none of the chlorotoluenes form compounds. The eutectic points and the corresponding compositions are for the ortho-compound, $-38·5°$ and $SbBr_3,23·8C_6H_4MeCl$; for the meta-compound, $-50°$ and $SbBr_3,32·3C_6H_4MeCl$, and for the para-compound, 2·5° and $SbBr_3,9·4C_6H_4MeCl$.

o-Nitrotoluene has m. p. $-8·5°$ (Knoevenagel, A., 1907, i, 202, gave $-9·4°$, and Ostromisslensky, A., 1907, i, 120, $-10·56°$) for the more stable α-modification and $-4°$ for the less stable β-form; the solutions in antimony trihaloid always correspond with the α-compound. The meta- and para-isomerides melt at 16° and 52·5° respectively.

o-Nitrotoluene and antimony trichloride give the compound

$$SbCl_3,C_6H_4Me·NO_2,$$

crystallising in slender needles, m. p. 34·5°; the eutectic points are $-18·5°$, corresponding with $SbCl_3,7·28C_6H_4Me·NO_2$, and 27·5° with $SbCl_3,0·56C_6H_4Me·NO_2$. *m*-Nitrotoluene and antimony chloride form a compound, which apparently melts at a higher temperature than the corresponding para-compound, but could not be obtained crystalline.

p-Nitrotoluene and antimony chloride form a compound

$$SbCl_3,C_6H_4Me·NO_2,$$

which crystallises with difficulty; the eutectic points and compositions are: (1) 7·5° and $SbCl_3,1·55C_6H_4Me·NO_2$, and (2) 3° and

$$SbCl_3,0·76C_6H_4Me·NO_2.$$

With antimony tribromide, *o*-nitrotoluene forms the compound $SbBr_3,C_6H_4Me·NO_2$, crystallising in needles, m. p. 32° (decomp.), isomorphous with those of the corresponding compound of antimony trichloride. The system exhibits one eutectic point, $-13·5°$, corresponding with $SbBr_3,10·8C_6H_4Me·NO_2$, and one transition point, 31°, corresponding with $SbBr_3,1·3C_6H_4Me·NO_2$. *m*-Nitrotoluene and antimony tribromide form no compound, the system showing only one eutectic point, $-9°$, corresponding with $SbBr_3,2C_6H_4Me·NO_2$. The para-derivative also forms no compound with the tribromide, the diagram consisting of two curves meeting at the eutectic point, 16°, for which the composition is $SbBr_3,1·3C_6H_4Me·NO_2$.

These results are discussed in relation to those obtained with benzene and its other substituted derivatives (*loc. cit.*). T. H. P.

Δ^1-Dihydronaphthalene. FRITZ STRAUS and LEO LEMMEL (*Ber.*, 1913, **46**, 232—241).—If Δ^2-dihydronaphthalene, which was obtained

by Bamberger and Lodter (A., 1888, 292; 1896, i, 99) by the action of sodium and ethyl alcohol on naphthalene, is heated with an alcoholic solution of sodium ethoxide, it quantitatively undergoes isomeric change into the hitherto unknown Δ^1-dihydronaphthalene.

Crude Δ^2-dihydronaphthalene was purified by shaking in ethereal solution with an aqueous solution of mercuric acetate; the crystalline mercury compound, after washing with ether, was dissolved in benzene, when a slight insoluble residue was obtained, apparently of the mercury compound of Δ^1-dihydronaphthalene, due to a trace of this hydrocarbon in the crude starting substance. The pure mercury compound, m. p. 119—120°, obtained on evaporation of the solution, when decomposed with a 30% solution of hydrochloric acid, gave pure Δ^2-dihydronaphthalene, leaflets, m. p. 24·5—25°, b. p. 94·5°/17 mm., which on heating for eight hours at 140—150° with sodium ethoxide in alcoholic solution was isomerised into Δ^1-*dihydronaphthalene*, b. p. 84—85°/12 mm., m. p. −8° to −7°, an unpleasant-smelling liquid which immediately decolorises permanganate; when shaken with mercuric acetate, it is slowly converted into a white *mercury* derivative, which is insoluble in benzene, and does not melt below 250°; the *dibromide*, colourless crystals, m. p. 70—71°, is quite distinct from that (m. p. 71·5—72°) of the Δ^2-isomeride, and when boiled with alcoholic potassium hydroxide gives an oily *substance* of characteristic odour, together with a little naphthalene.

When an emulsion of Δ^1-dihydronaphthalene in water is oxidised by the gradual addition of concentrated potassium permanganate solution, *o*-carboxyphenylpropionic acid is obtained, together with a quantity of a pungent *substance* of low m. p. The further reduction of Δ^1-dihydronaphthalene can be accomplished by the addition of its alcoholic solution to finely-divided sodium, the product being tetrahydronaphthalene.

The above method of formation of Δ^1-dihydronaphthalene disposes of the difficulty of reconciling the reduction of naphthalene through Δ^2-dihydronaphthalene to tetrahydronaphthalene with the behaviour of the analogous allylbenzene and propenylbenzene, only the latter of which is reducible by sodium and alcohol to a saturated homologue of benzene (Klages, A., 1903, i, 19, 329; 1904, i, 567); according to this, Δ^2-dihydronaphthalene should not be directly reducible. The preparation of tetrahydronaphthalene by Bamberger and Kitschelt (A., 1890, 1146) is to be attributed to the reduction occurring by the stages

$$C_6H_4{<}\begin{array}{l}CH{:}CH\\ CH{:}CH\end{array} \longrightarrow C_6H_4{<}\begin{array}{l}CH_2{\cdot}CH\\ CH_2{\cdot}CH\end{array} \longrightarrow C_6H_4{<}\begin{array}{l}CH{:}CH\\ CH_2{\cdot}CH_2\end{array} \longrightarrow$$

$$C_6H_4{<}\begin{array}{l}CH_2{\cdot}CH_2\\ CH_2{\cdot}CH_2\end{array}$$

D. F. T.

Triphenylmethyl. XXII. Ethers or Oxides in the Triphenylmethane Series. Moses Gomberg (*J. Amer. Chem. Soc.*, 1913, **35**, 200—210).—It is well known that diarylcarbinols can be converted into the corresponding ethers or oxides by heating them either alone or in presence of a dehydrating agent. A few oxides of the triaryl-

carbinols have also been reported in the literature, but the results of the present work show that most of the compounds thus designated were not in reality triarylmethyl ethers.

A general method is now described for the preparation of triarylmethyl ethers. These compounds are as stable as the peroxides, are not affected by exposure to the air, or by heating them to temperatures below their m. p.; they are not decomposed by water or dilute alkali hydroxide, even at 100°, but are hydrolysed when boiled with dilute acids, alcohol, acetic acid, or acetyl chloride.

When triphenylmethyl chloride is treated with silver oxide, oxidation takes place with formation of diphenylquinomethane and other products, but the ether is not obtained. If triphenylmethyl chloride is shaken with zinc oxide and ether in sealed tubes, it is reduced quantitatively to triphenylmethane, and this reaction furnishes a simple and rapid method for preparing the hydrocarbon. The oxides of cadmium, lead, nickel, cobalt, and magnesium do not react with triphenylmethyl chloride. When, however, a triarylmethyl chloride dissolved in a dry solvent, such as benzene, ether, carbon disulphide, or chloroform, is heated on the water-bath with mercuric oxide, the corresponding triarylmethyl ether is readily obtained in a good yield.

Triphenylmethyl ether, $CPh_3 \cdot O \cdot CPh_3$, m. p. 235—237° (decomp.), forms white crystals, and is soluble in about 25 parts of benzene at the ordinary temperature, or in 5 parts of boiling benzene; 1 gram dissolves in 11 c.c. of carbon disulphide or in 325 c.c. of ether.

Phenylfluorene ether, $\left(\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}>CPh\right)_2O$, m. p. 232—233°, forms colourless crystals, and is soluble in about 6·5 parts of benzene or 100 parts of ether; it is readily converted into the peroxide, m. p. 193° (Gomberg and Cone, A., 1906, i, 822). The compound obtained by Kliegl (A., 1905, i, 187) by the action of acetic and sulphuric acids on phenylfluorenol is not identical with the ether now described.

Phenylxanthenol ether, $\left(O<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>CPh\right)_2O$, m. p. 250—252°, forms pale yellowish-pink crystals, and is soluble to the extent of 1 gram in 12 c.c. of cold, or 5 c.c. of hot, benzene, or in 160 c.c. of ether.

p-*Methoxytriphenylmethyl ether*, m. p. 212°, is soluble to the extent of 1 gram in 25 c.c. of cold benzene.

p-*Acetoxytriphenylmethyl chloride*, m. p. 85—86°, obtained by the action of hydrogen chloride on a solution of the carbinol in benzene, forms white crystals; when treated with mercuric oxide, it is converted into p-*acetoxytriphenylmethyl ether*, m. p. 123—124° (decomp.), which crystallises in white needles, and is not identical with the substance to which this constitution was assigned by Bistrzycki and Herbst (A., 1901, i, 702); the latter was probably the carbinol as suggested by Auwers and Schröter (A., 1903, i, 821).

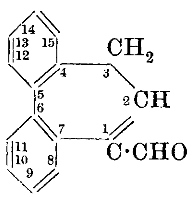
Another method has also been devised for preparing triarylmethyl ethers. When triphenylmethyl carbonate is heated under certain conditions, carbon dioxide is evolved and a nearly quantitative yield of triphenylmethyl ether is produced. The details of this method will be published subsequently. E. G.

Triphenylmethyl Ether. MOSES GOMBERG (*Ber.*, 1913, **46**, 225—228).—Although *triphenylmethyl ether* is not obtained in the action of silver oxide on triphenylmethyl chloride (compare Schlenk, this vol., i, 34), the application of mercuric oxide gives an almost quantitative yield of this substance (m. p. 235—237°). The reaction with mercuric oxide is a general one for the production of triarylmethyl ethers. Triphenylmethyl carbonate (m. p. 205—210°) when heated with copper as a catalyst to 140°, also decomposes into triphenylmethyl ether and carbon dioxide.

The opinion is expressed that the behaviour of triphenylmethyl and its analogues is best explained by an equilibrium between the three structures represented by the tervalent carbon, the hexaphenylethane, and Jacobson's (A., 1905, i, 186) formulæ.

D. F. T.

Synthesis of Pyrene. RICHARD WEITZENBÖCK (*Monatsh.*, 1913, **34**, 193—223).—Two schemes for the synthesis of pyrene have been followed. The first, which should have led to the preparation of diphenyl-2 : 2′-diacetaldehyde, which might have condensed in a manner analogous to the formation of β-phenylnaphthalene from phenylacetaldehyde (Auwers and Keil, A., 1904, i, 26), was unsuccessful. The tetramethylacetal of the dialdehyde was obtained, but on hydrolysis it gave 4 : 5 : 6 : 7-dibenzo-$\Delta^{1:4:6}$-*cyclo*heptatriene-2-aldehyde (annexed formula), the ready closing of the seven-membered ring recalling the formation of 2-imino-1-cyano-4 : 5 : 6 : 7-dibenzo-$\Delta^{4:6}$-*cyclo*heptadiene from diphenyl-2 : 2′-diacetonitrile (Kenner and Turner, T., 1911, **99**, 2104).



The other scheme was analogous to the preparation of 2 : 8-dihydroxychrysene from $\beta\gamma$-diphenyl-$\alpha\delta$-dihydromuconic acid (Beschke, A., 1911, i, 874), and consisted in the condensation of diphenyl-2 : 2′-diacetic acid to dihydroxypyrene which could be reduced by means of zinc dust or hydriodic acid and red phosphorus.

Scheme A.—It was first attempted to prepare diphenyl-2 : 2′-diacrylic acid by the distillation of *methyl* o-*iodocinnamate*, white needles, m. p. 40°, b. p. 300—310°, with copper, but the decomposition proceeded to the formation of phenanthrene. The ethyl ester could not be obtained pure, and gave still worse results. The acid was obtained, however, by Perkin's synthesis on 2 : 2′-dialdehydodiphenyl (compare Mayer, A., 1911, i, 870), being accompanied by the lactone of diphenyl-2-carbinol-2′-carboxylic acid (Kenner and Turner, *loc. cit.*), and was converted into the *diamide*, $C_{18}H_{16}O_2N_2$, white needles, by means of thionyl chloride and ammonia.

A better way to arrive at diphenyl-2 : 2′-diacetaldehyde was sought in the application of Weerman's method (A., 1907, i, 132) to the *amide* of o-*iodocinnamic acid.* This was obtained by the action of thionyl chloride and ammonia on the acid, in light brown, quadratic leaflets, m. p. 204—205°, the crude chloride having m. p. 63—64°. When treated with sodium hypochlorite in methyl alcohol, *methyl*

o-iodostyrylcarbamate, $C_6H_4I\cdot CH\colon CH\cdot NH\cdot CO_2Me$, was obtained in colourless leaflets, m. p. 128—130°, which on hydrolysis gave *o-iodophenylacetaldehyde*, C_8H_7OI, in pleasant smelling, white needles, m. p. 35—36°. When heated with copper, extensive decomposition took place, which was also the case with the *phenylbenzylhydrazone*,

$$C_{21}H_{19}N_2I,$$

stout, colourless needles, m. p. 104—105°. However, the *dimethylacetal*, $C_{10}H_{13}O_2I$, which was obtained by Fischer and Hoffa's method (A., 1898, i, 659) as a colourless, mobile oil, b. p. 144°/19 mm., gave a good yield of diphenyl-2 : 2′-diacetaldehyde,

$$C_{12}H_6\cdot[CH_2\cdot CH(OMe)_2]_2,$$

in the form of a viscid, yellow oil, b. p. 210—211°/13 mm. On hydrolysis, an unsaturated aldehyde was obtained, in white, pleasant smelling needles, m. p. 108—109°, which gave phenanthraquinone on oxidation with chromic acid, and is, therefore, to be regarded as 4 : 5 : 6 : 7-*dibenzo*-$\Delta^{1:4:6}$-cyclo*heptatriene*-1-*aldehyde*, rather than as phenanthryl-4-acetaldehyde. It gives a stable *dibromide*, $C_{16}H_{12}OBr_2$, in colourless needles, m. p. 133° (decomp.).

Scheme B.—Diphenyl-2 : 2′-diacetonitrile was hydrolysed by means of concentrated hydrochloric acid at 130—140° (compare Kenner and Turner, *loc. cit.*), and the acid was dehydrated with zinc chloride or, better, converted into the chloride with thionyl chloride and then condensed with aluminium chloride. The impure, reddish hydroxy-product gave pyrene when distilled with zinc dust or heated with hydriodic acid and red phosphorus at 200°. An attempt to convert dibromoditolyl into the nitrile by Mann's method for phenylacetonitrile (A., 1881, 1034) resulted in the formation of Kenner and Turner's 2-imino-1-cyano-4 : 5 : 6 : 7-dibenzo-$\Delta^{4:6}$-*cyclo*heptadiene. J. C. W.

Quaternary Salts of Alkylideneamines and a General Method of Converting Primary into Secondary Amines.

HERMAN DECKER and PAUL BECKER (*Annalen*, 1913, **395**, 362—377).—The formation of a quaternary ammonium salt by the addition of an alkyl iodide to an alkylideneamine is practicable, but the product is often contaminated by other substances formed by (i) the dissociation of the salt into its generators, (ii) heterospasis (Decker and Fellenberg, A., 1909, i, 116), (iii) intramolecular change, ring formation, or polymerisation of the salt.

Quaternary alkylideneammonium iodides are decomposed by water or alcohol in the sense of the equation:

$$CHR''\colon NRR'I + H_2O = R''\cdot CHO + NHRR' + HI,$$

whereby a very satisfactory method is secured of converting primary into secondary amines without any possibility of the formation of the tertiary amines or the quaternary salt. The yield of the secondary amine is usually more than 75%, being less, however, in the case of primary aromatic amines containing the amino-group in the nucleus.

β-Phenylethylamine reacts with benzaldehyde and with vanillin on the water-bath to form *β-phenylethylbenzylideneamine*,

$$CH_2Ph\cdot CH_2\cdot N\colon CHPh,$$

m. p. 33—34°, colourless prisms, and *β-phenylethylvanillylideneamine*

m. p. 108—109°, leaflets, respectively. The former and methyl iodide at 100° yield an additive compound which is decomposed by boiling 95% alcohol into benzaldehyde and *β-phenylethylmethylamine hydriodide*, $CH_2Ph\cdot CH_2\cdot NHMe,HI$, m. p. 113—115°. The base, which is also produced by heating β-phenylethylglycine above its m. p., forms a *hydrochloride*, m. p. 156—157° (decomp.), *platinichloride*, m. p. 225—226° (decomp.), and *picrate*, m. p. 141—143°. β-Phenylethylethylamine, prepared in a similar manner, forms a *hydriodide*, m. p. 166—168°. Methyl-*p*-toluidine, prepared in a similar manner from benzylidene *p*-toluidine or heptylidene-*p*-toluidine, forms a *hydriodide*, m. p. 134—137°, pale yellow leaflets, and a *picrate*, m. p. 130—132° (decomp.), which is very sparingly soluble in benzene. Ethylaniline, methylaniline, and methyl*iso*butylamine have also been prepared by this method. C. S.

The Nitro-derivatives of *o*-Cresyl Oxide [*o*-Tolyl Ether] and *o*-Cresylene Oxide [Di-*o*-tolylene Oxide]. ALPHONSE MAILHE (*Compt. rend.*, 1913, **156**, 241—243. Compare this vol., i, 173).—On nitrating *o*-tolyl ether in acetic acid solution, a viscous liquid is obtained which, by distillation under reduced pressure, yields 5-*nitro*-o-*tolyl ether*, $C_6H_4Me\cdot O\cdot C_6H_3Me\cdot NO_2$, yellow needles, m. p. 125°; this on reduction with iron and acetic acid gives the corresponding *amine*, m. p. 98°. If the nitration is effected in cold fuming nitric acid, by gradual addition of the ether to the acid, 5 : 5′-*dinitro*-o-*tolyl ether*, $O(C_6H_3Me\cdot NO_2)_2$, is obtained as a white powder, m. p. 270°, which on prolonged nitration with fuming nitric acid, containing a little sulphuric acid, is converted into 3 : 5 : 3′ : 5′-*tetranitro*-o-*tolyl ether*,

$$O[C_6H_2Me\cdot(NO_2)]_2,$$

m. p. 115°.

Di-*o*-tolylene oxide nitrates very readily in acetic acid solution on warming, giving *nitrodi*-o-*tolylene oxide* $O{<}\begin{matrix}C_6H_3Me\\|\\C_6H_2Me\cdot NO_2\end{matrix}$, m. p. 108—109°, giving by reduction the corresponding *amine*, m. p. 92°, which gives a red coloration in alcoholic solution with calcium chloride.

By warming di-*o*-tolylene oxide with fuming nitric acid, a *dinitro*-derivative is obtained, crystallising in yellow needles, m. p. 170°. By warming this compound with fuming nitric acid, *tetranitrodi*-o-*tolylene oxide*, $O{<}\begin{matrix}CHMe(NO_2)_2\\|\\C_6HMe(NO_2)_2\end{matrix}$, is obtained as a white powder, m. p. 210°.

W. G.

The Action of Aldehydes on Phenols. HERMANN WICHELHAUS (*Ber.*, 1913, **46**, 110—112).—A continuation of research as to the origin of the dyes in certain woods (compare A., 1910, i, 868).

Formaldehyde has been detected in certain trees (Curtius and Franzen, A., 1912, ii, 978; Kleinstück, A., 1912, ii, 1202), and the author has, therefore, examined the action on phenols of trithioformaldehyde, which possesses the advantage of a lower volatility. In the presence of zinc chloride, condensation occurs with β-naphthol, resor-

cinol, a- and β-anthrols, and dihydroxynaphthalene, producing deeply coloured fusions which are difficult to purify. It is probable that one molecule, CH_2S, condenses with two of the phenol.

If the aldehyde is first combined with sodium sulphite (D.R.-P. 87335), the condensation follows another course, involving two molecules of aldehyde and two of the phenol; the products are colloidal substances often yielding fluorescent solutions, and possess dyeing power.

β-Naphthol after conversion into the acid, $OH\cdot C_{10}H_6\cdot CH_2\cdot SO_3H$, gives a condensation product which in solution possesses a green fluorescence, dyes wool a rose colour, and gives brightly coloured lakes with aluminium, manganese, and zinc salts. The product from β-naphtholsulphonic acid dyes silk greyish-red.

2 : 7-Dihydroxynaphthalene when converted into 2 : 7-dihydroxynaphthylmethanesulphonic acid, and heated slowly with zinc chloride solution in a vacuum, undergoes condensation below 100°, giving a blue *substance*, $C_{22}H_{16}O_6$; this dyes silk, and also can be converted into *nitro*-derivatives which also possess dyeing properties.

D. F. T.

The Silver Equivalent of Quinol. M. A. GORDON (*J. Physical Chem.*, 1913, **17**, 47—82).—The number of molecules of silver salt reduced per molecule of quinol varies with the conditions up to at least 10·5. In presence of acid no reduction occurs. In alkaline solution the amount of silver liberated from precipitated silver bromide depends on the efficiency of stirring, the time, temperature, and concentration of the alkali, but not on the incident light. At 20° in presence of excess of sodium hydroxide, the action appears to proceed in two stages, namely, up to about 6 equivalents of silver in a few hours, and then to about 8 in eighteen days. At 100° at least 9 equivalents are liberated in six hours.

The silver equivalent of *p*-benzoquinone is about two less than that of quinol. The liberation of 6 equivalents of silver by quinol corresponds with the formation of dihydroxy-*p*-benzoquinone, thus: $C_6H_4(OK)_2 + 6AgBr + 6KOH = C_6H_2(OK)_2O_2 + 6Ag + 6KBr + 4H_2O$. *p*-Benzoquinone and monohydroxy-*p*-benzoquinone may be intermediate products as suggested by Luther and Leubner (*Brit. J. Photo.*, 1912, **59**, 632—747), although the presence of neither monohydroxy- nor dihydroxy-benzoquinone has been demonstrated. *p*-Benzoquinone is undoubtedly an intermediate product, and by the action of the alkaline solution is transformed into quinol plus a peroxidised product which may be hydrogen peroxide (Mees and Sheppard) or hydroxybenzoquinone (Luther and Leubner). The Mees and Sheppard theory demands an infinite liberation of silver by a small amount of quinol in presence of sodium sulphite, and is inadmissible. The Luther and Leubner theory restricts the silver equivalent of quinol to 6, and therefore does not express the whole truth.

In strongly alkaline solution an excess of sodium sulphite increases the silver equivalent of quinol by 2 (from 6 to 8) for short runs, and by 1 (from 8 to 9) for long runs. The effect on the equivalent of benzoquinone is about half as great. When sulphite is added after the reduction by quinol has started, its effect is restricted. Hence

sulphite probably intervenes in the first and second stages of the oxidation of quinol equally. Some of the sulphite is oxidised, presumably to dithionate, although sodium sulphite alone is without action on silver bromide.

Ammoniacal silver nitrate, silver sulphite dissolved in sodium sulphite, and silver oxide in presence of sodium hydroxide give quinol equivalents of 7, 8, and 10·5 respectively for five minute runs.

Pyrogallol with and without sodium sulphite has a silver equivalent of a little over 3 when tested with silver bromide in a one hour run. Catechol under like conditions has an equivalent of 4·5, increasing to 5·5 in presence of sulphite. R. J. C.

o-**Nitrophenyl Selenocyanate and** *o*-**Aminophenylselenol.** Hugo Bauer (*Ber.*, 1913, **46**, 92—98).—When a solution of potassium selenocyanate is added gradually to a diazotised solution of *o*-nitroaniline in which the excess of free mineral acid has been neutralised by the addition of sodium acetate, nitrogen is liberated and a quantitative yield of *o-nitrophenyl selenocyanate*, yellow needles, m. p. 142°, is obtained. This action appears to be a general one, and was also successful with *p*-nitroaniline (*p-nitrophenyl selenocyanate*, pale yellow leaflets, m. p. 135°), sulphanilic acid, *p*-aminobenzoic acid, and arsanilic acid. On moistening with alcohol and then adding sodium hydroxide solution, *o*- and *p*-nitrophenyl selenocyanates undergo hydrolysis, forming coloured solutions (violet and red respectively) of the *sodium* salts of o- and *p-nitrophenylselenols*; the free phenylselenols could not be isolated, but the addition of a solution of lead acetate precipitated the *lead* salts, both of an orange colour.

The coloured alkaline solution of *o*-nitrophenylselenol soon loses its colour, undergoing oxidation even in a hydrogen atmosphere to *di-o-nitrophenyl diselenide*, yellow needles, m. p. 209°, which precipitates. The alkaline solution of *o*-nitrophenylselenol can also be obtained by the interaction of *o*-chloronitrobenzene and sodium hydroselenide in dilute solution in cold alcohol, and the diselenide can then be again obtained, the oxidation being aided if necessary by the addition of hydrogen peroxide. The former method is, however, the more satisfactory.

If the alkaline solution of *o*-nitrophenylselenol is treated near its b. p. with sodium hyposulphite a clear yellow or colourless solution of the *sodium* salt of *o-aminophenylselenol* is obtained, which on careful oxidation with hydrogen peroxide gives a precipitate of *di-o-aminophenyl diselenide*, orange needles, m. p. 81°. When a solution of this in hot alcohol is treated with hydrochloric acid and the resultant suspension of the *hydrochloride* reduced by zinc dust, the addition of sodium acetate precipitates the stable *zinc* salt of *o*-aminophenylselenol; the action of lead acetate on a suspension of this gives the orange *lead* salt. The reduction of the diselenide can also be effected by alkali and dextrose (compare Clasz, A., 1912, i, 851).

The action of benzoyl chloride on the zinc salt of *o*-aminophenylselenol in the presence of ethyl acetate produces *1-phenylbenzoselenazole*, $C_6H_4{<}{}^{N}_{Se}{>}CPh$, colourless needles, m. p. 116—117° which could not

be obtained by the action of selenium on benzanilide (compare Hofmann, A., 1880, 386; 1887, 839). With picryl chloride the zinc salt undergoes condensation with the formation of 3:5-*dinitrophenoselenazine*, $C_6H_4<^{NH}_{Se}>C_6H_2(NO_2)_2$ (compare Kehrmann, A., 1900, i, 61).
D. F. T.

Some Compounds of Cholesterol giving Liquid Crystals. PAUL GAUBERT (*Compt. rend.*, 1913, **156**, 149—151. Compare A., 1907, ii, 932; 1908, i, 882; 1909, i, 920).—On heating cholesterol with the different tartaric acids for one minute a homogeneous isotropic liquid substance is obtained, which on cooling yields elongated rhombic crystals, possessing very great plasticity. The direction of the greatest refraction coincides with the long diagonal. At temperatures near to the point of fusion, the crystalline particles of the crystals arrange themselves so that the optical axis is perpendicular to the glass slide, and there are produced extensive, irregular films exhibiting all the characteristics of a uniaxial, optically positive substance. The hardness of the crystals rapidly increases up to that of gypsum as they become solid. Similar results are obtained by using malic and lactic acids instead of the tartaric acids. Maleic and malonic acids, but not fumaric acid, yield optically positive liquid crystals almost instantly on warming with cholesterol, but they are only stable within narrow temperature limits. The same applies to the compound obtained with succinimide and cholesterol. In order to obtain liquid crystals with cholesterol and succinic, cinnamic, or anisic acids, it is necessary to keep the mixture molten at 160° for one hour, when characteristic optically negative crystals are produced.
W. G.

Action of Magnesium on a Mixture of Allyl Bromide and Benzoin. V. JAKUBOVITSCH (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1858—1861).—*Diphenylallylethylene glycol* [$\delta\epsilon$-*diphenyl*-Δ^{α}-*pentene*-$\delta\epsilon$-*diol*], $C_3H_5\cdot CPh(OH)\cdot CHPh\cdot OH$, prepared by decomposing with water the product of the action of magnesium on allyl bromide and benzoin, forms small, colourless crystals, m. p. 89°, has the normal molecular weight in boiling benzene, and decolorises bromine. When boiled with 20% sulphuric acid, it is converted into the corresponding double *ether*, $\begin{array}{l}CHPh\text{---}O\text{---}CHPh\\ |\qquad\qquad\quad |\\ CPh(C_3H_5)\cdot O\cdot CPh\cdot C_3H_5\end{array}$, which crystallises in small, colourless needles, m. p. 125—126°.
T. H. P.

Influence of Constitution on the Rotatory Power of Optically Active Substances. V. Esters of *d*-Carvoxime. HANS RUPE and GEORG WOLFSLEBEN (*Annalen*, 1913, **395**, 136—148).—The following substances have been prepared generally by the interaction of *d*-carvoxime, pyridine (2 mols.), and the acyl chloride in benzene. Only the acetyl compound can be purified by distillation under diminished pressure; the others must be crystallised from absolute or dilute alcohol. Acetylcarvoxime has m. p. 63—64°, b. p. 158—161°/17 mm., and and $[\alpha]_D^{20}$ +43·02°. *Crotonylcarvoxime*, $C_{10}H_{14}:NO\cdot CO\cdot CH:CHMe$, oil,

$[\alpha]_D^{20}$ +33·46°; *diphenylacetylcarvoxime*, m. p. 65—66°, $[\alpha]_D^{20}$ +17·63°; *cinnamoylcarvoxime*, m. p. 79°, $[\alpha]_D^{20}$ +15·44°; *β-phenylpropionylcarvoxime*, oil, $[\alpha]_D^{20}$ +26·23°; *α-phenylcinnamoylcarvoxime*,

$$C_{10}H_{14}:N\cdot O\cdot CO\cdot CPh:CHPh,$$

m. p. 139—140°, $[\alpha]_D^{20}$ +37·06°; *αβ-diphenylpropionylcarvoxime*, m. p. 119—120°, $[\alpha]_D^{20}$ +12·52°; *β-phenylcinnamoylcarvoxime*, m. p. 74—75°, $[\alpha]_D^{20}$ +26·37°; *di-β-phenylpropionylcarvoxime*, m. p. 89—90°, $[\alpha]_D^{20}$ +20·09°; *α-methylcinnamoylcarvoxime*, m. p. 68—69°, $[\alpha]_D^{20}$ +16·33°; *β-phenyl-α-methylpropionylcarvoxime*, oil, $[\alpha]_D^{20}$ +23·85°; *β-methylcinnamoylcarvoxime*, m. p. 78°, $[\alpha]_D^{20}$ +22·45°; *β-phenyl-β-methylpropionylcarvoxime*, oil, $[\alpha]_D^{20}$ +22·76°.

Excluding the α- and the β-phenylcinnamoyl- and diphenylpropionylcarvoximes, the rotation of the saturated or the alkyl derivatives is distinctly greater than that of the corresponding unsaturated or phenyl derivatives. A parallelism cannot be traced between the carvoxime esters and the menthyl esters of the acids.

The entrance of a phenyl group into acetic acid or phenylacetic acid or the replacement of methyl by phenyl in acetic acid or crotonic acid diminishes the rotatory power of the carvoxime; the entrance of phenyl into the α- or the β-position in cinnamic acid increases the rotatory power. Just the converse behaviour is observed with the menthyl esters of the acids. The author is of opinion that the work so far recorded proves the necessity of dealing with substances containing one, or at most two, asymmetric carbon atoms in connexion with the problem of the relation between constitution and rotatory power. C. S.

The Determination of the Configuration of the Stereoisomeric Cinnamic Acids. CARL LIEBERMANN (*Ber.*, 1913, **46**, 214—216).—A reply to Stoermer and Heymann (A., 1912, i, 974), indicating that theirs is not the first experimental proof of the steric configuration of *allo*cinnamic acid. D. F. T.

Fixation of the Alkali Hydrogen Sulphites by the Salts and Esters of the Acetylenic Acids. ED. LASAUSSE (*Compt. rend.*, 1913, **156**, 147—149).—Under given conditions the salts or esters of the acetylenic acids of the type $R\cdot C:C\cdot CO_2H$ will unite with one or two molecules of an alkali hydrogen sulphite, giving an alkali salt of a monosulphonic acid, containing an ethylenic linking, or of a saturated disulphonic acid.

On heating phenylpropiolic acid (1 mol.) with normal sodium sulphite (1·5 mol.) in aqueous solution, in a sealed tube for eight hours at 100°, crystals of *disodium-β-sulphocinnamate*,

$$SO_3Na\cdot CPh:CH\cdot CO_2Na,$$

are obtained, which rapidly decolorise potassium permanganate in the cold. When heated in sealed tubes at 130° with concentrated hydrochloric acid it is decomposed, giving carbon dioxide, sulphur dioxide, and acetophenone. On fusion with sodium hydroxide at 200—220°, it yields sodium benzoate, sodium acetate, and sodium sulphite. The corresponding *potassium* salt has been prepared, starting with potassium sulphite. Methyl phenylpropiolate and sodium hydrogen sulphite under similar conditions yield *sodium methyl sulphocinnamate*,

$$SO_3Na\cdot CPh:CH\cdot CO_2Me.$$

If the heating is carried on for forty hours under reflux instead of in sealed tubes, three compounds are obtained, namely, *methyl disodium disulphophenylpropionate*, $C_2H_2Ph(SO_3Na)_2\cdot CO_2Me$, disodium sulphocinnamate, and *sodium phenyldisulphopropionate*,

$$C_2H_2Ph(SO_3Na)_2\cdot CO_2Na.$$

These three substances can be separated by their varying solubility in alcohol. The *barium* salt corresponding with the last compound has been prepared.

By similar methods the author has prepared *methyl disodium disulpho-octoate*, $C_5H_{11}\cdot C_2H_2(SO_3Na)_2\cdot CO_2Me$, which is saponified by cold aqueous sodium hydroxide, giving the corresponding *trisodium* salt, which when heated with hydrochloric acid in sealed tubes at 120° yields the *acid*, $C_5H_{11}\cdot C_2H_2(SO_3Na)_2\cdot CO_2H$.

He also prepared *methyl disodium disulphononoate*,

$$C_6H_{13}\cdot C_2H_2(SO_3Na)_2\cdot CO_2Me,$$

the *trisodium* derivative, and the *acid*, $C_6H_{13}\cdot C_2H_2(SO_3Na)_2\cdot CO_2H$.

W. G.

Synthesis of β-m-Tolyl-α-methylhydracrylic Acid. A. Gubarev (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1865—1867).—*Ethyl β-m-tolyl-α-methylhydracrylate*, $C_6H_4Me\cdot CH(OH)\cdot CHMe\cdot CO_2Et$, obtained by decomposing with water the product of the action of zinc on a mixture of ethyl α-bromopropionate and *o*-tolualdehyde, is a colourless, viscous liquid, with a pleasant odour, b. p. 171—172°/15—16 mm. The *acid* forms crystals, m. p. about 90°, but was not obtained pure. The *potassium* ($+H_2O$), *silver*, *zinc*, *copper*, and *lead* salts were prepared, and the first two analysed.

T. H. P.

Influence of Constitution on the Rotatory Power of Optically Active Substances. IV. Hans Rupe (*Annalen*, 1912, **395**, 87—135).—[With Eduard Lenzinger.]—The following menthyl esters have been prepared by heating menthol and the substituted ethyl acetoacetate; acetoacetate, m. p. 36°, b. p. 154°/10 mm.; *methylacetoacetate*, $CH_3\cdot CO\cdot CHMe\cdot CO_2\cdot C_{10}H_{19}$, b. p. 148—149°/8 mm., $[\alpha]_D^{20}$ $-63\cdot59°$ in benzene, n_α 1·45436, n_D 1·45733, n_β 1·46317, n_γ 1·46797, D_4^{20} 0·9697, violet coloration with alcoholic ferric chloride; ethylacetoacetate, b. p. 155°/8 mm., $[\alpha]_D^{20}$ $-60\cdot26°$ in benzene, violet coloration with ferric chloride. The following menthyl esters are prepared by heating menthyl sodioacetoacetate and the requisite alkyl haloid in ethyl alcohol: *propylacetoacetate*, b. p. 162°/8 mm., $[\alpha]_D^{20}$ $-57\cdot27°$ in benzene, reddish-violet coloration with alcoholic ferric chloride; sec.-*octylacetoacetate*, b. p. 139°/0·1 mm., $[\alpha]_D^{20}$ $-47\cdot82°$ in benzene, brownish-red coloration with ferric chloride. *Menthyl phenylacetoacetate*, prepared from menthol and ethyl phenylacetoacetate at 140°, has m. p. 69°, b. p. 131—133°/0·1 mm., and develops a violet coloration with alcoholic ferric chloride. A freshly prepared solution of the ester in benzene is dextrorotatory, $[\alpha]_D^{20}$ $+19\cdot07°$, but rapidly becomes lævorotatory, and has $[\alpha]_D^{20}$ $-67\cdot55°$ constant after ten days. In another experiment, $[\alpha]_D^{20}$ was initially $+28\cdot70°$, and finally constant at $-67\cdot16°$ after sixty-seven days. In alcohol, $[\alpha]_D^{20}$ is initially $-28\cdot27°$, and becomes constant at $-67\cdot15°$ after forty-seven hours.

Menthyl benzylacetoacetate, prepared from menthol and ethyl benzylacetoacetate at 155°, has m. p. 68°, and $[\alpha]_D^{20}$ $-106{\cdot}97°$, and produces with alcoholic ferric chloride a yellow coloration changing to greyish-yellow. By treatment with benzyl bromide and alcoholic sodium ethoxide at 0°, it yields *menthyl dibenzylacetoacetate*, m. p. 70°, $[\alpha]_D^{20}$ $-25{\cdot}28°$.

Menthyl sodioacetoacetate and the requisite haloid in alcohol yield the following menthyl esters: *β-phenylethylacetoacetate*,

$$CH_2Ph{\cdot}CH_2{\cdot}CHAc{\cdot}CO_2{\cdot}C_{10}H_{19},$$

b. p. 143°/0·1 mm., $[\alpha]_D^{20}$ $-51{\cdot}64°$ in benzene and $-53{\cdot}79°$ in alcohol, violet coloration with ferric chloride; *γ-phenylpropylacetoacetate*, b. p. 157°/0·1 mm., $[\alpha]_D^{20}$ $-45{\cdot}44°$ in benzene and $-48{\cdot}99°$ in alcohol; *allylacetoacetate*, b. p. 169—171°/13 mm., $[\alpha]_D^{20}$ $-58{\cdot}27°$ in benzene; *cinnamylacetoacetate*, $CHPh\colon CH{\cdot}CH_2{\cdot}CHAc{\cdot}CO_2{\cdot}C_{10}H_{19}$, $[\alpha]_D^{20}$ $-41{\cdot}31°$ in benzene.

Menthyl benzoylacetate, $CH_2Bz{\cdot}CO_2{\cdot}C_{10}H_{19}$, prepared from ethyl benzoylacetate and menthol at 120°, has m. p. 41°, $[\alpha]_D^{20}$ n benzene initially $-55{\cdot}36°$ and finally $-63{\cdot}97°$ after fifty hours, $[\alpha]_D^{20}$ in alcohol initially $-56{\cdot}41°$ and finally $-56{\cdot}89°$ after six hours, is slightly soluble in alkalis, develops a deep red coloration with alcoholic ferric chloride, and forms a *semicarbazone*, m. p. 163°, which produces a dark green coloration with ferric chloride.

The following menthyl esters are obtained by treating menthyl sodiobenzoylacetate with the requisite alkyl haloid in alcohol; *α-benzoylpropionate*, $CHMeBz{\cdot}CO_2{\cdot}C_{10}H_{19}$, m. p. 68°, $[\alpha]_D^{20}$ $-57{\cdot}73°$ in alcohol; *α-benzoylbutyrate*, b. p. 208°/10 mm., $[\alpha]_D^{20}$ $-55{\cdot}86°$ in alcohol and $-54{\cdot}27°$ in benzene; *α-benzoylvalerate*, decomp. 180°/0 mm., $[\alpha]_D^{20}$ $-52{\cdot}35°$ in alcohol, violet-red coloration with alcoholic ferric chloride.

Ethyl benzoylphenylacetate and menthol at 160—165° yield *menthyl benzoylphenylacetate*, m. p. 116°, $[\alpha]_D^{20}$ $+20{\cdot}14°$ in benzene and $-12{\cdot}12°$ initially and $-62{\cdot}60°$ after eighty-nine hours in alcohol.

The following menthyl esters are obtained from menthyl sodiobenzoylacetate and the requisite haloid in alcohol: *α-benzoyl-β-phenylpropionate*, m. p. 117°, $[\alpha]_D^{20}$ $-60{\cdot}83°$ in benzene; *α-benzoyl-γ-phenylbutyrate*, m. p. 77°, $[\alpha]_D^{20}$ $-56{\cdot}70°$ in benzene; *α-benzoyl-δ-phenylvalerate*, $[\alpha]_D^{20}$ $-43{\cdot}97°$; *α-benzoyl-Δ^γ-pentenoate*, m. p. 53°, $[\alpha]_D^{20}$ $-51{\cdot}40°$ in benzene, violet-red coloration with ferric chloride in alcohol; *α-benzoyl-δ-phenyl-Δ^γ-pentenoate*, m. p. 82—83°, $[\alpha]_D^{20}$ $-48{\cdot}10°$.

By esterifying α-benzoyl-δ-phenyl-Δ^γ-pentenoic acid with menthol and repeatedly extracting the product with gasolin, it can be resolved in the sparingly soluble l-*menthyl* l-*α-benzoyl-δ-phenyl-Δ^γ-pentenoate*, m. p. 102—103°, $[\alpha]_D^{20}$ $-86{\cdot}66°$ in benzene, colourless needles, and the more soluble l-*menthyl* d-*α-benzoyl-δ-phenyl-Δ^γ-pentenoate*, m. p. 77°, $[\alpha]_D^{20}$ $-25{\cdot}95°$ in benzene; the esters do not develop a coloration with alcoholic ferric chloride.

Menthyl benzoylacetate and benzaldehyde and a little piperidine, cooled in a freezing mixture, yield *menthyl α-benzoylcinnamate*, $CHPh\colon CBz{\cdot}CO_2{\cdot}C_{10}H_{19}$, m. p. 65°, $[\alpha]_D^{20}$ $-77{\cdot}43°$ in benzene white leaflets.

[With PAUL HÄUSSLER.]—α-Benzylcinnamoyl chloride and menthol

in benzene containing pyridine yield *menthyl α-benzylcinnamate*,

$$CHPh:C(CH_2Ph)\cdot CO_2\cdot C_{10}H_{19},$$

m. p. 64—65°, $[\alpha]_D^{20}$ − 144·86° in benzene, and *α-benzylcinnamic anhydride*, $O[CO\cdot C(CH_2Ph):CHPh]_2$, m. p. 108—109°. The latter, which is stable to boiling aqueous sodium carbonate and is only slowly esterified by boiling alcohol and sulphuric acid, is also obtained directly from the acid chloride and pyridine.

Menthyl β-phenyl-α-benzylpropionate, m. p. 42—43°, $[\alpha]_D^{20}$ − 24·41° in benzene, is prepared from the acid chloride, menthol, and pyridine in benzene.

[With GEORG WOLFSLEBEN.]—The reaction between potassium γ-phenylbutyrate and an excess of benzaldehyde and of acetic anhydride at 106° for forty-eight hours, and subsequently on the water-bath for 290 hours, leads to the formation of *γ-phenyl-α-benzylidenebutyric acid*, $CH_2Ph\cdot CH_2\cdot C(:CHPh)\cdot CO_2H$, m. p. 124—125°. Its *menthyl* ester, prepared from the acid chloride, menthol, and pyridine in benzene, is a yellow oil, $[\alpha]_D^{20}$ − 23·00°.

Ethyl sodiomalonate and β-phenylethyl bromide in boiling alcohol yield *ethyl β-phenylethylmalonate*, $CH_2Ph\cdot CH_2\cdot CH(CO_2Et)_2$, b. p. 179°/10 mm., which reacts with alcoholic sodium ethoxide and benzyl bromide to form *ethyl benzyl-β-phenylethylmalonate*,

$$CH_2Ph\cdot CH_2\cdot C(CH_2Ph)(CO_2Et)_2,$$

b. p. 230°/10 mm. By hydrolysis with methyl alcoholic potassium hydroxide, the latter yields *benzyl-β-phenylethylmalonic acid*, m. p. 153° (decomp.), which is converted at 160° into *γ-phenyl-α-benzylbutyric acid*, $CH_2Ph\cdot CH_2\cdot CH(CH_2Ph)\cdot CO_2H$, m. p. 59—61°, b. p. 230°/8 mm. The acid chloride of the latter yields the *menthyl* ester, m. p. 102°, $[\alpha]_D^{20}$ − 36·69°, by treatment with menthol and pyridine in benzene, and is converted by distillation under 15 mm. partly into *2-β-phenylethylhydrindone*, $C_6H_4{<}{\substack{CO\\CH_2}}{>}CH\cdot CH_2\cdot CH_2Ph$, m. p. 56—57° (*semicarbazone*, m. p. 227—228° [decomp.]). γ-Phenylpropyl bromide and potassium cyanide yield *γ-phenylbutyronitrile*, b. p. 132—133°/11 mm. The acid is converted by phosphorus trichloride in benzene into the *chloride*, b. p. 119°/9 mm., from which *menthyl γ-phenylbutyrate*, b. p. 205°/10 mm., $[\alpha]_D^{20}$ − 57·00°, is obtained by means of menthol and pyridine in benzene.

The variations with time of the rotations of the preceding menthyl esters of β-ketonic acids in alcohol and in benzene have been measured in order to gain some idea of the magnitude and the velocity of the keto-enolic transformation. The acetoacetate and benzoylacetate rapidly acquire a constant rotation in a alcohol, but only after many hours or even days in benzene; the methylacetoacetate, benzoylpropionate, and benzoylphenylpropionate have constant rotations in benzene as well as in alcohol.

An unexpected fact of great importance has been found in the resolution by crystallisation of the menthyl esters of β-ketonic acids of enantiomorphous configuration. Such esters, the phenylacetoacetate, benzylacetoacetate, benzoylphenylacetate, and benzoylphenylpentenoate, all of which, it will be observed, contain a phenyl group, must have the ketonic structure. The case of the menthyl phenyl-

acetoacetate is interesting. Only *l*-menthyl *d*-phenylacetoacetate has been isolated, and it is dextrorotatory. As it changes to the enol in benzene, the activity due to the acidic portion disappears, the activity finally being due to the *l*-menthyl group only; the time required for the attainment of a constant lævorotation varies in different experiments (probably owing to the action of a catalyst in the glass), in one case being ten days and in another sixty-five days. The converse is observed with *l*-menthyl *d*-benzoylphenylacetate, which has a constant dextrorotation in benzene, but is lævorotatory in alcohol, reaching a maximum after four days.

Menthyl benzyl-, dibenzyl-, and benzylidene-acetoacetates, and the methyl-, phenyl-, benzyl-, *s*-phenylethyl-, cinnamyl-, and benzylidene-derivatives of menthyl benzoylacetate do not develop a coloration with alcoholic ferric chloride. In some cases the enolisation must be repressed by the ferric chloride, because menthyl benzoylphenylacetate, for example, which does not give a coloration with alcoholic ferric chloride, shows in alcohol a lævorotation which increases with time.

The author's results show that valuable conclusions regarding structure can be drawn from the molecular rotations, provided strictly homologous esters are being compared; comparisons are not justifiable when an alkyl group is replaced by a phenyl group. C. S.

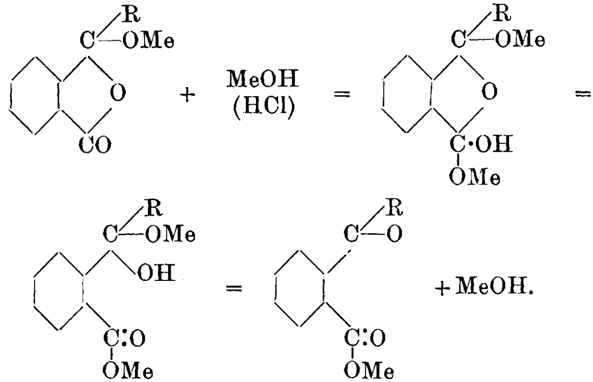
α-Hydroxy-γ-phenylcrotonic Acid. An Example of an Ether of a Ketone Hydrate. J. BOUGAULT (*Compt. rend.*, 1913, **156**, 236—239. Compare A., 1912, i, 770, and Fittig, A., 1898, i, 196).—By the controlled action of dilute sodium hydroxide on α-hydroxy-γ-phenylcrotonamide, and subsequent neutralisation with acid, an *acid amide* is obtained having the constitution

$$\begin{array}{l}CH_2Ph\cdot CH_2\cdot C(OH)\cdot CO_2H \\ \qquad\qquad\quad >O \\ CH_2Ph\cdot CH_2\cdot C(OH)\cdot CO\cdot NH_2\end{array},$$

which on heating loses two molecules of water, giving another *acid amide*, $C_{20}H_{19}O_4N$. The first compound is readily decomposed by alkalis or alkali carbonates quantitatively into ammonia and benzylpyruvic acid, but unlike the acid anhydrides is not hydrated by boiling with water or dilute acetic acid. W. G.

Esters of Aromatic Keto-acids. GRETE EGERER and HANS MEYER (*Monatsh.*, 1913, **34**, 69—93. Compare A., 1908, i, 26).—The pseudo- and normal esters of some benzoylated benzoic acids are described. In most cases the ψ-methyl esters, for which the sensitive colour reaction with concentrated sulphuric acid is characteristic, are produced by the action of thionyl chloride, but Goldschmiedt and Lipschitz had already shown (A., 1905, i, 132) that the *n*-ester resulted in the case of naphthoylbenzoic acid, whilst ψ-ethyl esters were hitherto unknown. It is now demonstrated that the ψ-ester is the primary product in all cases, but that under the influence of alcohol and mineral acids it may undergo further changes which result in the *n*-ester. To prevent this rearrangement, for example, in the case of the naphthoylbenzoate, the mixture of the acid chloride and the alcohol is immediately poured into sodium carbonate solution. On the other hand, any ψ-ester may be converted into its isomeride by the action of

a mineral acid or thionyl chloride and an alcohol. In this way a ψ-methyl ester may be transformed into a *n*-ethyl ester, which might be supposed to be due to the effect of mass action on the already rearranged *n*-methyl ester. Since, however, prolonged heating with methyl alcohol is necessary to convert ethyl *n*-benzoylbenzoate into the *n*-methyl ester, whereas the ψ-ethyl ester gives the *n*-methyl ester in a short time, the conclusion is drawn that the transformation of the ψ-form into the *n*-form is not due to any instability of the chloride or of the ester, but to the addition of alcohol to the lactone system under the catalytic influence of hydrogen ions and the subsequent elimination of alcohol from the methane carbon atom according to the scheme:



It thus becomes evident why the action of ammonia on the isomerides always results in the same amide, namely, that of the ketone acid (compare Meyer, A., 1905, i, 133).

Some of the acids employed were derived from the chlorophthalic acid which Auerbach obtained by the action of hypochlorites on phthalic acid. Since this may be condensed with benzene and transformed into β-chloroanthraquinone, it is to be regarded as 4-chlorophthalic acid.

Whereas methyl ψ-benzoylbenzoate may be prepared without precaution, by the action of thionyl chloride and methyl alcohol, the formation of the *ψ-ethyl* ester only succeeds when the mixture of the chloride with excess of cold absolute alcohol is at once poured into cold sodium carbonate solution. It crystallises in triangular tablets, m. p. 51—53°, and dissolves with lemon-yellow colour in concentrated sulphuric acid. The *n*-ethyl ester (rhombic, $a:b:c = 1.9725:1:1.267$) may be prepared by leaving the chloride with alcohol, by the usual means or by boiling the ψ-methyl ester for a few minutes or the *n*-methyl ester for a few hours with alcohol and thionyl chloride or sulphuric acid. Conversely, methyl alcohol and thionyl chloride transform the ψ-ethyl ester into the *n*-methyl ester in a short time, whereas the *n*-ethyl ester must be heated for fifty hours. In the same way, methyl ψ-toluoylbenzoate and methyl ψ-methoxybenzoylbenzoate (Meyer and Turnau, A., 1909, i, 710; m. p. 83° and not 63°) may be converted into the *n*-esters.

The preparation of 4-chlorophthalic anhydride by Auerbach's

method has been improved; the compound has b. p. 291—295°, and when crystallised from dry ether has m. p. 94°, but after contact with moist ether the m. p. rises to that of the acid. When condensed with benzene in presence of an excess of aluminium chloride, it yields *benzoyl-4-chlorobenzoic acid*, m. p. 180·5°, which gives β-chloroanthraquinone (Graebe and Rée, T., 1886, 531) in concentrated sulphuric acid. The *acid chloride*, $COPh \cdot C_6H_3Cl \cdot COCl$, long needles, m. p. 114—117°, also readily yields the quinone on heating. The *ψ-methyl* ester forms colourless needles, m. p. 68·5—69·5°, and the n-*ester* forms monoclinic crystals ($a:b:c = 1·8252:1:0·6878$; $\beta = 76°59'$), m. p. 102—104°.

The acid obtained by the condensation of 4-chlorophthalic anhydride with chlorobenzene dissolves in sulphuric acid with the formation of 2 : 6-dichloroanthraquinone, and is, therefore, 2-p-*chlorobenzoyl-4-chlorobenzoic acid*, which confirms the position of the halogen in the above benzoyl-4-chlorobenzoic acid. The acid has m. p. 195·5°, gives a well-defined *acid chloride*, m. p. 115—120°, from which, however, the ψ-ester could not be obtained crystalline. The n-*methyl* ester, from the transformation of the crude isomeride or by direct esterification, melts at 98°.

*Methyl ψ-*p-*chlorobenzoylbenzoate*, m. p. 101—102·5°; the n-*ester*, m. p. 109—110°, monoclinic crystals ($a:b:c = 0·92461:1:?$; $\beta = 73°40'$), and the n-*ethyl* ester, m. p. 88°, have also been prepared.

Phthalic anhydride condenses with *p*-dichlorobenzene when boiled with an excess of aluminium chloride in nitrobenzene; the 2-om-*dichlorobenzoylbenzoic acid*, radiating needles, m. p. 168°, yields 1 : 4-dichloroanthraquinone (Ullmann and Billig, A., 1911, i, 490). Similarly, 4-chlorophthalic anhydride and *p*-dichlorobenzene give 2-om-*dichlorobenzoyl-4-chlorobenzoic acid*, m. p. 157—160°, which condenses to form 1 : 4 : 7-trichloroanthraquinone and yields a *ψ-methyl* ester, m. p. 115—120°.

The constitution of the isomeric esters (A., 1908, i, 26) receives support from the molecular refractions, for methyl *n*-benzoylbenzoate, $[M.R.]_D = 67·98$, being a benzophenone derivative, shows exaltation (compare Auwers and Eisenlohr, A., 1911, ii, 782), whereas the ψ-ester gives the theoretical value for a hydroxylactone, $[M.R.]_D = 65·40$.

J. C. W.

Isomeric Esters of Trichlorobenzoylbenzoic Acids. STEPHAN JAROSCHY (*Monatsh.*, 1913, **34**, 1—6. Compare preceding abstract).—The product of the condensation of 1 : 4-dichlorophthalic anhydride with chlorobenzene, 2-p-*chlorobenzoyl-3 : 6-dichlorobenzoic acid*,

$$C_{14}H_7O_3Cl_3,$$

crystallises in colourless leaflets, m. p. 157°, and yields 1 : 4 : 7-trichloroanthraquinone in concentrated sulphuric acid. The *ψ-methyl* ester, colourless crystals, m. p. 153—154°, and the *ψ-ethyl* ester, a white, crystalline powder, m. p. 150—151°, may be obtained by immedia ely adding the mixture of alcohol and acid chloride to sodium carbonate solution, and may be transformed into the *n*-esters by heating with thionyl chloride and the corresponding alcohol for some hours. The normal esters may also be obtained by the usual methods, give no

coloration in sulphuric acid, and melt at 90° and 105—106° respectively. J. C. W.

Preparation of Amides and Acylation of the Amino-group. HERMAN DECKER (*Annalen*, 1913, **395**, 282—299).—Hofmann's classical method of preparing amides and substituted amides by heating the ammonium salts of carboxylic acids or their salts with primary and secondary amines, which has fallen into disuse owing to its supposed disadvantages, is shown to be a simple and convenient method of preparation provided the optimum temperature (the temperature at which water is eliminated, it may be slowly, from the salt, whilst the dissociation of the latter is still hardly appreciable) is obtained, and is retained to the end of the reaction. A whole series of amides and substituted amides have thus been prepared by simply heating the acid and the amine at the optimum temperature. The reaction, which is analogous to the formation of an ester from an acid and an alcohol, is accelerated, as in the case of esterification, by catalysts.

[With WALTER KROPP, HEINRICH HOYER, CLEMENS ZOELLNER, and PAUL BECKER.]—Formophenylethylamide is obtained free from β-phenylethylamine formate, and in 96% yield by heating β-phenylethylamine and anhydrous formic acid in slight excess at 170—180° for four hours. In a similar manner, phenylacetyl-β-phenylethylamine (95% yield) is obtained from phenylacetic acid and the amine at 180°, and acetyl-β-phenylethylamine from acetic acid and the amine.

Piperonylacetamide, $CH_2O_2\!:\!C_6H_3\cdot CH_2\cdot CH_2\cdot CO\cdot NH_2$, m. p. 122—123°, colourless leaflets, can be prepared from the acid chloride and 25% aqueous ammonia, from *ethyl piperonylacetate*, b. p. 303°, and aqueous ammonia at 160—180° (bad yield), or from 3:4-methylenedioxyphenylpropionyl chloride and 25% aqueous ammonia, is readily obtained by heating piperonylacetic acid for two hours at 200—220° in a current of dry ammonia. It is readily converted by the sodium hypochlorite method into homopiperonylamine (hydrochloride, m. p. 207—208°; picrate, m. p. 174—176°; *carbonate*, m. p. about 110°; *platinichloride*, m. p. about 225° [decomp.]).

Formohomopiperonylamide, $CH_2O_2\!:\!C_6H_3\cdot CH_2\cdot CH_2\cdot NH\cdot CHO$, m. p. 61—62°, is obtained almost quantitatively from the amine and anhydrous formic acid at 180—200°. *Phenylacetohomopiperonylamide*, $CH_2O_2\!:\!C_6H_3\cdot CH_2\cdot CH_2\cdot NH\cdot CO\cdot CH_2Ph$, m. p. 96°, is obtained from the amine and phenylacetic acid at 160°.

Homopiperonoylhomopiperonylamine,

$$CH_2O_2\!:\!C_6H_3\cdot CH_2\cdot CH_2\cdot NH\cdot CO\cdot CH_2\cdot C_6H_3\!:\!CH_2O_2,$$

m. p. 119°, is prepared from the amine and homopiperonylic acid at 160° for eight hours. Homopiperonylic acid is obtained in 5% yield by oxidising safrole in well-cooled acetone with potassium permanganate and treating the precipitate with sulphurous acid, whereby piperonylic acid is precipitated; the homopiperonylic acid is extracted from the filtrate by ether.

Anhydrous oxalic acid reacts with β-phenylethylamine at 180—200° to form oxalodi-β-phenylethylamide, m. p. 186°, in 61% yield, and with homopiperonylamine at 170—180° to form *oxalodihomopiperonyl-*

amide, $C_2O_2(NH\cdot CH_2\cdot CH_2\cdot C_6H_3:CH_2O_2)_2$, m. p. 196—197° (corr.), colourless needles.

Fagaramide (Thoms and Thümen, A., 1912, i, 115) can be synthesised by heating piperonylacrylic acid and *iso*butylamine at 190—200° for two and a-half hours. C. S.

The Oxidation of Substituted Aceanthrenequinones. D. BUTESCU (*Ber.*, 1913, **46**, 212—214. Compare Liebermann and Butescu, A., 1912, i, 467).—The substituted aceanthrenequinones behave on oxidation in a similar manner to aceanthrenequinone itself, yielding anthraquinonecarboxylic acids (Liebermann and Zsuffa, A., 1911, i, 202). The oxidation is effected in acetic acid solution by chromic acid.

β-Methylanthraquinone-α-carboxylic acid, yellow needles, m. p. 295°, is obtained in the oxidation of β-methylaceanthrenequinone.

β-Chloroanthraquinone-α-carboxylic acid, yellow needles, m. p. 260°, obtained from β-chloroaceanthrenequinone, is distinct from the β-chloroanthraquinonecarboxylic acid described by Heller and Schülke (A., 1908, i, 994).

α-Chloroanthraquinone-α-carboxylic acid, obtained by the oxidation of α-chloroaceanthrenequinone, forms leaflets, m. p. 205°, which can be sublimed to give yellow needles; it is distinct from the isomeric substances described by Heller and Schülke (*loc. cit.*) and Fischer and Sapper (A., 1911, i, 279).

1 : 5-*Dichloroanthraquinone*-4-*carboxylic acid*, obtained from 1 : 5-dichloroaceanthrenequinone, has m. p. 250°.

1 : 8-*Dichloroanthraquinone*-5-*carboxylic acid*, from the corresponding aceanthrenequinone, forms yellow needles, m. p. 240°. D. F. T.

Action of Magnesium on a Mixture of Allyl Bromide and Phthalic Anhydride. A. ORLOV (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1868—1870. Compare Bauer, Abstr., 1904, i, 417; 1905, i, 210).

Diallylphthalide, $C_6H_4<\substack{C(C_3H_5)_2 \\ CO}>O$, prepared by the action of water on the product of the interaction of magnesium, allyl bromide, and phthalic anhydride, is a pale yellow, slightly mobile liquid of pleasant odour, b. p. 184—185°/14 mm., D_4^{25} 1·0546, n_D^{25} 1·53614, and develops fluorescence on prolonged keeping. It unites with 4 atoms of bromine, giving a liquid *bromide*, $C_{14}H_{14}O_2Br_4$, of pleasant odour. T. H. P.

The Reaction between 5-Bromo-2 : 4 : 6-tri-iodo-1 : 3-dinitrobenzene and Ethyl Sodiomalonate. C. LORING JACKSON and F. C. WHITMORE (*Ber.*, 1913, **46**, 67—70).—The explanation (Jackson and Bigelow, A., 1911, i, 101) of the reaction between ethyl sodiomalonate and halogen-nitrobenzenes in which one of the halogen atoms of the latter becomes replaced by hydrogen is now tested by applying it to 5-bromo-2 : 4 : 6-tri-iodo-1 : 3-dinitrobenzene; this substance is found, in accordance with the hypothesis, first to form with the ethyl sodiomalonate, an *additive* compound which probably has the constitution

$CO_2Et\cdot CHI\cdot C(ONa)(OEt)\cdot C_6BrI_2(NO_2)_2$, which when acidified undergoes scission into $C_6HBrI_2(NO_2)_2$ and $CHI(CO_2Et)_2$, the latter substance then reacting with a second molecule of ethyl sodiomalonate with the formation of ethyl ethanetetracarboxylate.

The additive compound could not be isolated, but a mixture of 2-bromo-1 : 3 : 5-tri-iodo-4 : 6-dinitrobenzene and ethyl sodiomalonate in alcohol gives a deep red liquid; if an excess of the halogen compound or of ethyl sodiomalonate is taken and a little of the filtered red liquid is evaporated, the percentages of sodium in the residue in the former case and of halogen in the latter are in accord with the above composition.

The direct coupling of the substituted benzene ring with the ethyl sodiomalonate is attributed to the possibility that the substituted ring is more negative than the iodine atom, and it is held that the formation of *p*-toluenesulphinic acid and ethyl ethanetetracarboxylate from *p*-toluenesulphonyl chloride and ethyl sodiomalonate (Kohler and MacDonald, A., 1899, i, 907) is in support of such a view.

D. F. T.

Polymerisation of Cinnamylideneacetic Acid by Light. C. N. RIIBER (*Ber.*, 1913, **46**, 335—338).—The author has obtained the dimolecular form of cinnamylideneacetic acid by the action of light on cinnamylideneacetic acid.

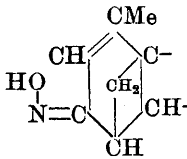
Cinnamylideneacetic acid was exposed to the action of light until the product had a mean mol. wt. of about 260 in acetone. The complex mixture so obtained was treated with a large quantity of benzene, whereby considerable quantities of oxidation products were isolated. The residue obtained by evaporation of the benzene mother liquor, after successive treatment with cold and boiling benzene, left a white, crystalline residue of *bimolecular cinnamylideneacetic acid*, needles, m. p. 219°, mol. wt. in acetone solution 320, which was purified by solution in methylal and addition of benzene. The acid is very sparingly soluble in the usual solvents. The *silver* salt was examined. The formula $\begin{array}{l}Ph\cdot CH\cdot CH\cdot CH:CH\cdot CO_2H\\ CO_2H\cdot CH\cdot CH\cdot CH:CHPh\end{array}$ is assigned to the acid, since when oxidised by potassium permanganate in alkaline solution, it yielded oxalic and benzoic acids, and an *acid* which could not be obtained in the pure state but gave a *silver* salt, $C_{13}H_9O_6Ag_3$, and a *methyl* ester, $C_{16}H_{18}O_6$. Since it was stable towards potassium permanganate, its composition is probably represented by the formula $\begin{array}{l}Ph\cdot CH\cdot CH\cdot CO_2H\\ CO_2H\cdot CH\cdot CH\cdot CO_2H\end{array}$.

*allo*Cinnamylideneacetic acid is similarly, but more readily, polymerised by the action of light.

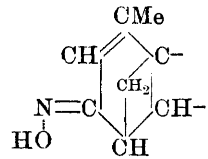
Bimolecular cinnamylideneacetic acid (m. p. 219°) differs greatly from the isomeric acid (m. p. 204°) obtained by the action of light on cinnamylidenemalonic acid (A., 1902, i, 617), particularly in regard to solubility in acetone. The latter acid, when oxidised by potassium permanganate, yielded benzoic and oxalic acids, together with a saturated *acid*, m. p. 134°. α-Truxillic acid could not be isolated. The formula

$$\begin{array}{l}\quad\ \ Ph\cdot CH\cdot CH\cdot CH\!:\!CH\cdot CO_2H \\ \quad\quad\quad\ \ | \\ CO_2H\cdot CH\!:\!CH\cdot CH\cdot CHPh\end{array}$$ is advanced for the acid m. p. 204°. H. W.

New Oxime of Santonin. GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 796—800).—When nitrosohydroxylamino-β-santoninoxime (Francesconi and Cusmano, A., 1909, i, 724) is heated with an equimolecular quantity of *N*-sodium hydroxide on the water-bath, nitrous oxide is evolved, and an oxime is formed, which is identical with the santoninoxime of Cannizzaro (A., 1886, 73). If, however, nitrosohydroxylamino-α-santoninoxime is similarly treated, a new *santoninoxime* of the same composition is produced; it differs from Cannizzaro's oxime in physical and to a certain extent in chemical properties, and is regarded by the author as representing the oxime of formula II, which is stereoisomeric with the oxime of formula I (Cannizzaro's oxime), adopting the formulæ deduced from the work of Angeli and Marino (A., 1907, i, 321).



(I.)



(II.)

The new oxime crystallises with $1\frac{1}{2}H_2O$, in scales or in lustrous needles; on heating, it becomes red towards 180°, m. p. 230° (decomp.). In addition this α-oxime differs from the β-oxime of Cannizzaro in having a bitter taste, and in yielding the corresponding *santoninic acid*, $C_{15}H_{21}O_4N,3\frac{1}{2}H_2O$, m. p. 80°, when its solution in sodium hydroxide is exactly precipitated with acid. If this acid is kept at 100° for twenty hours, the original oxime is formed. The *hydrochloride* of the oxime crystallises in colourless scales, which change on keeping into large prisms; on heating, the hydrochloride undergoes gradual change until it melts at 168°. With water it yields the oxime, together with santonin and hydroxylamine hydrochloride.

When treated with sodium nitrite and acetic acid, the new oxime yields a *pernitroso*-derivative, $C_{15}H_{18}O_4N_2,H_2O$, which forms prismatic crystals, which become red at 175°, m. p. 197° (with evolution of gas). This compound differs from that obtained from the other oxime in m. p. and in water of crystallisation, but resembles it in giving santonin when heated with alkali, and yielding a blue coloration with a solution of diphenylamine in sulphuric acid.

Treatment of the β-oxime with methyl sulphate yields a *monomethyl ether*, $C_{16}H_{23}O_4N$ (which forms silky, acicular crystals, m. p. 184°), and also another *substance* having the same composition, but crystallising in long, thin needles, m. p. 196°.

Under the same conditions the α-oxime gives a *methyl ether* of the same composition, which forms large, prismatic crystals, m. p. 185°. A mixture of this ether with that of m. p. 184° has m. p. about 160°.

R. V. S.

The Action of Oxalyl Chloride on Polynuclear Hydrocarbons. CARL LIEBERMANN and M. KARDOS (*Ber.*, 1913, **46**, 198—212. Compare A., 1911, i, 202, 387, 656; 1912, i, 464).—2 : 4 : 2′ : 4′-Tetramethyldiphenyl, when oxidised by prolonged boiling with sodium dichromate and diluted sulphuric acid, gives in poor yield diphenyl-2 : 4 : 2′ : 4′-tetracarboxylic acid (compare Liebermann and Kardos, A., 1912, i, 465); the same acid is obtained with still more difficulty by the oxidation of 2 : 7-dimethylphenanthraquinone, in which phenanthraquinone-2-carboxylic acid can be isolated as an intermediate product.

Oxalyl chloride reacts with 2 : 4 : 5 : 2′ : 4′ : 5′-hexamethyldiphenyl at the ordinary temperature in carbon disulphide solution in the presence of aluminium chloride, giving a mixture of 1 : 2 : 4 : 5 : 7 : 8-*hexamethylphenanthra*-9 : 10-*quinone*, yellow prisms, m. p. 223—224° (the *monoxime*, yellow flakes, m. p. 178°, when submitted to the Beckmann rearrangement gives a *substance*, possibly the mononitrile of hexamethyldiphenic acid; the *monophenylhydrazone* exists in two forms, α- red needles, m. p. 187°, β- yellow needles, m. p. 143°, which are possibly *cis*- and *trans*-isomerides respectively), with 2 : 4 : 5 : 2′ : 4′ : 5′-*hexamethyldiphenyldicarboxylic acid*, a microcrystalline powder, m. p. 284—285°, which is turned yellow by light. This acid when oxidised in alkaline solution by potassium permanganate is converted into *diphenyl*-2 : 4 : 5 : 2′ : 4′ : 5′ : ? : ?′-*octacarboxylic acid*, a hygroscopic solid which gives a fluorescein reaction when fused with resorcinol; *calcium* salt, very soluble; *silver* salt, colourless; when dried at 110°, the acid loses carbon dioxide and water, giving the *monoanhydride* of *diphenylhexacarboxylic acid*, $C_{12}H_4(CO_2H)_4{<}{}^{CO}_{CO}{>}O$; the *silver* salt was prepared.

3 : 4 : 5 : 3′ : 4′ : 5′-Hexamethyldiphenyl was prepared from 5-aminohemimellithene (Noelting and Forel, A., 1886, 58; Limpach, A., 1888, 464); in the preparation of this latter substance by heating a mixture of *s*-xylidine hydrochloride and methyl alcohol at 250—260° under 30—33 atmospheres' pressure, a relatively large quantity of acridine bases was obtained as a high boiling, feebly basic mixture, which gave fluorescent solutions in organic solvents; there could be isolated from this mixture a *substance*, m. p. 223°, another substance (probably *tetramethylacridine*), m. p. 172—175°, and a *hexamethylacridine*, m. p. 220—225°; *hydrochloride*, yellow; *platinichloride*, yellow and sparingly soluble. Aminohemimellithene was converted through the corresponding diazonium salt into 5-*iodohemimellithene*, crystals, m. p. 35°, which on heating with finely divided copper (compare Ullmann, A., 1904, i, 725) at 230—250°, loses iodine with the formation of 3 : 4 : 5 : 3′ : 4′ : 5′-*hexamethyldiphenyl*, m. p. 132—133°. In an experiment on a small scale, in which hexamethyldiphenyl and oxalyl chloride were kept for six weeks in carbon disulphide solution in contact with aluminium chloride, the product was a mixture of carboxylic acids with a neutral yellow *substance*, doubtless the expected 1 : 2 : 3 : 6 : 7 : 8-hexamethylphenanthra-9 : 10-quinone.

In extension of the earlier result with phthalic acid which was converted by acetyl chloride into phthalyl chloride (Liebermann, A.,

1912, i, 464), it is found that terephthalic and *iso*phthalic acids in like manner with acetyl chloride at 130° give *terephthalyl chloride*, needles or leaflets, m. p. 83—84° (compare Schreder, this Journ., 1874, 990), and *isophthalyl chloride*, prisms, m. p. 43—44°, respectively; in the former case the product is accompanied by a little *terephthalyl acid chloride*, $C_6H_4 \cdot COCl \cdot CO_2H$, needles, m. p. above 300°. D. F. T.

Compounds of Benzaldehyde and Benzonitrile with Antimony Trichloride and Tribromide. BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1929—1938. Compare A., 1912, ii, 920, and *ante*).—For benzaldehyde, Haase (A., 1893, ii, 357) gave the m. p. $-26°$, and Altschul and von Schneider (A., 1895, ii, 206) $-13·5°$. The author finds that different preparations of the aldehyde melt at temperatures varying from $-26°$ to $-15°$. This behaviour is probably due to the ready oxidisability of the aldehyde in the air, most samples containing dissolved peroxide and acid. With the systems containing benzaldehyde, difficulties were encountered in determining temperatures lying between the melting point of the aldehyde and the first eutectic point.

Benzaldehyde and antimony trichloride form the compound

$$SbCl_3, Ph \cdot CHO,$$

m. p. 43·5°, crystallising in elongated plates, often united in stellar aggregates. The eutectic point between this compound and the pure trichloride lies at 25°, and corresponds with the composition

$$SbCl_3, 0·44 Ph \cdot CHO.$$

The compound $SbBr_3, Ph \cdot CHO$ forms rhombic plates and crystals resembling rhombohedra, m. p. 41·5°, and the eutectic point,

$$SbBr_3, Ph \cdot CHO–SbBr_3,$$

lies at 37·8°, and corresponds with the composition

$$SbBr_3, 0·63 Ph \cdot CHO.$$

Benzonitrile has m. p. $-13·2°$ (Hofmann, *Jahresbericht*, 1862, 335, gave $-17°$, and von Schneider, A., 1896, ii, 290, and 1897, ii, 304, $-12·9°$).

The compound $SbCl_3, Ph \cdot CN$ crystallises in quadratic plates, m. p. 21·5°, and the eutectic temperatures and compositions of the system are (1) for $Ph \cdot CN–SbCl_3, Ph \cdot CN$, $-19°$ and $SbCl_3, 10·6 Ph \cdot CN$, and (2) for $SbCl_3, Ph \cdot CN–SbCl_3$, $-15°$ and $SbCl_3, 0·59 Ph \cdot CN$.

The compound $SbBr_3, Ph \cdot CN$ forms long plates or needles, m. p. 38°, and the eutectic points are 18° for $SbBr_3, 8·7 Ph \cdot CN$ and 35° for

$$SbBr_3, 0·74 Ph \cdot CN.$$

The diagrams of all the above systems have the form typical of the formation from the components of a single stable compound.

T. H. P.

New Synthesis of Syringaldehyde. FERDINAND MAUTHNER (*Annalen*, 1913, **395**, 273—281).—Syringaldehyde is readily obtained in good yield by Guyot's process (A., 1909, i, 935; 1910, i, 40) A mixture of pyrogallol 1 : 3-dimethyl ether, ethyl mesoxalate, anhydrous zinc chloride, and a little carbamide is kept in glacial acetic acid for fourteen days, whereby *ethyl 4-hydroxy-3 : 5-dimethoxyphenyltartronate*, $OH \cdot C_6H_2(OMe)_2 \cdot C(CO_2Et)_2 \cdot OH$, m. p. 60°, is obtained in almost

quantitative yield. The ester, by hydrolysis by boiling aqueous potassium hydroxide, acidification below 10°, and treatment with aqueous copper sulphate finally at the b. p., is converted into *4-hydroxy-3 : 5-dimethoxyphenylglyoxylic acid* (*syringoylcarboxylic acid*),

$$OH{\cdot}C_6H_2(OMe)_2{\cdot}CO{\cdot}CO_2H,$$

m. p. 128—129°, yellow needles (*p-nitrophenylhydrazone*, m. p. 225° [decomp.], yellow needles), which yields syringaldehyde by treatment with boiling dimethyl-*p*-toluidine as in Guyot's method. The relative positions of the aldehydo- and hydroxyl groups in the aldehyde are proved by the fact that it yields gallaldehyde trimethyl ether by treatment with methyl sulphate in alkaline solution.

Syringaldehyde forms a *p-nitrophenylhydrazone*, m. p. 216—217°, yellow needles, and an *aldazine*, $C_9H_{12}O_3N_2$, m. p. 208—209°, yellow needles, and reacts with 1-phenyl-3-methyl-5-pyrazolone in hot glacial acetic acid to form *1-phenyl-4-p-hydroxydi-m-methoxybenzylidene-3-methyl-5-pyrazolone*, $C_{19}H_{18}O_4N_2$, m. p. 208—209°, red leaflets, with acetophenone and 33% sodium hydroxide in alcohol at 80° to form, after acidification, *4-hydroxy-3 : 5-dimethoxybenzylidenebisacetophenone*, $C_{25}H_{24}O_5$, m. p. 112—113°, faintly yellow leaflets, and with β-naphthylamine and pyruvic acid in boiling alcohol to form *α-p-hydroxydi-m-methoxyphenyl-β-naphthacinchonic acid*, $C_{22}H_{17}O_5N$, m. p. 275° (decomp.), yellow needles. C. S.

α-Chlorocyclopentanone and its Derivatives. MARCEL GODCHOT and FÉLIX TABOURY (*Compt. rend.*, 1913, **156**, 332—334).—By passing dry chlorine over *cyclo*pentanone kept at a temperature below 25°, a mixture of substances is obtained, which on fractionation yields *2-chlorocyclopentanone*, C_5H_7OCl, b. p. 80°/10 mm., D_{14} 1·870, n_D^{14} 1·4782, which on boiling with water or an aqueous suspension of barium carbonate is converted into *cyclopentanone-2-ol*, $C_5H_8O_2$, b. p. 80°/12 mm., D 1·1680. It is very soluble in water, and in solution gives a reddish-brown colour with potassium hydroxide and a violet-red with ferric chloride. It forms a *phenylhydrazone*, yellow needles, m. p. 142—143°, and a *semicarbazone*, a yellow powder decomposing at 170°. This hydroxy-ketone is readily oxidised by 1% potassium permanganate to glutaric acid.

On distilling 2-chloro*cyclo*pentanone either alone or, better, with diethylaniline, it loses hydrogen chloride and is converted into Δ^2-*cyclopentenone*, a colourless liquid, b. p. 135—136°, which gives a *semicarbazone*, m. p. 214—215°, and an *oxime*, m. p. 52—53°. W. G.

Terpenes and Ethereal Oils. CXIII. Autoreduction of Hydroaromatic Compounds at the Moment of their Formation. OTTO WALLACH and PAUL FRY (*Annalen*, 1913, **395**, 74—86). —β-Methyl-Δ^β-hepten-ζ-one and zinc chloride form at the ordinary temperature after two to three weeks a very viscous, brown mass which is probably an additive compound, since it is decomposed into its generators by water. At 100°, however, methylheptenone reacts vigorously in the presence of zinc chloride or phosphoric oxide; hydrogen is not evolved and the product is a complex mixture from

which an oil is obtained by distillation with steam. By distillation this oil yields a very large fraction, b. p. 130—140°, which is not 1 : 3-dimethyl*cyclo*-$\Delta^{1:3}$-hexadiene as stated previously, but is proved to be a mixture of *m*-xylene and 1 : 3-dimethyl-Δ^3-*cyclo*hexene by treatment with 3% potassium permanganate at 0°, whereby the *m*-xylene is unattacked, whilst the 1 : 3-dimethyl*cyclo*hexene is converted into 1 : 3-*dimethyl*cyclo*hexane*-3 : 4-*diol*, $OH\cdot CMe<\substack{CH(OH)\cdot CH_2 \\ CH_2\text{---}CHMe}>CH_2$, m. p. 89°. The constitution of the glycol is proved by the fact that it yields 1 : 3-dimethyl*cyclo*hexan-4-one, b. p. 179—179·5°, D^{21} 0·9066, n_D^{21} 1·4464 (*semicarbazone*, m. p. 189°; *oxime*, m. p. 98—99°), by treatment with warm dilute sulphuric acid. This ketone in an impure state (b. p. 176·5°, D^{16} 0·9124, n_D 1·446) has been described by Sabatier and Mailhe, in 1906. By oxidation with chromic and dilute sulphuric acids on the water-bath, it yields a keto-acid (*semicarbazone*, m. p. 136—137°), which is converted into bromoform and β-methyladipic acid by alkaline hypobromite.

Since hydrogen is not evolved and 1 : 3-dimethyl-$\Delta^{1:3}$-*cyclo*hexadiene is not obtained by the auto-condensation of the methylheptenone, it follows that one molecule of 1 : 3-dimethyl*cyclo*hexadiene loses hydrogen and changes to *m*-xylene, the hydrogen converting a second molecule into 1 : 3-dimethyl*cyclo*-Δ^3-hexene. C. S.

Synthetic *p*-Dialkylated Dihydroxyquinones and Hydroxyperezone. FRITZ FICHTER, MAX JETZER, and ROBERT LEEPIN (*Annalen*, 1913, **395**, 1—25. Compare A., 1904, i, 678; 1908, i, 658).—The following substances have been prepared by the reaction, as described previously, between sodium, ethyl oxalate, and a fatty ester in ether or benzene. The reaction proceeds more slowly the greater the molecular weight of the fatty acid, and reaches its limit with *n*-decoic ester; ethyl laurate or palmitate do not yield a *p*-dialkylated dihydroxyquinone. 3 : 6-*Dihydroxy*-2 : 5-*di*iso*butyl*-p-*benzoquinone*, $C_{14}H_{20}O_4$, m. p. 217—218° (in closed tube), red spangles (*diacetate*, m. p. 113·5°, yellow crystals), from ethyl *iso*hexoate, develops a blue coloration in concentrated sulphuric acid and a violet in aqueous sodium hydroxide. 3 : 6-*Dihydroxy*-2 : 5-*diamyl*-p-*benzoquinone*, $C_{16}H_{24}O_4$, m. p. 164°, red leaflets (*diacetate*, m. p. 74°, yellow needles), from ethyl *n*-heptoate; 3 : 6-*dihydroxy*-2 : 5-*dihexyl*-p-*benzoquinone*, $C_{18}H_{28}O_4$, m. p. 154°, red scales (*diacetate*, m. p. 68°, yellow needles), from ethyl *n*-octoate; 3 : 6-*dihydroxy*-2 : 5-*diheptyl*-p-*benzoquinone*, $C_{20}H_{32}O_4$, m. p. 145°, red leaflets (*diacetate*, m. p. 77·5°, yellow needles), from ethyl *n*-nonoate; 3 : 6-*dihydroxy*-2 : 5-*dioctyl*-p-*benzoquinone*, m. p. 141°, red leaflets, from ethyl *n*-decoate. In the colour of their solutions and of their alkali salts, and in their inactivity towards hydroxylamine and ortho-diamines, *p*-dialkylated dihydroxybenzoquinones show a greater similarity to chloroanilic acid than to the unsubstituted dihydroxybenzoquinone. The same is true of their ethers; 3 : 6-*dimethoxy*-2 : 5-*di*iso*propyl*-p-*benzoquinone*, $CPr^\beta \lessgtr \substack{C(OMe)\cdot CO \\ CO\cdot C(OMe)} \gtrless CPr^\beta$, m. p. 142°, prepared from the silver derivative, crystallises in almost black leaflets.

Ethyl iso*valerylacetate*, $CH_2Pr^{\beta}\cdot CO\cdot CH_2\cdot CO_2Et$, b. p. 99·5°/12·5 mm., D^{15} 0·964, prepared by hydrolysing ethyl *iso*valerylacetoacetate with aqueous ammonia, is soluble in alkalis, develops an intense red coloration with ferric chloride, yields 1-*phenyl*-3-iso*butyl*-5-*pyrazolone*,

$$CH_2Pr^{\beta}\cdot C{<}\begin{matrix}CH_2\cdot CO \\ N{-\!\!-}NPh\end{matrix},$$

m. p. 105·5°, with phenylhydrazine, and condenses with resorcinol and concentrated sulphuric acid to form 5-*hydroxy*-4-iso*butylcoumarin*, $C_{13}H_{14}O_3$, m. p. 117°, glistening needles, which dissolves in alkalis with a blue fluorescence.

By treatment with ozonised oxygen, 3 : 6-dihydroxy-2 : 5-dialkyl-*p*-benzoquinones in dry chloroform at 0° do not yield ozonides, but are decomposed in the sense of the equation:

$$C_6R_2(OH)_2O_2 + 6O + 2H_2O = 2H_2C_2O_4 + 2R\cdot CO_2H,$$

the necessary water being produced by the complete oxidation of a portion of the quinone; thus dihydroxydi*iso*propyl-*p*-benzoquinone yields oxalic and *iso*butyric acids, dihydroxy-*p*-xyloquinone yields oxalic and acetic acids (the same products are also obtained by the oxidation of the quinone by alkaline potassium permanganate), dihydroxydiethyl-*p*-benzoquinone yields oxalic and propionic acids, and dihydroxythymoquinone yields oxalic and *iso*butyric acids, acetic acid not being detected.

The study of dialkylated dihydroxybenzoquinones has thrown considerable light on the constitution of perezone (pipitzahoic acid). This substance is converted through the anilino-derivative into hydroxyperezone by Mylius's method (A., 1885, 777, 805). Hydroxyperezone, $C_{15}H_{20}O_4$, m. p. 138—139°, yellowish-red needles, resembles the dialkylated dihydroxy-*p*-benzoquinones in its colour, in the colorations it develops with concentrated sulphuric acid and with aqueous sodium hydroxide respectively, and in its conversion into a *tetra-acetate*, $C_{23}H_{30}O_8$, m. p. 97—98°, colourless crystals, by reductive acetylation. By treatment in chloroform with ozonised oxygen, it yields oxalic acid and not a volatile fatty acid as expected, but $\alpha\beta$-diketobutyric acid, which is isolated and identified by treating its aqueous solution with phenylhydrazine, whereby $\alpha\beta$-diketobutyric acid phenylosazone (completely identified by its conversion by warm alkali into 4-benzeneazo-1-phenyl-3-methyl-5-pyrazolone) is obtained. The formation of the diketobutyric acid is accounted for if one of the side-chains in hydroxyperezone is a propenyl group. Consequently, the other side-chain must be a hexyl group, since the sum of the carbon atoms in the side-chains is 9. Hydroxyperezone, therefore, has the constitution

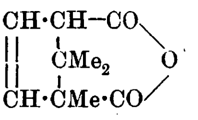
$$C_6H_{13}\cdot C{<}\begin{matrix}C(OH)\cdot CO \\ CO\cdot C(OH)\end{matrix}{>}C\cdot CH{:}CHMe.$$

Since hydroxyperezone readily loses water to form perezinone (Mylius, *loc. cit.*), whilst perezone does not suffer an analogous change, perezone has the constitution $C_6H_{13}\cdot C{<}\begin{matrix}C(OH)\cdot CO \\ CO{-\!\!-}CH\end{matrix}{>}C\cdot CH{:}CHMe$, and perezinone is $\begin{matrix}C(OH){-\!\!-}CO\cdot C{-}CH \\ C(C_6H_{13})\cdot CO\cdot C\cdot CH_2\end{matrix}{>}CH$. By reduction with sodium amalgam and aqueous sodium hydroxide at 100°, hydroxyperezone yields

hexylpropenyldihydroresorcinol, $C_{15}H_{24}O_2$, m. p. 140—144°, colourless needles. By similar treatment, dihydroxythymoquinone yields *methyl*iso*propyldihydroresorcinol*, $C_{10}H_{16}O_2$, m. p. 170°, softening at 145°, colourless leaflets. C. S.

Camphor and its Derivatives. XII. JULIUS BREDT (*Annalen*, 1913, **395**, 26—63).—[With J. HOUBEN, P. LEVY, and S. LINK.]—*Methyl* 4-*chlorocamphorate*, $\begin{matrix} CH_2-CCl(CO_2Me) \\ | \\ CH_2\cdot CMe(CO_2Me) \end{matrix}\!\!>\!CMe_2$, m. p. 56°, b. p. 158°/15 mm., is prepared from 4-chlorocamphoryl chloride and sodium methoxide in methyl alcohol. By slow distillation at 254—285° under ordinary pressure, it yields hydrogen chloride and *methyl dehydrocamphorate*, $C_{12}H_{18}O_4$, b. p. 137°/15 mm., and also methyl chloride and methyl camphanate, the latter decomposition resembling that which occurs during the distillation of the ester of a γ-halogenated fatty acid. *Phenyl* 4-*chlorocamphorate*, $C_{22}H_{23}O_4Cl$, m. p. 89°, obtained in a similar manner from sodium phenoxide in petroleum (b. p. 70—100°), yields, by slow distillation or by heating with quinoline, only hydrogen chloride and *phenyl dehydrocamphorate*, $C_{22}H_{22}O_4$, m. p. 155°. *Phenyl* dl-4-*chlorocamphorate*, m. p. 74°, yields *phenyl* dl-*dehydrocamphorate*, m. p. 133°, by similar treatment.

By hydrolysis with aqueous methyl alcoholic potassium hydroxide, removal of the alcohol and phenol, and subsequent acidification, phenyl dehydrocamphorate yields *d*-dehydrocamphoric acid, m. p. 202—203°, $[\alpha]_D^{21}$ +118·6° in chloroform and +113·8° in alcohol, which is converted into iso*dehydrocamphoric anhydride* (annexed formula), m. p. 185·5—186°, and camphonenic acid by distillation under ordinary pressure. iso*Dehydrocamphoric acid* has m. p. 181—182°, and readily yields the anhydride by treatment with cold acetyl chloride. Dehydrocamphoric acid yields camphoronic acid by oxidation with dilute nitric acid or alkaline potassium permanganate, and forms a *methyl hydrogen* ester, $C_{11}H_{16}O_4$, m. p. 96°, *silver* salt, $C_8H_{12}(CO_2Ag)_2,H_2O$, and *calcium* salt,



$C_{10}H_{12}O_4Ca,4H_2O$.

It does not form an anhydride, and yields the *chloride*, $C_{10}H_{12}O_2Cl_2$, b. p. 139°/13·5 mm., m. p. about 50°, by treatment with phosphorus pentachloride or acetyl chloride. The non-formation of an anhydride and the fact that its chloride reacts with aqueous ammonia at 0° to form the *diamide*, $C_{10}H_{16}O_2N_2,H_2O$, m. p. 191°, colourless needles (compare A., 1912, i, 411), show that dehydrocamphoric acid has something approaching the *cis-trans* configuration. Reference to the tetrahedral model shows that the two carboxyl groups are in what the author terms the *meso-trans* position, in which the spatial separation of the acidic groups is almost as great as in the *cis-trans* modification of the isomeric *iso*dehydrocamphoric acid.

The non-existence of dehydrocamphoric anhydride explains why hydrogen chloride or bromide cannot be eliminated from the C_5-ring of 4-chloro- or bromo-camphoric anhydride.

With S. LINK and TH. FUSSGÄNGER.]—When heated at 100° for

six hours with hydrobromic acid saturated at 0°, *d*-dehydrocamphoric acid yields a mixture of cis-3-*bromocamphoric acid*, m. p. 158—160°, and trans-3-*bromocamphoric acid*, m. p. 232°, of which the former is easily soluble in benzene. The *cis*-acid, which is the chief product of the action of hydrobromic acid at 0°, yields *cis*-camphoric acid, and the *trans*-acid yields *trans*-camphoric acid, by reduction with zinc and glacial acetic and 24% hydrochloric acids. The action of hydrobromic acid at 100° on *dl*-dehydrocamphoric acid yields a mixture of two stereoisomeric dl-3-*bromocamphoric acids*, m. p. 188—189° (decomp.) and 239—240° respectively, of which the less fusible is the chief product, is insoluble in benzene, and yields *trans-dl*-camphoric acid by reduction. Unlike the active acid, *dl*-dehydrocamphoric acid is not attacked by hydrobromic acid at 0°, even after three months.

By boiling with aqueous sodium carbonate and subsequently acidifying, *cis*-3-bromocamphoric acid yields 3-*hydroxycamphorolactone*, $C_{10}H_{14}O_4$, m. p. 228°, whilst *trans*-3-bromocamphoric acid yields trans-3-*hydroxycamphoric acid*, $C_{10}H_{16}O_5$, m. p. 194°, and camphonenic acid, m. p. 155°, identical with that mentioned above and with the unsaturated acid obtained by Noyes from the nitroso-derivative of aminolauronolic anhydride (A., 1906, i, 397). The constitution of camphonenic acid is proved by the formation of camphoronic acid by oxidation with nitric acid or potassium permanganate.

3-Hydroxycamphorolactone boils unchanged, but *trans*-3-hydroxycamphoric acid yields dehydrocamphoric acid and *iso*dehydrocamphoric anhydride by slow distillation. *trans*-3-Hydroxycamphoric anhydride yields only the latter by distillation.

By heating equal molecular quantities of bromine and dehydrocamphoryl chloride at 100° for six hours, decomposing the product with aqueous sodium carbonate, and acidifying, an unsaturated *acid*, $C_9H_{12}O_2$, m. p. 149°, colourless needles, is obtained, which is probably *dehydrolaurolenic acid.*

From the behaviour of the two acids, it is probable that in *cis*-3-bromocamphoric acid the two carboxyl groups are each in the *cis*-position to the bromine atom, whilst in *trans*-3-bromocamphoric acid the bromine is in the *cis*-position to the neighbouring carboxyl and in the trans-position to the other carboxyl group, because lactone formation does not occur by the distillation of its esters, although the halogen is in the γ-position to the carboxyl group. C. S.

Action of Magnesium and Allyl Haloids on Camphor.

METSCHISLAV CHOJN (*J. Russ. Phys. Chem. Soc.* 1912, **44**, 1844—1853). —*Allylborneol* (1 : 7 : 7-*trimethyl*-2-*allyl*-1 : 2 : 2-bicyclo*heptan*-2-*ol*),

$$\begin{array}{l} CH_2\cdot CH-CH_2 \\ |\quad\ CMe_2\ | \\ CH_2\cdot CMe-C(OH)\cdot CH_2\cdot CH{:}CH_2, \end{array}$$

obtained by decomposing with water the product of the interaction of magnesium, allyl bromide or iodide, and camphor, is a colourless, viscous liquid with a pleasant camphor-like odour, b. p. 118—119°/17 mm., 120—121°/21 mm., $D_4^{21\cdot8}$ 0·9474, $n_D^{21\cdot8}$ 1·48943, and exhibits the normal molecular weight in freezing benzene or boiling ether. It

unites with two atoms of bromine and, when treated in ethereal solution and in presence of anhydrous sodium sulphate with dry hydrogen chloride at 0°, gives the analogous chloro-derivative, which is converted into the corresponding unsaturated hydrocarbon when heated with dry pyridine.

Oxidation of allylborneol with 1% potassium permanganate solution yields *βγ-dihydroxypropylborneol* (1 : 7 : 7-*trimethyl*-2-*propan*-*βγ*-*diol*-1 : 2 : 2-bicyclo*heptan*-2-*ol*),

$$\begin{array}{l} CH_2\cdot CH{-}{-}CH_2 \\ \Big| \quad\; CMe_2 \;\Big| \\ CH_2\cdot CMe\cdot C(OH)\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH \end{array},$$

which forms radiating or beard-like masses of tasteless, odourless, snow-white crystals, m. p. 119—120°, and exhibits normal ebullioscopic behaviour in benzene.

When oxidised with 4% potassium permanganate (4 atoms of oxygen), allylborneol is converted into the hydroxy-acid, *borneolacetic acid*,

$$\begin{array}{l} CH_2\cdot CH{-}CH_2 \\ \Big| \quad\; CMe_2 \;\Big| \\ CH_2\cdot CMe\cdot C(OH)\cdot CH_2\cdot CO_2H \end{array}$$

, which was not obtained in the pure state; the *ammonium*, *silver*, and *calcium* ($+2H_2O$) salts of the acid were prepared and analysed. T. H. P.

Bupleurol. The Alcohol from the Essential Oil of Bupleurum fructicosum. LUIGI FRANCESCONI and E. SERNAGIOTTO (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 34—40).—This alcohol, which the authors named *bupleurol*, can be isolated by the aid of phthalic anhydride from the higher fractions of the essential oil. It has the composition $C_{10}H_{20}O$, b. p. 209—210°/762 mm., D^{17} 0·8490, n_D 1·4508, and is optically inactive; the substance has a slight, pleasant odour of roses. From its physical properties the substance is probably an olefinic alcohol, and this is supported by the fact that it yields an oily *dibromide*. It forms a *urethane*, which crystallises in lustrous needles, m. p. 45°. Oxidation of bupleurol with chromic acid yields: (1) an *aldehyde*, which shows Schiff's reaction, and gives a *semicarbazone*, m. p. 135°; (2) an *aldehyde*, of which the *semicarbazone* has m. p. 97°; (3) a *ketone* (b. p. 217°, n_D^{25} 1·4419), which yields a *semicarbazone*, m. p. 189—190°; (4) a red oil, b. p. 207°, which is the *ester* of bupleurol and the corresponding *acid*, which was also isolated. Bupleurol is isomeric with citronellol and with androl, and the authors assign to it the formula $CHMe_2\cdot[CH_2]_3\cdot C(CH_2)\cdot CH_2\cdot CH_2\cdot OH$, which is that of a dihydro-derivative of nerol.

When the *phthalic* ester of bupleurol is dissolved in ammonia and treated with silver nitrate, the *silver* salt, $C_{18}H_{23}O_4Ag$, is obtained, m. p. 135°.

In the isolation of bupleurol, a *substance*, $C_{10}H_{16}O$, is als met with; it has an acrid odour, gives a coloration with Schiff's reagent, reduces ammoniacal silver nitrate, and has D 0·9264, $[\alpha]_D$ 14·93°, n_D 1·4909.

R. V. S.

Insoluble Constituents of Ceara- and Rambong-Caoutchouc. CLAYTON BEADLE and HENRY P. STEVENS (*Zeitsch. Chem. Ind.*

Kolloide, 1913, **12**, 46—48).—The influence of the insoluble constituents on the properties of Ceara- and Rambong-caoutchouc has been investigated, and the results compared with those of similar experiments carried out previously with Hevea-caoutchouc (A., 1912, i, 789). "Benzine" was added to the caoutchouc, and the products recovered from the upper clear solution and the lower turbid solution were separately examined, the latter containing practically the whole of the insoluble constituent. The data compared are the nitrogen content, the proportion of free and fixed sulphur in the vulcanised material, and the mechanical properties. Although the relationships involved are of a complicated character, it would appear that the insoluble constituents play an important part in connexion with the vulcanisation of the caoutchouc, and are more or less independent of the percentage content of nitrogenous substances in the caoutchouc. H. M. D.

Artificial Caoutchoucs. II. CARL D. HARRIES (*Annalen*, 1913, **395**, 211—264).—Replies are given to the remarks of Lebedev (A., 1911, i, 959), Kondakov, Ostromisslenski, and Perkin (A., 1912, i, 636) in connexion with the author's first paper (A., 1911, i, 798).

[With MAX HAGEDORN.]—The identity of natural and of artificial caoutchoucs cannot be satisfactorily tested by a comparison of their derivatives except in the case of the ozonides. The products of their decomposition contain similar amounts of lævualdehyde and its acid and diperoxide. Also the comparison of the velocity of decomposition, under proper conditions, of the diozonides and dioxozonides (Harries and Neymann, A., 1908, i, 967; Harries, A., 1912, i, 706) gives satisfactory results. The decomposition curves of the diozonides of Para caoutchouc (purified by twice precipitating its benzene solution by alcohol, and by two extractions with acetone in a Soxhlet apparatus for twelve hours), of gutta-percha, and of artificial caoutchouc obtained by the autopolymerisation of isoprene at 95°, are the same; the decomposition curve of artificial caoutchouc, obtained from isoprene by the acetic acid process, is slightly different. The decomposition curve of "sodium" caoutchouc diozonide is quite different. The same is true of the butadiene caoutchoucs. "Sodium" butadiene-caoutchouc (purified by the alcohol-benzene method) forms a diozonide, the decomposition products of which do not contain a trace of succindialdehyde or lævulaldehyde, and the decomposition curve of which is quite different from that of the diozonide of butadiene-caoutchouc polymerised by heat.

Like natural caoutchouc, artificial "normal" caoutchoucs form diozonides and dioxozonides. Artificial "sodium" caoutchoucs also form diozonides and dioxozonides, although with greater difficulty; the products of their decomposition by water are similar, but the diozonides yield a larger proportion of aldehydes, the dioxozonides a larger amount of acids.

Gutta-percha, purified by alcohol and chloroform and by prolonged extraction with acetone, yields, with washed 9—10% ozone, a *diozonide*, $C_{10}H_{16}O_6$, which so closely resembles the diozonide of natural or of artificial caoutchouc that most probably they are identical. By further treatment with 18% ozone in chloroform, gutta-percha diozonide yields

a *dioxozonide*, $C_{10}H_{16}O_8$, which behaves like the dioxozonide of Para caoutchouc.

The authors have been able to account for a phenomenon which has frequently been observed. Caoutchouc diozonides, prepared apparently in the same manner, frequently yield, by decomposition with water, different amounts of the crystalline lævulaldehyde diperoxide, m. p. 196°; it has now been shown that the quantity of this product increases with amount of dioxozonide in the diozonide.

In partial agreement with Gottlob (A., 1908, i, 436), the authors find that the diozonides of African (Congo) caoutchoucs yield quantities of decomposition products distinctly different from those of the decomposition products of the diozonides of Para caoutchouc, artificial caoutchouc, and gutta-percha. Congo caoutchoucs yield dioxozonides only with difficulty.

[With WILHELM SCHÖNBERG.]—The exhaustive methylation of piperidine is not a suitable method for the preparation of piperylene in quantity. It can be obtained readily as follows: (1) acraldehyde and magnesium ethyl bromide yield by the usual process the alcohol, $CH_2:CH\cdot CHEt\cdot OH$, which is then dehydrated by phthalic anhydride; (2) the alcohol, $CHEt_2\cdot OH$, prepared in the usual manner from ethyl formate and magnesium ethyl bromide, yields Δ^{β}-pentene by distillation with phosphoric oxide; the olefine forms a *dibromide*,

$$CHMeBr\cdot CHEtBr,$$

b. p. 65—70°/15 mm., which is converted into piperylene by the sodium carbonate process at about 600°. This is the best method.

By heating for about fourteen days at 105—110° in an atmosphere of carbon dioxide, piperylene polymerises to "normal" *piperylene-caoutchouc*, $C_{10}H_{16}$, which is elastic and very closely resembles "normal" isoprene-caoutchouc in most of its properties. It forms a *nitrosite*-a, $C_{10}H_{16}O_5N_2$ (?), decomp. 118—122°, yellow powder, insoluble in acetone or ethyl acetate, and a *nitrosite*-c, $2C_{10}H_{15}O_7N_3$, decomp., 162—164°, easily soluble in acetone or ethyl acetate, and an unstable *bromide*, $C_{10}H_{15}Br_3$ (?), decomp. 150—160°, pale yellow, amorphous powder; these three derivatives are almost indistinguishable from the corresponding derivatives of "normal" isoprene-caoutchouc. The ozonides of the two caoutchoucs, however, are quite dissimilar. By treatment with washed ozone in chloroform, piperylene-caoutchouc yields the *diozonide*, $C_{10}H_{16}O_6$, which explodes violently by heating, and exhibits the usual properties of ozonides. It forms a dioxozonide only with very great difficulty. The decomposition curve of piperylene-caoutchouc diozonide is similar to, yet quite distinct from, that of normal caoutchouc diozonide, but the decomposition products are quite different. The former diozonide does not yield lævulaldehyde, but a substance which is most probably methylsuccindialdehyde. Hence "normal" piperylene-caoutchouc (which is a true structural isomeride of "normal" caoutchouc, piperylene being $\Delta^{\alpha\gamma}$-pentadiene) is a derivative of 1 : 5-dimethyl-2 : 6-*cyclo*octadiene,

$$2CHMe:CH\cdot CH:CH_2 \longrightarrow \begin{array}{l} CHMe\cdot CH:CH\cdot CH_2 \\ CH_2—CH:CH—CHMe \end{array} \longrightarrow$$
$$2CHO\cdot CH_2\cdot CHMe\cdot CHO.$$

During the polymerisation of piperylene by heating, a by-product is obtained in the form of a *terpene*, $C_{10}H_{16}$, b. p. 58—59°/11 mm., $D_4^{20\cdot5}$ 0·8313, $n_D^{20\cdot5}$ 1·46916, n_α 1·46620, n_γ 1·48373, which forms a crystalline *bromide*, m. p. 178°, and a white *diozonide*, $C_{10}H_{16}O_6$; the velocity of decomposition of the latter by water at 125° is very great, but definite substances could not be isolated from the products owing to lack of material.

The polymerisation of piperylene by sodium at 60° yields a "sodium" piperylene-caoutchouc which is brittle after purification; it forms a *nitrosite*, decomp. 140—145°, and a *bromide*, the analyses of which do not correspond with the formulæ of the normal compounds.

[By the AUTHOR.]—The proof of the presence of an 8-ring in "normal" caoutchoucs is of fundamental importance in the chemistry of caoutchoucs. To test this point, the velocity of decomposition of "normal" butadiene-caoutchouc diozonide has been compared with that of the diozonide of Willstätter's 1 : 5-*cyclo*octadiene. (A serious difficulty is encountered in separating the "normal" butadiene-caoutchouc from the terpenoid hydrocarbon, C_8H_{12}, obtained as a by-product during the polymerisation. Both substances form almost colourless *diozonides*, $C_8H_{12}O_6$; the diozonide of the terpenoid hydrocarbon is decomposed very rapidly by water at 125°, and the products of decomposition contain hydrogen peroxide, but do not respond to the pyrrole test.) The comparison shows that both decompose at the same rate (at first the "normal" butadiene-caoutchouc decomposes more rapidly, but this is probably due to the presence of a little of the easily decomposable diozonide of the terpenoid hydrocarbon), and yield practically the same amount of succindialdehyde. Since the decomposition curve of 1 : 5-*cyclo*octadiene diozonide is very characteristic, and since the decomposition products of the two diozonides are quite alike in not responding to the hydrogen peroxide test and in containing the same percentage of succindialdehyde, the statement is made with considerable confidence that "normal" caoutchoucs contain an 8-ring.

[With RICHARD SEITZ.]—Although Zelinsky and Gorsky (A., 1908, i, 619) have resolved 1-methyl-$\Delta^{2:4}$-*cyclo*hexadiene into its active forms, their method of preparing the substance does not necessarily lead to the formation of a compound of this constitution (compare Harries and Neymann, A., 1909, i, 218). The authors, therefore, have used a method similar to that by which Harries obtained pure $\Delta^{1:3}$-*cyclo*hexadiene (A., 1912, i, 343). 1-Methyl-Δ^3-*cyclo*hexene and bromine in acetic acid yield 3 : 4-*dibromo*-1-*methyl*cyclo*hexane*, b. p. 94—95°/12 mm., which reacts with 33% alcoholic trimethylamine (2 mols.) at about 95° for twenty hours to form 1-*methyl*-Δ^4-cyclo-*hexenyl*-3-*trimethylammonium bromide* or 1-*methyl*-Δ^2-cyclo*hexenyl*-4-*tri-methylammonium bromide*, $C_{10}H_{20}NBr$, m. p. 166—167°. The bromide, whichever constitution it may have, must yield 1-methyl-$\Delta^{2:4}$-*cyclo*hexadiene by treatment with water and silver oxide and subsequent distillation. The hydrocarbon agrees well in its physical constants (b. p. 100·5—101·5°, $D_4^{22\cdot5}$ 0·8252, n_α 1·46225, $n_D^{22\cdot5}$ 1·46619, n_γ 1·48519) with Zelinsky and Gorsky's compound (*loc. cit.*). By treatment with unwashed 18—20% ozone in chloroform, it yields a *diozonide*, $C_7H_{10}O_6$,

which is decomposed in ether by copper hydride, yielding probably methylsuccindialdehyde and glyoxal; these substances, however, could not be definitely identified. C. S.

Comparative Researches on the Polymerisation Products of βγ-Dimethylbutadiene obtained Spontaneously and by Heat. CARL D. HARRIES (*Annalen*, 1913, **395**, 264—272).—[With MAX HAGEDORN.]—"Normal" βγ-dimethylbutadiene-caoutchouc, produced by heating βγ-dimethylbutadiene in a closed vessel, yields very readily the diozonide and the dioxozonide, both of which are decomposed by water, giving an almost quantitative yield of acetonylacetone. Kondakov's white, insoluble polymeride, produced by the prolonged keeping of βγ-dimethylbutadiene at the ordinary temperature, also readily forms a *diozonide*, $C_{12}H_{20}O_6$, and *dioxozonide*, $C_{12}H_{20}O_8$, by the decomposition of which by water only about 20% of acetonylacetone is produced. Also the decomposition curves of the two diozonides are very different.

By exposure to air for a few hours, Kondakov's polymeride changes to a yellow, soluble resin. This forms a *diozonide*, $C_{12}H_{20}O_6$, and *dioxozonide*, $C_{12}H_{20}O_8$, by the decomposition of which about 36% of acetonylacetone is obtained.

The author is of opinion that Kondakov's polymeride is not a true caoutchouc, and by analogy, therefore, that the caoutchouc obtained by Pickles (T., 1910, **97**, 1085) by the prolonged keeping of isoprene is not true caoutchouc. C. S.

Chlorophyll. LÉON MARCHLEWSKI (*Annalen*, 1913, **395**, 194—210). —A reply to Willstätter and Isler (A., 1912, i, 710). The author maintains his contention that Willstätter's phaeophytin is chlorophyllan under another name. The heterogeneity of chlorophyllan was established by the author and Malarski (A., 1909, i, 947) before Willstätter (A., 1911, i, 393).

The proportion of the components *a* and *b* in chlorophyll is determined far more conveniently by Marchlewski and Jacobson's method (A., 1912, ii, 705) than by Willstätter and Isler's process (*loc. cit.*).

C. S.

Alkaloids of Aconitum Lycoctonum. HEINRICH SCHULZE and ERICH BIERLING (*Arch. Pharm.*, 1913, **251**, 8—49).—A detailed résumé is first given of the work of Hübschmann (*Schweiz. Woch. Pharm.*, 1865, **3**, 269), Dragendorff and Spohn (A., 1885, 403), Einberg (*Diss. Dorpat.*, 1887), Dohrmann (*ibid.*, 1888), and van der Bellen (*ibid.*, 1890) on these alkaloids. The author's results extend, and to some extent confirm, those of Dragendorff and his pupils. It is shown that the alkaloids of this species differ from the typical "aconitines" in not yielding two monobasic acids on hydrolysis.

The coarsely ground roots were exhausted with 94% alcohol, the extract concentrated, and set aside to deposit sucrose, the mother liquor further concentrated, and diluted with three times its volume of water to separate resin and oil, and the filtrate, after extraction with ether to remove the last traces of oil, made alkaline with sodium

hydroxide and the liberated lycaconitine extracted with ether. The alkaline liquor was then shaken with chloroform, and the amorphous alkaloids so obtained freed from traces of lycaconitine by extraction with ether. This partly purified mixture of alkaloids was dissolved in dilute hydrochloric acid (3%), the solution treated with potassium thiocyanate in excess to remove an alkaloid giving an insoluble thiocyanate, and the filtrate made alkaline with sodium hydroxide and extracted with chloroform, which removed myoctonine.

Lycaconitine, $C_{36}H_{46}O_{10}N_2$, $[\alpha]_D^{20}$ $+42{\cdot}47°$ in alcohol, was decolorised by means of animal charcoal, and thus obtained as a colourless powder, easily soluble in alcohol or chloroform, less so in ether; it is a weak base from which no crystalline derivatives could be prepared. On hydrolysis by water or dilute hydrochloric acid, it yields succinic acid and anthranoyl-lycoctonine. Alkalis hydrolyse it to lycoctonine and lycoctoninic acid.

Myoctonine, $(C_{36}H_{42}O_{10}N_2)_2$, $[\alpha]_D^{20}+44{\cdot}79°$ in alcohol, is a colourless, amorphous powder, soluble in alcohol or chloroform, but sparingly so in ether; the solution in alcohol fluoresces bluish-violet. No crystalline derivatives were obtained. On hydrolysis by hydrochloric acid or alkalis, it furnishes the same products as lycaconitine.

The unnamed base giving an insoluble thiocyanate was not analysed; on hydrolysis by alkalis, it also yields lycoctonine and lycoctoninic acid.

Lycoctonine, $C_{25}H_{39}O_7N,H_2O$, m. p. 131—133°, $[\alpha]_D^{20}+49{\cdot}64°$ in alcohol, crystallises in long, colourless needles from dilute alcohol, is a strong base, contains four methoxyl groups and a methylimino-group, and becomes amorphous when dehydrated by drying at 100°/40 mm. The *hydrochloride*, B,HCl,H_2O, m. p. 75° (decomp.), forms colourless prisms; the *hydrobromide*, $B,HBr,2H_2O$, has m. p. 88—89°, and the *perchlorate*, $B,HClO_4,1\frac{1}{2}H_2O$, m. p. 68—69° (decomp.), forms heavy prisms. The *methiodide*, B,MeI, m. p. 178°, forms pale yellow needles from alcohol on addition of ether, and the *methochloride aurichloride*, $B,Me,HAuCl_4$, small, heavy, yellow prisms. Lycoctonine contains at least two hydroxyl groups.

Lycoctoninic acid, $C_{11}H_{11}O_5N$, m. p. 179°, forms bright brown needles or leaflets from dilute alcohol, and appears to be succinanil-carboxylic acid (Riedel, A., 1912, i, 774).

Anthranoyl-lycoctonine, $C_{32}H_{44}O_8N_2$, m. p. 154—155°, forms bright brown, glancing leaflets, is easily soluble in chloroform, but sparingly so in other solvents; the solutions fluoresce bluish-violet. The alkaloid contains four methoxyl groups and a methylimino-group. The *perchlorate*, $B,2HClO_4$, alone was obtained crystalline; it forms aggregates of colourless needles, and does not melt completely even at 235°. On hydrolysis by sodium hydroxide in alcohol, the free base yields lycoctonine and anthranilic acid. Anthranoyl-lycoctonine is probably identical with Dragendorff's "lycaconine," but as it is not analogous with the other "aconines," lycoctonine being the corresponding substance in this instance, it is proposed to abandon this name.

The reactions of these alkaloids with the usual alkaloidal reagents and precipitants are tabulated in the original.

Hildebrandt reports that in doses of 0·01 gram, lycaconitine stills the

frog's heart in five hours and myoctonine in seven hours, death occurring three hours later. Lycoctonine causes paralysis after seven hours, but does not still the heart, whilst the action of the relatively insoluble anthranoyl-lycoctonine only becomes apparent after six days. When paralysis of the heart's action does not come on too quickly, all the alkaloids show the characteristic action of the aconitines on the heart. T. A. H.

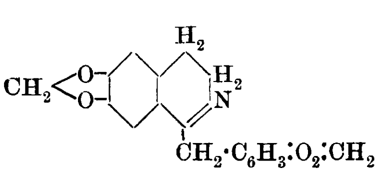
ψ-Laudanine. HERMAN DECKER and THEODOR EICHLER (*Annalen*, 1913, **395**, 377—381).—The reduction of an alcoholic solution of *N*-methylnorpapaverinium phenolbetaine (Decker and Dunant, A., 1908, i, 204) by tin and concentrated hydrochloric acid on the water-bath yields the *stannochloride*, $C_{20}H_{25}O_4N,HCl,SnCl_2$, of a *base*, $C_{20}H_{25}O_4N$, m. p. 111°, which has the constitution:

$$C_6H_3(OMe)_2\cdot CH_2\cdot CH{<}{\substack{C_6H_2(OH)(OMe)\\ NMe\text{———}CH_2}}{>}CH_2,$$

and is called *ψ-laudanine*, since it differs from laudanine only by the interchange in position of a hydroxyl and a methoxyl group. The *hydrochloride*, *platinichloride*, *chromate*, *picrate*, m. p. 162—163°, and *perchlorate* of the base are mentioned. C. S.

Syntheses of Dihydro*iso*quinoline Derivatives. HERMAN DECKER, WALTER KROPP, HEINRICH HOYER, and PAUL BECKER (*Annalen*, 1913, **395**, 299—320. Compare Pictet and Kay, A., 1909, i, 513; Decker and Kropp, *ibid.*, i, 513).—Derivatives of 3 : 4-dihydro-*iso*quinoline are obtained by the interaction of acyl-β-phenylethyl-amides and phosphorus pentachloride and phosphoryl chloride in boiling benzene, toluene, or xylene, moisture being carefully excluded. Formo-β-phenylethylamide yields very little 3 : 4-dihydro*iso*quinoline (*picrate*, m. p. 174—176°), the chief products being β-phenylethylamine and β-phenylethylaminomalon-β-phenylethylamide (Decker and Becker, A., 1911, i, 714). Phenylaceto-β-phenylethylamide, treated as in Decker and Kropp's method (*loc. cit.*), yields *di-β-phenylethylamine* (?), $NH(CH_2\cdot CH_2Ph)_2$, b. p. 220—230°/30 mm. (*picrate*, m. p. 229—231°), and 1-benzyl-3 : 4-dihydro*iso*quinoline (picrate, m. p. 182°, not 174—175° [Pictet and Kay, *loc. cit.*]). Oxalodi-β-phenylethylamide yields a *substance* (*hydrochloride*, m. p. 191—193°; *picrate*, $C_{24}H_{21}O_8N_5$, m. p. 167—168°, canary-green needles), which is probably 3 : 4-*dihydro*iso-*quinolyl*-1-*carboxy*-β-*phenylethylamide*, $C_9NH_8\cdot CO\cdot NH\cdot CH_2\cdot CH_2Ph$, since it yields β-phenylethylamine and a derivative of *iso*quinoline by hydrolysis by hydrochloric acid at 120°. Even by energetic treatment, the substance cannot be converted into bis-3 : 4-dihydro*iso*-quinolyl.

Homopiperonoylhomopiperonylamine yields 1-*piperonylnorhydrastinine* (annexed formula), m. p. 136—137°, colourless plates (*picrate*, m. p. 220—223° [decomp.]; *platinichloride*, decomp. 175—180°), together with another base, *picrate*, m. p. 228°.



Phenylacetohomopiperonylamide yields 1-benzylnorhydrastinine

(*picrate*, m. p. 205—206° [decomp.]), whilst *benzohomopiperonylamide*, $CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}COPh$, m. p. 122°, colourless needles, prepared by heating *homopiperonylamine benzoate*, m. p. 115°, yellowish-green needles, at 180° (compare this vol., i, 272), or from homopiperonylamine by the Schotten-Baumann method, yields 1-*phenylnorhydrastinine*, $C_{16}H_{13}O_2N$, m. p. 141°, colourless prisms (*methiodide*, m. p. 241°; *picrate*, m. p. 188—190°).

Formohomopiperonylamide yields by condensation *norhydrastinine*, $CH_2O_2{:}C_6H_2{<}{\begin{array}{l}CH_2{\cdot}CH_2\\CH{=}N\end{array}}$, m. p. 90—91°, stout needles (*picrate*, m. p. 237—238°; *hydrochloride*, m. p. 192°; *platinichloride*, decomp. about 240°), the chief product, however, being *homopiperonylaminomalondihomopiperonyldiamide*,

$$CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CH(CO{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_3{:}CH_2O_2)_2,$$

m. p. 124—126° (decomp.), colourless needles, which forms a *picrate*, m. p. 210—211° (decomp.), yellow plates, and *hydrochloride*, m. p. 182—183°. C. S.

Syntheses of Hydrastinine and its *N*-Homologues. HERMAN DECKER (*Annalen*, 1913, **395**, 321—328).—Norhydrastinine (preceding abstract) and methyl sulphate react in toluene at 100° to form 2-*methylnorhydrastinine methosulphate* (*hydrastinine methosulphate*),

$$C_{10}H_9O_2NMe{\cdot}SO_4Me,$$

m. p. 117—119°, pale yellow, crystalline powder, from which hydrastinine is liberated by 15% sodium hydroxide at 0°.

Norhydrastinine in alcohol reacts with benzyl chloride at 50° to form the *benzylochloride*, $C_{10}H_9O_2NCl{\cdot}CH_2Ph$, m. p. 215°, pale yellow powder, and with ethyl iodide to form the *ethiodide*, $C_{10}H_9O_2NEtI$, m. p. 222°, yellow leaflets; 2-*ethylnorhydrastinine picrate* has m. p. 175°. C. S.

Synthesis of Cotarnine and Third Synthesis of Hydrastinine. HERMAN DECKER and PAUL BECKER (*Annalen*, 1913, **395**, 328—342). —*Formylhomomyristicylamine*, $CH_2O_2{:}C_6H_2(OMe){\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CHO$, m. p. 105—106° (corr.), colourless needles, obtained by heating homomyristicylamine formate at 160—170° for three hours, is converted, by phosphoryl chloride in boiling toluene and subsequently basifying the aqueous solution of the product, into *norcotarnine*,

$$CH_2O_2{:}C_6H(OMe){<}{\begin{array}{l}CH_2{\cdot}CH_2\\CH{=}N\end{array}},$$

(*picrate*, m. p. 182—184°, yellow needles), the methiodide of which, m. p. 184—186° (decomp.), is identical with cotarnine hydriodide, and the methosulphate of which is converted into cotarnine picrate (Salway T., 1911, **97**, 1208) by alcoholic picric acid.

Equal molecular quantities of homopiperonylamine and benzaldehyde react on the water-bath to form *benzylidenehomopiperonylamine*, $CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}CH_2{\cdot}N{:}CHPh$, m. p. 36°, pale yellow prisms, which is converted by methyl iodide (without a solvent) at 100° into the *methiodide*. The latter is hydrolysed by boiling 95% alcohol or by steam, yielding benzaldehyde and *homopiperonylmethylamine hydriodide*,

m. p. 135—136° (corr.), colourless leaflets. *Homopiperonylmethylamine*, $C_{10}H_{13}O_2N$, b. p. 156—158°/24 mm., pale yellow oil (*carbonate*, m. p. 72—75°; *hydrochloride*, m. p. 183—185°; *picrate*, m. p. 166—167° [corr.]), is converted into formylhomopiperonylmethylamine by heating its formate at 150—160° for seven hours. By condensation with phosphoryl chloride in boiling toluene and basification of the product, the formyl derivative is converted into hydrastinine.

By processes similar to the preceding, *benzylidenehomopiperonylamine* and its *ethiodide*, *homopiperonylethylamine hydriodide*, m. p. 126—128°, white leaflets, and the corresponding *hydrochloride*, m. p. 183—185°, and *picrate*, m. p. 135—136°, orange-red leaflets, *formylhomopiperonylethylamine*, and 2-ethylnorhydrastinine (preceding abstract) have been prepared.

When a certain temperature or duration of heating is exceeded, by-products are obtained in the interaction of benzylidenehomopiperonylamine and an alkyl haloid. Their production is due to the formation of homopiperonyl haloid, which reacts with the benzylidene compound in the same manner as does the alkyl haloid, a derivative of dimethylamine being produced simultaneously. As an illustration of such heterospasis (compare Decker and Fellenberg, A., 1909, i, 116), equal molecular quantities of benzylidenehomopiperonylamine and methyl iodide have been heated in benzene at 140° for six hours and the product has been hydrolysed by steam, whereby *dihomopiperonylamine hydriodide*, $NH(CH_2{\cdot}CH_2{\cdot}C_6H_3{:}CH_2O_2)_2,HI$, m. p. 234—236°, pale yellow prisms, has been obtained. The corresponding *base* has m. p. 72—75° (decomp.).

Moreover, quaternary ammonium haloids are formed when moisture is present during the interaction of benzylidenehomopiperonylamine and an alkyl haloid; in the preceding example, *homopiperonyltrimethylammonium iodide*, m. p. 260—261°, is formed. C. S.

Syntheses of Tetrahydro*iso*quinoline Derivatives. HERMAN DECKER and PAUL BECKER (*Annalen*, 1913, **395**, 342—362).—Homopiperonylamine or a similar derivative of β-phenylethylamine reacts readily at the ordinary temperature with an equal molecular quantity of an aldehyde to form the alkylidene derivative, which is converted into a tetrahydro*iso*quinoline derivative by a suitable catalyst; homopiperonylamine (or similar base) and the aldehyde, reacting directly in the presence of the catalyst, yield quite different products.

By adding slowly a benzene solution of benzylidenehomopiperonylamine to moderately warm, concentrated hydrochloric acid, the *hydrochloride*, m. p. 309—311°, of 1-*phenyldihydronorhydrastinine*,

$$CH_2O_2{:}C_6H_2{<}\begin{matrix}CH_2\text{—}CH_2\\ CHPh{\cdot}NH\end{matrix},$$

m. p. 97—98°, large, hexagonal leaflets, is obtained; the *nitrate* and *picrate*, m. p. 169—170° (decomp.), dark yellow prisms, are described. The same base is produced by reducing 1-phenylnorhydrastinine (preceding abstract) by alcohol and 2·5% sodium amalgam, the solution being kept acid by the addition of glacial acetic acid.

Piperonylidenehomopiperonylamine, m. p. 117—118° (unstable *picrate*, m. p. 143—145°), and *cinnamylidenehomopiperonylamine*, m. p.

61—63°, are respectively prepared from equal molecular quantities of the components on the water-bath.

The slow addition of homopiperonylamine to 20% formaldehyde yields *homopiperonylmethyleneamine*, $CH_2O_2{:}C_6H_3{\cdot}CH_2{\cdot}CH_2{\cdot}N{:}CH_2$, a liquid, which is converted by hydrochloric acid on the water-bath into the *hydrochloride*, m. p. 274—276°, of *dihydronorhydrastinine*, $C_{10}H_{11}O_2N$, m. p. 81—83°. This base, the hydrochloride of which is also obtained by reducing norhydrastinine with tin and hydrochloric acid, forms a *hydrobromide*, m. p. 256—258°, *picrate*, m. p. 229—231° (decomp.), and *carbonate*, m. p. 114—115° (decomp. corr.), and reacts in benzene with methyl iodide to form the hydriodide, m. p. 239—241° (Freund and Will record 232°) of dihydrohydrastinine. Dihydronorhydrastinine and methyl sulphate react in benzene to form a crystalline substance, m. p. 135—137°, which is converted, by successive treatment with sodium hydrogen carbonate and hydrochloric acid, into dihydrohydrastinine hydrochloride, m. p. 276—278°. Dihydrohydrastinine in the form of its hydrochloride is obtained directly from homopiperonylamine hydrochloride by heating it with 40% formaldehyde at 130° for three hours. The same hydrochloride is also produced from homopiperonylmethylamine hydrochloride or dihydronorhydrastinine hydrochloride and an excess of 40% formaldehyde at 120°.

The paper closes with an explanation of Eschweiler's process of methylation by means of formaldehyde which is represented by the scheme:

$$\mathrm{RR'NH,HX} \longrightarrow \mathrm{RR'N}{<}\begin{matrix}\mathrm{CH_2{\cdot}OH}\\ \mathrm{CH_2{\cdot}OH}\\ \mathrm{X}\end{matrix} \longrightarrow$$

$$\mathrm{RR'N}{<}\begin{matrix}\mathrm{Me}\\ \mathrm{CHO}\\ \mathrm{X}\end{matrix} \xrightarrow{\mathrm{HO}} \mathrm{RR'NMeX} + \mathrm{H{\cdot}CO_2H}.$$

This explanation is in harmony with the fact that quaternary ammonium salts are not produced by Eschweiler's method, and, applied to phenols, will account for the frequent occurrence of the methoxyl group in plant substances. C. S.

Synthesis of Pyrroles from Amino-ketones and Ketones or Ketonic Esters. OSCAR PILOTY and PAUL HIRSCH (*Annalen*, 1913, **395**, 63—74).—The synthesis of pyrrole derivatives by Knorr's method of condensing amino-ketones and esters of β-ketonic acids in glacial acetic acid fails in many cases. The authors now find that condensation in alkaline solution is much more satisfactory, and that ketones can be used instead of ketonic esters. An aqueous solution of the amino-ketone hydrochloride is treated with an excess of an alkali hydroxide, the ketone or ketonic ester is added, and the closed vessel is kept at a gentle heat or left for several days at the ordinary temperature; thus aminoacetone yields 2 : 4-dimethylpyrrole with acetone, *2-phenyl-4-methylpyrrole*, m. p. 152°, with acetophenone, 2 : 3 : 4-trimethylpyrrole with methyl ethyl ketone, *3 : 4-dimethyl-2-ethylpyrrole*, an oil (*picrate*, m. p. 122·5°), with diethyl ketone, whilst methyl α-aminoethyl ketone yields *2 : 3 : 5-trimethylpyrrole*, b. p. 75·5—76·5°/16 mm. (and tetramethylpyrazine as a by-product), with

acetone, and 2 : 3 : 4 : 5-*tetramethylpyrrole* (*picrate*, m. p. 125—126°), and chiefly tetramethylpyrazine, with methyl ethyl ketone.

Aminoacetone yields ethyl 2 : 4-dimethylpyrrole-3-carboxylate with ethyl acetoacetate, and *ethyl hydrogen* 3-*methylpyrrole*-4 : 5-*dicarboxylate*, $NH<\begin{matrix}CH{=\!=\!=}CMe \\ C(CO_2H)\cdot C\cdot CO_2Et\end{matrix}$, m. p. 196°, with ethyl oxalacetate; by hydrolysis the ethyl hydrogen ester is converted into 3-*methylpyrrole*-4(or 5)-*carboxylic acid*, m. p. 149°, which yields 3-methylpyrrole by heating.

Methyl α-aminoethyl ketone yields *ethyl hydrogen* 2 : 3-*dimethylpyrrole*-4 : 5-*dicarboxylate*, m. p. 201° (decomp.), and tetramethylpyrazine, with ethyl oxalacetate. By hydrolysis the ester yields 2 : 3-*dimethylpyrrole*-4(or 5)-*carboxylic acid*, m. p. 188°, which decomposes at 190—195° in carbon dioxide to form 2 : 3-*dimethylpyrrole*, b. p. 62°/11 mm. (*picrate*, $2C_6H_9N,C_6H_2(NO_2)_3\cdot OH$, m. p. 146·5°).

C. S.

A New Method of Preparing Cyclamine-aldehydes and -alcohols. II. ADOLF KAUFMANN and LOUIS G. VALLETTE (*Ber.*, 1913, **46**, 49—57. Compare A., 1912, i, 655).—In the earlier paper, the aldehydes obtained by the scission of the condensation products of nitrosodimethylaniline with 2-methylquinoline ethiodide or α-picoline methiodide were isolated only as phenylhydrazones; processes are now described for the separation of the aldehydes in a free state.

6-*Methoxylepidine ethiodide*, yellow or brown needles decomposing at 177—179°, gives in dilute aqueous solution a beautiful blue fluorescence; it condenses with nitrosodimethylaniline when heated in alcoholic solution, with the formation of the p-*dimethylaminoanil* of 6-*methoxyquinoline*-4-*aldehyde ethiodide*, green columns, m. p. 214—215°, which gives blue solutions in alcohol and carmine-red in water; this substance dissolves in dilute hydrochloric acid, undergoing scission into *p*-aminodimethylaniline and 6-*methoxyquinoline*-4-*aldehyde ethiodide*, the latter of which can be easily separated as the *phenylhydrazone*, red needles decomposing near 248°.

The dimethylaminoanil of quinoline-2-aldehyde ethiodide (*loc. cit.*) is hydrolysed by mineral acid, and phenylhydrazine precipitates the phenylhydrazone of quinoline-2-aldehyde ethiodide; if the addition of the phenylhydrazine be delayed for a time, the precipitate obtained is a mixture of the above with the *phenylhydrazone* of *quinoline*-2-*aldehyde ethochloride*, red needles, m. p. 180° (decomp.), which on reduction with zinc and dilute hydrochloric acid yields a pungent smelling, oily *base*, together with some aniline.

The hydrolysis of the dimethylaminoanil of pyridine-2-aldehyde methiodide likewise yields the methiodide and *methochloride* of the aldehyde, which can be separated as the phenylhydrazones, that of the methochloride decomposing near 235° after previous fusion in its water of crystallisation near 70°.

If the phenylhydrazone of pyridine-2-aldehyde methiodide, after previous careful removal of water of crystallisation, is heated below its m. p. (244°) under 0·1—0·2 mm. pressure (obtained by Wohl's

method with liquid air and charcoal), methyl iodide is liberated with the formation of *pyridine-2-aldehyde phenylhydrazone*, yellow needles or leaflets, m. p. 180—182°; *hydrochloride*, orange-yellow needles, m. p. 188° (decomp.). The methochloride can also be used for the reaction.

In a similar manner the phenylhydrazone of quinoline-2-aldehyde ethiodide can be decomposed to produce *quinoline-2-aldehydephenylhydrazone*, yellowish-brown needles or leaflets, m. p. 203—204°; *hydrochloride*, red needles, m. p. about 237° (decomp.) (compare von Miller and Spady, A., 1886, 370).

Pyridine-2-aldehydephenylhydrazone undergoes reversible hydrolysis when treated with warm mineral acid, but the addition of dinitrobenzaldehyde causes the removal of the phenylhydrazine by forming a very sparingly soluble phenylhydrazone, and the hydrolysis then proceeds to completion; free *pyridine-2-aldehyde* is a pungent liquid, b. p. 210°/725 mm., which gives the usual aldehyde reactions except with Fehling's solution.

Quinoline-2-aldehyde, obtained by hydrolysis of the phenylhydrazone at 120—130° under pressure, forms colourless tablets, m. p. 70—71° (compare von Miller and Spady, *loc. cit.*). D. F. T.

4-Quinolyl Ketones. II. ADOLF KAUFMANN, MAX KUNKLER, and HEINRICH PEYER (*Ber.*, 1913, **46**, 57—64. Compare A., 1912, i, 1017).—From a comparison of the cinchona alkaloids the conclusion is drawn that a substance of the structure 6-alkyloxy-4(β-dialkylamino-α-hydroxyalkyl)-quinoline should possess properties similar to those of quinine.

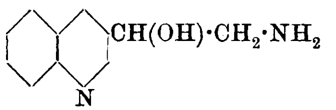
4-Quinolyl methyl ketone has b. p. 99°/0·08 mm., and 4-quinolyl phenyl ketone, m. p. 59°, b. p. 142°/0·12 mm.

6-Ethoxyquinoline (Kaufmann and Peyer, A., 1912, i, 650) readily unites with methyl sulphate with the formation of a yellow solid, the fluorescent solution of which when treated with potassium cyanide yields *4-cyano-6-ethoxy-1-methyl-1 : 4-dihydroquinoline*; the ethereal extract of this substance is oxidised by alcoholic iodine to red needles of *4-cyano-6-ethoxyquinoline methiodide*, m. p. 183—184° (decomp.), which when heated near its m. p. in a vacuum liberates methyl iodide, leaving free *4-cyano-6-ethoxyquinoline* as yellow needles m. p. 118°, which give fluorescent solutions. When treated in benzene solution with an ethereal solution of magnesium methyl iodide the cyano-compound is converted into *6-ethoxy-4-quinolyl methyl ketone*, golden-yellow leaflets or needles, m. p. 80—81°, whilst with magnesium ethyl iodide in an analogous manner, *6-ethoxyquinolyl ethyl ketone*, golden-yellow crystals, m. p. 92°, is produced; both ketones with dilute acids give yellow solutions with a greenish fluorescence.

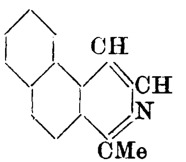
6-Methoxy-4-quinolyl methyl ketone, dissolved in acetic acid of 50% concentration, is reduced by zinc dust to *6-methoxy-4-quinolyl methyl carbinol*, needles, m. p. 120—121°, which gives a blue fluorescence in dilute sulphuric acid, and an emerald-green coloration with chlorine water and ammonia.

4-Quinolyl methyl ketone in alcoholic solution containing sodium

ethoxide is converted by amyl nitrite into 4-*quinolyl oximinomethyl ketone*, colourless needles, m. p. 237—242° (decomp.), which gives a yellow *substance* with phenylhydrazine, and is reduced by an acid solution of stannous chloride to *β-amino-α-hydroxy-4-quinolylethane* (annexed formula); *hydrochloride*, a greyish-white powder, m. p. 208—210° (decomp.); *picrate*, leaflets, m. p. 202°. D. F. T.



A Methylnaphtha*iso*quinoline. AMÉ PICTET and B. MANEVITCH (*Arch. Sci. phys. nat.*, 1913, [iv], **35**, 40—47. Compare Pictet and Gams, A., 1909, i, 671).—The preparation of 1-methyl-α-naphtha*iso*quinoline (annexed formula) is described.



A mixture of α- and β-naphthyl methyl ketones was obtained by the addition of aluminium chloride to a solution of naphthalene and acetyl chloride in carbon disulphide. The two isomerides were separated by treatment of their alcoholic solution with a saturated solution of picric acid, whereby the α-naphthyl methyl ketone picrate was precipitated, from which, by decomposition with sodium carbonate, α-naphthyl methyl ketone, b. p. 292—293°, was isolated in 25—30% yield. β-Naphthyl methyl ketone, b. p. 171—172°/12 mm., m. p. 51°, was obtained from the mother liquor, the yield being 12—15%. Attempts to prepare the α-ketone by the action of acetyl chloride on an ethereal solution of magnesium α-naphthyl bromide were less successful.

α-*Naphthyl oximinomethyl ketone*, m. p. 183°, was formed by the gradual addition of amyl nitrite to an alcoholic solution of α-naphthyl methyl ketone in the presence of sodium ethoxide, and was transformed into α-*naphthyl aminomethyl ketone hydrochloride*, m. p. 245—250° (decomp.) by reduction with stannous chloride. The free *base* was unstable.

α-*Naphthyl acetylaminomethyl ketone*, $C_{10}H_7\cdot CO\cdot CH_2\cdot NHAc$, m. p. 103°, prepared by the action of acetic anhydride and potassium hydroxide on a concentrated aqueous solution of the above hydrochloride, was reduced by means of sodium amalgam to the corresponding *carbinol*, needles, m. p. 145—146°, which, when treated with phosphoric oxide in boiling xylene solution, was transformed into 1-*methyl-α-naphtha*iso*quinoline*, m. p. 95—96°. H. W.

Amino-Imino-Desmotropy. KURT H. MEYER and HANS SCHLÖSSER (*Ber.*, 1913, **46**, 29—32).—It has already been shown (Meyer, A., 1911, i, 193) that 9-hydroxyanthracene exhibits tautomerism between its enolic and ketonic isomeric structures (anthranol and anthrone), and it is now discovered that similar tautomerism can exist in the anthracene group with 9-aminoanthracene derivatives.

The oxidation of 9-aminoanthracene by amyl nitrite (Kaufler and Suchannek, A., 1907, i, 225) or by bromine in alcoholic solution gives

rise to a substance, m. p. 204—205°, which from its lack of colour and of fluorescence must be dianthronedi-imine,

$$NH:C<\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}>CH\cdot CH<\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}>C:NH\,;$$

it is a diacid base, and the course of the oxidation is evidently analogous to that of anthranol (Meyer, *loc. cit.*). When the substance is boiled for an hour with a methyl-alcoholic solution of potassium hydroxide, it is converted into the isomeric diaminodianthryl,

$$NH_2\cdot C<\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}>C\cdot C<\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}>C\cdot NH_2,$$

golden-yellow leaflets, m. p. 334° (compare Gimbel, A., 1887, 1049), which dissolves in benzene to a solution with a green fluorescence. The same isomeric change can be induced less readily by boiling with acetic acid or by fusion, but the reverse change from the amino- to imino-compound could not be accomplished. D. F. T.

Phenylbenzylidenehydrazine. GEORG LOCKEMANN and FRANZ LUCIUS (*Ber.*, 1913, **46**, 150—152).—Thiele and Pickard (A., 1898, i, 474) obtained by the action of acetic anhydride and zinc chloride or sulphuric acid on phenylbenzylidenehydrazine an isomeric β-modification of the hydrazine, m. p. 136°. On repetition the only product now obtained is α-acetyl-α-phenyl-β-benzylidenehydrazine, m. p. 122°. E. F. A.

Constitution of "Anilipyrine." EZIO COMANDUCCI (*Boll. chim. farm.*, 1912, **51**, 741—743).—Two "anilipyrines" have been described, of which one was supposed to result from the condensation of equimolecular quantities of antipyrine and acetanilide, and the other from two molecules of antipyrine with one molecule of acetanilide. By the method of thermal analysis, the author now shows that these substances are neither compounds nor even mixed crystals, but consist simply of crystalline mixtures. When fused mixtures of the antipyrine and acetanilide are cooled, an eutectic is observed corresponding with 45% of antipyrine and 45°. The behaviour of the "anilipyrines" with solvents supports the above results. R. V. S.

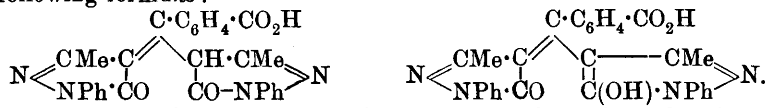
Constitution of "Anilipyrine." LINO METELLO ZAMPOLLI (*Boll. chim. farm.*, 1912, **51**, 780—782. Compare preceding abstract).—Polemical. The author appears to be in agreement with Comanducci's conclusions as now stated. From his preliminary experiments, however, the eutectic temperature is at least 48·5°. R. V. S.

Reaction Products from 1-Phenyl-3-methyl-5-pyrazolone and Phthalic Anhydride. GUSTAV SCHULTZ and GEORG ROHDE (*J. pr. Chem.*, 1913, [ii], **87**, 119—142).—When crystallised from ethyl acetate or acetone, the product, formed by fusing 1-phenyl-3-methyl-5-pyrazolone with phthalic anhydride in equimolecular proportions at 120°, yields an orange-yellow, crystalline *substance*, which becomes red and melts at 202—204°, and on crystallisation from methyl alcohol and acetic acid, or on treatment with aqueous alkalis, loses phthalic

acid and is converted into the red substance first observed by Knorr (A., 1887, 601).

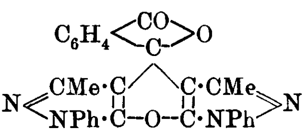
The latter compound is best prepared by boiling the product of the fusion with water until it is completely soluble in chloroform. It crystallises in clusters of dark red prisms or thin, lancet-shaped leaflets, m. p. 208—210° or above, according to the rapidity of heating, and when heated with phthalic acid in acetone or ethyl acetate solution is transformed into the above-mentioned yellow substance.

The constitution of the red substance is represented by one of the following formulæ:



It separates from methyl alcohol and chloroform in red prisms, containing the solvent, and dissolves in aqueous alkalis and alkaline carbonates, forming orange-red salts; the red mono- and di-*silver* salts are mentioned. With methyl-alcoholic hydrogen chloride, it forms a *methyl* ester, $C_{29}H_{24}O_4N_2$, which crystallises in orange-yellow prisms or plates having a bluish glance, m. p. 178—179°, and yields a red *silver* salt, $C_{29}H_{23}O_4N_4Ag$. When heated in nitrobenzene solution or in other solvents of high b. p., the red substance decomposes into 1-phenyl-3-methyl-5-pyrazolone and *1-phenyl-3-methyl-4-pyrazol-5-onylidenephthalide*, $\begin{matrix}N{=}CMe\\|\\NPh\cdot CO\end{matrix}\!\!>C{:}C\!<\!\begin{matrix}C_6H_4\\O\end{matrix}\!\!>CO$. This crystallises in slender, red needles, which sinter at 208°, and have m. p. 212—219°, according to the rapidity of heating. It combines with 1-phenyl-3-methyl-5-pyrazolone in boiling cumene solution to form the original red compound, and is resolved by aqueous alkalis into the ketonic *acid*, $\begin{matrix}N{=}CMe\\|\\NPh\cdot CO\end{matrix}\!\!>CH\cdot CO\cdot C_6H_4\cdot CO_2H$, which forms lustrous, yellow leaflets of variable m. p. (145—160°), and is reconverted by the action of acetic anhydride into the phthalide.

When warmed with acetic anhydride and a little sulphuric acid, the original red substance is transformed into an *anhydride* (annexed formula), crystallising in slender, colourless needles, m. p. 261°; the reverse transformation may be effected by boiling the anhydride with alcoholic alkali hydroxides. F. B.



The Constitution of the Pyrazolinecarboxylic Acids. AUGUST DARAPSKY (*Ber.*, 1913, **46**, 218—225).—Polemical; a reply to Bülow (this vol., i, 101). D. F. T.

A New Example of the Reversed Pinacolin Rearrangement. HEINRICH BILTZ and KARL SEYDEL (*Ber.*, 1913, **46**, 138—142).—4:5-Diphenyldihydroglyoxalone, $\begin{matrix}CPh\cdot NH\\||\\CPh\cdot NH\end{matrix}\!\!>CO$, is oxidised by nitric acid to

4 : 5-diphenyldihydroglyoxalone glycol, $\begin{array}{l}\mathrm{HO{\cdot}CPh{\cdot}NH} \\ \mathrm{HO{\cdot}CPh{\cdot}NH}\end{array}\!\!>\mathrm{CO}$, which in presence of alkaline hydroxides undergoes a normal pinacolin rearrangement into 5 : 5-diphenylhydantoin, $\begin{array}{l}\mathrm{CPh_2{\cdot}NH} \\ \mathrm{CO{-}{-}NH}\end{array}\!\!>\mathrm{CO}$ (compare Biltz, A., 1909, i, 525).

When this hydantoin is energetically reduced with hydrogen iodide and phosphorus, 4 : 5-diphenyldihydroglyoxalone is obtained together with decomposition products, the phenyl group returning to its original place.

The decomposition products include diphenylacetic acid and diphenylmethane, indicating that in the hydantoin the two phenyl residues are attached to the same carbon atom.

On reducing 5 : 5-diphenylhydantoin by distillation with zinc dust, diphenylmethane and benzonitrile are formed, the latter being due to the rearrangement into diphenylglyoxalone which gives rise to benzonitrile when distilled with zinc dust.

Di-*p*-bromo-4 : 5-diphenylhydantoin is very resistant to hydrogen iodide and phosphorus. Only bis-*p*-bromophenylmethane could be isolated from the reaction products; the presence of di-*p*-bromodiphenylacetic acid and of di-*p*-bromodiphenyldihydroglyoxalone was made probable. E. F. A.

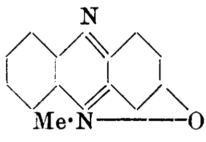
Phenazine. FRIEDRICH KEHRMANN and EM. HAVAS (*Ber.*, 1913, **46**, 341—352).—The authors have obtained good yields of phenazine by the action of *o*-aminodiphenylamine on *o*-nitrodiphenylamine in the presence of anhydrous sodium acetate, and have examined several of its derivatives.

o-Nitrodiphenylamine was obtained in 85—90% yield by heating *o*-chloronitrobenzene, aniline, and anhydrous sodium acetate during twelve to fifteen hours at 215°. Reduction of its alcoholic solution by stannous chloride and hydrochloric acid gave *o*-aminodiphenylamine. For the preparation of phenazine, *o*-nitrodiphenylamine, *o*-aminodiphenylamine, and anhydrous sodium acetate were heated at about 250°, when a violent reaction occurred. The phenazine was isolated by distillation of the crude product, or, better, by treatment with superheated steam; yield, 60—70%. In the absence of sodium acetate, only traces of phenazine could be obtained.

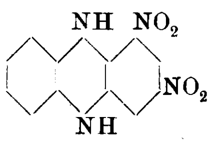
When dissolved in nitrobenzene and treated with methyl sulphate, phenazine yielded *methylphenazonium methosulphate* as greenish-yellow prisms. The corresponding *platinichloride*, $C_{26}H_{22}N_4Cl_6Pt$, and *dichromate*, $C_{26}H_{22}N_4O_7Cr_2$, were analysed, but the *chloride*, *bromide*, and *nitrate* were found to be so readily soluble in water that they could not be precipitated from a solution of the sulphate. When concentrated aqueous potassium iodide was added to an aqueous solution of methylphenazonium methosulphate, an orange-coloured solution was obtained, which, after a short time, deposited greenish-black needles. The latter dissolved readily in hot alcohol with formation of a greenish-yellow solution, which, when rapidly cooled, yielded bluish leaflets, which could be ground to a dirty-green powder.

Analyses of the crystals yielded figures agreeing with those required by the normal iodide, $C_{13}H_{11}N_2I$. The authors, however, are led to the conclusion that this substance is only contained in the yellow solution, and that the crystals probably consist of a quinhydrone salt composed of 1 mol. of methylphenazonium tri-iodide and 2 mols. of methyldihydrophenazine.

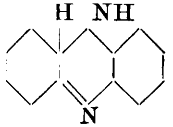
In the presence of air, sodium hydroxide transformed a solution of methylphenazonium methosulphate into phenazine mixed with small quantities of a red *substance*, probably having the annexed formula. Similarly, aqueous ammonia yielded mainly phenazine when brought into reaction with methylphenazonium salts, but, in the absence of water, salts of 3-aminomethylphenazonium were readily obtained. Of these, the following were isolated, namely, the *chloride*, *bromide*, and *nitrate*, green needles which yielded magenta-red solutions, and the *platinichloride*.



1 : 3-*Dinitrophenazine* was obtained by cautiously heating phenazine with sulphuric acid and rather more than the calculated amount of nitric acid to 130°. It crystallised in yellow needles, which had no definite m. p., but decomposed above 200°. Reduction of this substance by hydrogen sulphide in ammoniacal alcoholic solution led to the formation of dinitrodihydrophenazine (annexed formula), the constitution of which follows from its identity with the compound prepared by Kehrmann and Messinger (A., 1894, i, 55), and by Leemann and Grandmougin (A., 1908, i, 478), from *o*-phenylenediamine and picryl chloride. Attempts to reduce 1 : 3-dinitrophenazine or its dihydro-derivative to diaminophenazine were unsuccessful.



The authors have re-investigated the acetylation of dihydrophenazine (compare Hinsberg and Garfunkel, A., 1897, i, 123; Tichwinski and Wolochowitsch, A., 1905, i, 383; Hinsberg, A., 1905, i, 840). They find that pure acetic anhydride and pure dihydrophenazine yield only a monoacetyl derivative, whilst the diacetyl derivative is immediately formed if a trace of zinc chloride is added. They consider that dihydrophenazine and its diacetyl derivative possess a symmetrical structure, whilst the yellow monoacetyl derivative and dihydrophenazine sulphate are probably derived from the annexed unsymmetrical form.



A solution of dihydrophenazine diacetate in glacial acetic acid was mixed with concentrated nitric acid and warmed on the water-bath, whereby a mixture of 2-*nitrophenazine*, m. p. 214°, and *nitrodiacetyldihydrophenazine*, m. p. 166°, was obtained. The latter substance yielded 3-aminophenazine when warmed with concentrated sulphuric acid.

2-Aminophenazine (compare Fischer and Hepp, A., 1889, 500) was obtained by reduction of an alcoholic solution of nitrodiacetyldihydrophenazine by stannous chloride and hydrochloric acid, oxidation of the tin salt so obtained by ferric chloride solution, and liberation of the base by means of ammonia. H. W.

New Methods of Preparation of Asymmetric $\alpha\beta$-Naphthazine. FRITZ REITZENSTEIN and FRANZ ANDRE (*J. pr. Chem.*, 1913, [ii], **87**, 97—118).—*as*-$\alpha\beta$-Naphthazine (Fischer and Junk, A., 1893, i, 283) has been prepared (1) from β-naphthylamine by the action of sulphur monochloride or sulphuryl chloride in pyridine solution, and also by distillation over magnesium and barium peroxides; (ii) from α-naphthylamine by heating with calcium oxide, and (iii) by sublimation of aceto-β-naphthylamide over a mixture of barium peroxide and calcium oxide. It forms greenish-yellow crystals, m. p. 278—281°, according to the method of preparation, and yields a dinitro-derivative, m. p. 330—332°, which is reduced by aqueous sodium sulphide to diaminonaphthazine (compare D.R.-P. 166363). When warmed with alcohol and hydrochloric acid, it forms an unstable red *hydrochloride*.

In pyridine solution, sulphuryl chloride reacts with α-naphthylamine, yielding a red *substance*, m. p. 169°, and with aceto-β-naphthylamide to form aceto-1-chloro-β-naphthylamide.

When distilled over a mixture of barium peroxide and calcium oxide, benzidine yields a substance, m. p. 122°, probably identical with the azine, $NH_2\cdot C_6H_4\cdot C_6H_3{<}\overset{N}{\underset{N}{|}}{>}C_6H_3\cdot C_6H_4\cdot NH_2$, isolated by Kalb (*Diss.*, München, 1905) from the product obtained by oxidising benzidine. The action of sulphuryl chloride on benzidine in pyridine solution gives rise to a *substance*, m. p. 126°, which is considered to be a chloro-derivative of benzidine or of the above-mentioned azine. F. B.

Synthesis of Two Isomeric Oxytetrazoles from Azoimide and Fulminic Acid. F. CARLO PALAZZO and G. MAROGNA (*Gazzetta*, 1913, **43**, i, 69—80).—The interaction of azoimide and fulminic acid yields, not only the 1-hydroxytetrazole previously described (compare Palazzo, A., 1910, i, 342), but also an isomeride of this substance. Its formation is favoured by a low temperature. The *sodium* salt of iso-*oxytetrazole*, $CHON_4Na,3H_2O$, forms large crystals, which have been described by Rosati (this vol., i, 207). It yields other salts by double decomposition, and gives also a *benzoyl* derivative, which crystallises in needles, m. p. 94°. The sodium salt is stable towards water and alkalis, but with sulphuric acid or with fuming hydrochloric acid suffers a decomposition analogous to that of its isomeride. The iso-*oxytetrazole*, $CHON_3{:}NH$, is obtained by treating the sodium salt with cold, dilute sulphuric acid; it has m. p. 155° (softening a few degrees previously). The decomposition of this substance with sulphuric acid is similar to that of the isomeride, but hydrochloric acid acts somewhat differently. The acid and its salts explode on percussion and also when heated.

The 1-hydroxytetrazole previously described forms when treated with diazomethane an ether containing a methoxyl group; it has m. p. 93—94°. The *iso*oxytetrazole forms an *N*-ether.

The authors consider that the *iso*oxytetrazole probably has the following structure: $\begin{matrix}CH{:}NO\\ |\\ N{=\!=}N\end{matrix}{>}NH$. They regard the production of these two isomerides from fulminic acid as a further proof of the tautomeric nature of that substance. R. V. S.

Halogen Substitution Products of Azo-dyes. S. WEBER (*Monatsh.*, 1913, **34**, 243—254).—The influence of halogen substitution on the shade and usefulness of some dyes has been systematically studied.

Group A.— *o*-, *m*- and *p*-Chloro-, bromo-, and iodo-anilines, diazotised and coupled with β-naphthol-8-sulphonic acid in sodium carbonate solution, give yellow to red dyes, the *p*-compounds being darker and the *m*-compounds lighter than the *o*-members, whilst the shades deepen from chlorine to iodine.

Group B.—The same bases give redder dyes with α-naphthol-2 : 8-disulphonic acid, but the same generalisations may be made.

Group C.—Aniline, *m*- and *p*-bromoaniline do not couple so readily with 1-amino-β-naphthol-6-sulphonic acid, and the dyes are dark red tinged with blue.

Group D.—2 : 4-Dibromoaniline is less easily diazotised and coupled than the mono-derivatives, but gives deeper colours with the above sulphonates.

The dyes are faster than the unsubstituted analogues, and their colouring power is much enhanced. The ortho- and para-compounds are more valuable than the meta-, and the bromo- and iodo-derivatives are much more effective that the chloro-dyes. J. C. W.

Congo-Red. I. Experimental Part. F. I. BOGOJAVLENSKI. **II. Theoretical Part.** VLADIMIR G. SCHAPOSCHNIKOV (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1813—1844).—The action of either strong or weak acids (even carbonic acid) on Congo-red results in the replacement of the sodium by hydrogen. With strong acids the action proceeds rapidly and yields a dark blue precipitate, which when washed gives a blue colloidal solution; the latter cannot be freed from admixed impurities by washing or dialysis. This solution of Congo-blue exhibits electrical conductivity, which is, however, probably conditioned by the impurities present. The action of weak acids gives the same product, but in a crystalline condition. Very small crystals of Congo-blue are capable of forming suspensions which closely resemble the colloidal solutions; both the colloidal particles and the crystals carry negative charges, both are coagulated without change of structure by acids or acid salts, and both the colloidal solution and the filtered crystalloidal suspension show Brownian movement under the ultramicroscope, the crystals passing through the filter.

The theoretical considerations of Part II lead to the following conclusions. The change in colour of substantive bisazo-colouring matters is conditioned by change in their intramolecular structure. The red forms of amino- and hydroxybisazo-colouring matters of the Congo-red type correspond with the azoid configuration of the molecules, whilst the blue forms correspond with the quinonoid structure. The instability of these forms and their ready interconversion are regarded as due to the agency of so-called "suspensive" linkings and of mobile hydrogen. T. H. P.

Aniline-Black and Allied Compounds. III. ARTHUR G. GREEN and SALOMON WOLFF (*Ber.*, 1913, **46**, 33—49).—See P., 1912, **28**, 250.

The Density and Solution Volume of Some Proteins. (Miss) HARRIETTE CHICK and CHARLES J. MARTIN (*Biochem. J.*, 1913, **7**, 92—96).—A comparison was instituted in the case of four proteins, caseinogen, egg-albumin, serum-albumin, and serum-globulin, between the density directly determined with dry specimens and that calculated from the specific gravity of concentrated solutions. The latter is found to be 5 to 8% in excess of the former, showing the extent of shrinkage in volume taking place when these proteins enter into colloidal solution. W. D. H.

The Hydrolysis of Organic Phosphorus Compounds by Dilute Acid and Dilute Alkali. R. H. ADERS PLIMMER (*Biochem. J.*, 1913, **7**, 72—80).—Ethyl dihydrogen phosphate, glycerophosphoric acid, and phytic acid are hydrolysed by acid, but are stable to alkali. Hexose-phosphoric acid and phospho-protein behave so differently to alkali from the other three compounds mentioned, that they are probably not esters. In phospho-proteins, the phosphoric acid is probably united to one of the amino-acids. Hexose-phosphoric acid reduces Fehling's solution, which points to the presence of a functioning aldehyde or ketone group. Some suggestions as to atomic grouping are made to explain the differences in reaction referred to.
W. D. H.

Protein Compounds. WALTER H. EDDY (*Biochem. Bull.*, 1912, **2**, 111—122).—A description is given of protein salts formed by combining organic bases (strychnine, morphine, etc.) with acid reacting proteins (mucoids, nucleoproteins) and by combining the latter with basic reacting proteins, such as histone. It is pointed out that so-called histone, however, is itself probably a protein salt.
W. D. H.

Bilirubin and Hæmin. HANS FISCHER (*Zeitsch. physiol. Chem.*, 1913, **83**, 170).—Polemical. A reply to Küster (this vol., i, 210).
E. F. A.

The Action of Pepsin-Hydrochloric Acid on Proteins Partly Digested with Trypsin. VALDEMAR HENRIQUES and J. K. GJALDBÆK (*Zeitsch. physiol. Chem.*, 1913, **83**, 83—92).—Egg-white and caseinogen partly digested with trypsin behave differently when submitted to the subsequent action of pepsin-hydrochloric acid, the former being more readily changed, and the yield of formaldehyde-titratable nitrogen being greater. W. D. H.

Activity of Koji Sucrase [Invertase] in the Presence of Different Acids. GABRIEL BERTRAND, M. ROSENBLATT, and (Mme.) M. ROSENBLATT (*Compt. rend.*, 1913, **156**, 261—263. Compare A., 1912, i, 148, 327, 401).—A study of the diastatic activity of the

sucrase, known as "taka-diastase," extracted from the Japanese Koji, in the presence of various acids. This sucrase, unlike those obtained from yeast and *Aspergillus niger*, shows a maximum activity in solutions the concentration of which with respect to hydrogen ions practically corresponds with neutrality to helianthin, and is independent of the nature of the acid. W. G.

Enzymic Decomposition of Glucosides and Galactosides. HENRY BIERRY (*Compt. rend.*, 1913, **156**, 265—267. Compare A., 1909, ii, 747).—A résumé of the work already published on the enzymic hydrolysis of α- and β-glucosides and galactosides by various ferments. The author finds that the digestive juice of the *Helix* attacks both α- and β-galactosides. The lactase obtained from the intestine of a dog appears to be much more specific in its action, only attacking derivatives of galactose, and of these only the β-derivatives, from which it seems to make a restricted choice in that it hydrolyses lactose itself, but neither α- or β-methyl galactoside. W. G.

The Rate of Destruction of Ptyalin by the Direct Electric Current. W. E. BURGE (*Amer. J. Physiol.*, 1913, **31**, 328—333).—The passage of the direct electric current destroys ptyalin, but this is not due to electrolytic products. The rate of destruction is uniform, and was 2·5% per coulomb for the solutions used. W. D. H.

Resistance of Emulsin to the Action of Heat in Presence of Strong Alcohol. ÉMILE BOURQUELOT and MARC BRIDEL (*J. Pharm. Chim.*, 1913, [vii], **7**, 65—67).—In a previous paper (this vol., i, 212), it was shown that the temperature at which emulsin is rendered inactive falls as the concentration of alcohol increases to 50%, but that with stronger alcohols the temperature of inhibition rises with the concentration of the alcohol. It was suggested that this phenomenon is due to the fact that in the stronger alcohols the ferment is precipitated, and in this condition is more resistant to heat. Experiments are now described which prove this contention; thus, it was found that emulsin was scarcely weakened in action when mixed with dry alcohol, and the latter heated slowly to the boiling point and maintained at this temperature during two minutes. In sterilising plants containing enzymes, therefore, it is best to use alcohol of such a strength as to produce a liquid containing about 60% of alcohol when the plants are immersed in it, allowance being made for the water in the plants. T. A. H.

Enzyme Action. III. Action of Manganous Sulphate on Castor Bean Lipase. K. GEORGE FALK and MARSTON L. HAMLIN (*J. Amer. Chem. Soc.*, 1913, **35**, 210—219. Compare Falk and Nelson, A., 1912, i, 523, 593).—Experiments are described which show that when a preparation of castor bean lipase which has been rendered inactive by heating with water is treated with manganous sulphate it becomes slightly active again. In order to explain this behaviour, it is suggested, that although the active enzyme is hydrolysed by the action of hot water, the inactive zymogen present in the pre-

paration is not wholly destroyed, and that the manganous sulphate effects the conversion of the inactive zymogen into active enzyme by a process of oxidation. E. G.

Enzymic Decomposition of Hydrogen Peroxide. IV. PERCY WAENTIG and OTTO STECHE (*Zeitsch. physiol. Chem.*, 1913, **83**, 315—337. Compare A., 1911, i, 759; 1912, i, 228; ii, 839).—The action of several proteoclastic and other enzymes on active preparations of catalase has been studied. Trypsin alone destroys the catalase, indicating the protein nature of this substance. The experiments are not in favour of the possible destruction of a protective colloid by the trypsin, thereby destroying the catalase as well. The resistance of catalase to hydrolysis by pepsin suggests that it has a polypeptide structure, but it is possible that the experimental conditions were adverse to the action of pepsin, since the solutions could not be made more than faintly acid.

The gastric juice of the cray fish was especially active in destroying catalase—this confirms its tryptic nature. The action on catalase affords a method of detecting and possibly of measuring tryptic enzymes. Differences are noted in the resistance of blood catalase to the tryptic ferments of vertebrates and of the crayfish, and also in the behaviour of catalases of different origin to the same trypsin. E. F. A.

Neutralisation of Solutions of Diaminodihydroxyarsenobenzene Hydrochloride. J. CHARLES BONGRAND (*J. Pharm. Chim.*, 1913, [vii], **7**, 49—55).—Theoretically this drug requires 4 mols. of sodium hydroxide to neutralise it by conversion into the disodium derivative. The author shows by means of cryoscopic and electrical conductivity determinations that in dilute solutions, as used in practice, hydrolytic dissociation occurs, and that more than the theoretical amount of sodium hydroxide is then required to maintain the drug in solution, as the disodium derivative. T. A. H.

Phenylstibines. PAUL CARRÉ (*Bull. Soc. chim.*, 1913, [iv], **13**, 102—104).—Magnesium phenyl bromide reacts with antimony trichloride to form triphenylstibine together with the chlorides of phenylstibine and diphenylstibine, the first being almost the sole product when a small proportion of the magnesium compound is used, whilst with 1 or 2 mols. larger quantities of the two latter substances are simultaneously produced. Phenylstibine and diphenylstibine chlorides are decomposed by heat into antimony trichloride and triphenylstibine (compare Michaelis and Günther, A., 1911, i, 1056). T. A. H.

Mercury Dibenzyl. PAUL WOLFF (*Ber.*, 1913, **46**, 64—66).—The description of mercury dibenzyl given by Campisi, in 1865, is erroneous, and endeavours to prepare this substance by the action of sodium amalgam on benzyl chloride have been futile, producing only dibenzyl. The substance has been successfully obtained by the application of magnesium benzyl chloride [see Pope, following abstract].

Mercury dibenzyl is formed, and crystallises in long, colourless needles, m. p. 111° [Pope and Gibson give 104°], which decompose above the m. p. into mercury and dibenzyl. When heated in alcoholic solution with mercuric chloride, *mercury benzyl chloride*, leaflets, m. p. 104°, is obtained; *mercury benzyl bromide* and *mercury benzyl iodide*, prepared in an analogous manner, also form colourless leaflets, m. p. 119° and 117° respectively; *mercury benzyl cyanide*, needles, m. p. 124°, for its formation requires mercury dibenzyl and mercuric cyanide to be heated together in alcoholic solution at 130°. *Mercury benzyl acetate* is produced by the interaction of mercury dibenzyl and mercuric acetate in alcoholic solution, and also of mercury benzyl chloride and silver acetate in alcoholic solution.

Mercury dibenzyl when heated with acetic acid for two or three hours at 170° undergoes decomposition into mercury, toluene, benzyl acetate, and dibenzyl. D. F. T.

Mercury Dibenzyl. WILLIAM J. POPE (*Ber.*, 1913, **46**, 352).—Mercury dibenzyl has been obtained previously to Wolff (preceding abstract) by Pope and Gibson, using the same method (T., 1912, **101**, 735). T. S. P.

Physiological Chemistry.

The Effects of Muscular Exercise in Man. FRANK COOK and MARCUS S. PEMBREY (*J. Physiol*, 1913, **45**, 429—446).—The average composition of alveolar air in healthy men is oxygen, 14·9%, and carbon dioxide, 5·57%. The mean respiratory quotient was 0·9. Directly after muscular exercise the alveolar air contained 14·33% oxygen and 6·52% carbon dioxide; the mean respiratory quotient was 1. During muscular dyspnœa the respiratory quotient affords no definite indication of the metabolism, for the vigorous ventilation of the lungs washes out the carbon dioxide. The administration of oxygen is of value only in pathological conditions. The pulse rate in healthy men at rest varies from 45 to 90 per minute. In a trained man the pulse rate is slower during rest, has a wider range in response to muscular work, and rapidly recovers after exercise. "Second wind" is an adjustment of the respiratory and circulatory systems to the demands of the muscles for an adequate supply of blood; carbon dioxide is the chief factor in effecting the accommodation. W. D. H.

Influence of Calcium and Potassium in the Respiratory Rhythm in Frogs. DONALD R. HOOKER (*Proc. Amer. physiol. Soc.*, 1912; *Amer. J. Physiol.*, **31**, xvii—xviii).—In the absence of calcium from a perfusion fluid, the respiratory centre is excited; in the absence of potassium it is depressed. In the presence of potassium decrease in the calcium causes depression, and an increase excita-

tion. In the presence of calcium, a decrease in the potassium causes excitation, and an increase causes depression. W. D. H.

The Oxygen Capacity of Blood in Relation to the Concentration of Hæmoglobin. J. H. BURN (*J. Physiol.*, 1913, **45**, 482—488).—No alteration in the oxygen capacity of the blood was discovered when the blood is diluted. Manchot states that it is increased. W. D. H.

Determination of the Constant of the Differential Blood-Gas Apparatus and the Specific Oxygen Capacity of Blood. JOSEPH BARCROFT and J. H. BURN (*J. Physiol.*, 1913, **45**, 493—497). —This apparatus can be best calibrated by the liberation of a known quantity of oxygen from a standard solution of hydrogen peroxide by potassium permanganate. The constant obtained is then higher than by previous methods. Applying this constant, the specific oxygen capacity of hæmoglobin becomes 401·8, the theoretical figure being 400·8 c.c. of oxygen per gram of iron. W. D. H.

The Effect of Exercise on the Dissociation Curve of Blood. JOSEPH BARCROFT, R. A. PETERS, FF. ROBERTS, and J. H. RYFFEL *Proc. physiol. Soc.*, 1913; *J. Physiol.*, **45**, xlv).—The following new terms are introduced. The blood is said to be *mesectic* when the dissociation curve is normal; *pleonectic* when at any given pressure of oxygen the hæmoglobin takes up more of that gas than normal; and *meionectic* when it takes up less. The immediate effect of severe exercise is to shift the curve in the direction of greater acidity, even though the carbon dioxide tension is reduced. After rapid climbing, the curve becomes meionectic; after slow climbing, it remains mesectic. W. D. H.

The Effect of Altitude on the Dissociation Curve of Blood. JOSEPH BARCROFT, MARIO CAMIS, G. C. MATHISON, FF. ROBERTS, and J. H. RYFFEL (*Proc. physiol. Soc.*, 1913; *J. Physiol.*, **45**, xlvi).— Although altitudes up to 15,000 feet lower the carbon dioxide alveolar pressure, the blood of the resting subject remains mesectic, for other acids in the blood compensate for the carbon dioxide. Meionexy is brought on by exercise more readily than at the sea level. W. D. H.

The Effect of Carbohydrate-free Diet on the Dissociation Curve of Blood. JOSEPH BARCROFT, G. GRAHAM, and HAROLD L. HIGGINS (*Proc. physiol. Soc.*, 1913; *J. Physiol.*, **45**).—In three out of five cases the curve remained mesectic, although the carbon dioxide tension fell. In two cases it became pleonectic, and the subjects felt knocked up and faint. W. D. H.

The Effect of Moist Heat on the Dissociation Curve of Blood. JOSEPH BARCROFT, MARIO CAMIS, G. C. MATHISON, FF. ROBERTS, and J. H. RYFFEL (*Proc. physiol. Soc.*, 1913; *J. Physiol.*, **45**, xlvii—xlviii).—With the wet bulb at 24·5° the carbonic acid

tension fell (as it often does in factories under similar conditions), and the blood became pleonectic. In all these conditions the subject feels well if his blood is mesectic; but variations in either direction produce symptoms of ill-health. W. D. H.

Sugar Loosely Combined in the Blood. RAPHAEL LÉPINE and RAYMOND BOULUD (*Compt. rend.*, 1913, **156**, 110—112. Compare A., 1904, ii, 56; 1907, ii, 562).—The authors have estimated not only the free sugar in the blood of dogs, but also the sugar liberated, after destroying the glycolytic ferment by heating the blood mixed with water at 58° for fifteen minutes, by the addition of emulsin and invertase and keeping the mixture at 39° for forty-five minutes. There is but little or no difference in the amounts of sugar liberated from arterial and venous blood, and but little and in some cases no sugar is liberated from the blood of normal dogs bled for the first time. The amount becomes considerable (up to 50% increase of total sugar) after the physiological equilibrium of the dog has been subjected to marked disturbance by such means as (*a*) severe hæmorrhage, (*b*) intravenous injection of amylase or pancreatin or extracts of liver or pancreas, (*c*) subcutaneous injection of phloridzin. In some cases, also, the intravenous injection of 2 grams of dextrose per kilo. of body-weight was followed by a rise in the amount of sugar liberated by the above method. W. G.

The Behaviour of Blood-Sugar in Normal and Pathological Cases. IV. The Blood-Sugar in Febrile and Dyspnœic Conditions of Man. FR. ROLLY and FR. OPPERMANN (*Biochem. Zeitsch.*, 1913, **48**, 259—267. Compare this vol., ii, 159).—In febrile conditions in man, there is an increase of blood-sugar which at times is quite considerable. There is, however, no parallelism between the increased amount and the rise in the height of the temperature. The hyperglycæmia is caused partly by the hyperthermia and bacterial toxins. In cases of dyspnœa, without high temperatures, where the carbon dioxide content of the blood is increased, hyperglycæmia also occurs. There are, therefore, in certain cases, two distinct causes for increased sugar in the blood, namely, febrile conditions and dyspnœa. Toxic substances, of varied origin, such as tolylenediamine, can also give rise to hyperglycæmia. S. B. S.

The Behaviour of Blood-Sugar in Normal and Pathological Cases. V. The Blood-Sugar in Nephritis, Arteriosclerosis, and Diseases of the Nerves. FR. ROLLY and FR. OPPERMANN (*Biochem. Zeitsch.*, 1913, **48**, 268—277).—Inflammation of the kidneys by itself does not give rise to hyperglycæmia. When such occurs in conjunction with inflammation of the kidneys, it is caused by other factors, which are concomitant pathological conditions, such as arteriosclerosis, dyspnœa, uræmic coma, or bacterial and other toxins. There is no parallelism between the hyperglycæmia and the degree of hypertension. In cases of diseases of the nerves the behaviour of the blood-sugar showed great variations, which depend largely on the seat and character of the affection. S. B. S.

Fibrinsæmia. J. O. WAKELIN BARRATT (*J. Path. Bact.*, 1913, **17**, 301—322).—If thrombin or thrombokinase is injected into the blood-stream of rabbits, separation of fibrin occurs in the circulating blood; the rate of intravascular clotting varies, and is specially readily produced in the right side of the heart; the circulation is by this means mechanically interfered with. W. D. H.

The Sodium and Carbonate Ions in the Serum, and the Question of the "Non-diffusible" Alkali. PETER RONA and PAUL GYÖRGY (*Biochem. Zeitsch.*, 1913, **48**, 278—290).—The method of compensation dialysis was employed in these experiments, the serum being placed in a dialysing membrane, and surrounded by water containing various amounts of salts, the mixtures being kept at the same hydrogen ion concentration as the serum by means of phosphate mixtures. By analysis, after a definite time the amount of salt in equilibrium with that in the serum was ascertained. It was found that the amount of sodium in equilibrium with that of the serum was 0·3260%, whereas the amount in serum determined directly was 0·3057%. There was therefore practically no non-diffusible sodium. The amount of potassium and sodium in equilibrium was found by dialysis to be 0·9214%, whereas the amounts in serum were 0·8532%. In taking into account these two numbers, the volume occupied by the serum proteins must also be considered. The amount of diffusible carbon dioxide was 0·1270%, and that estimated directly in the serum was 0·1270% in one experiment, and similar numbers were obtained from other series. The greater part of the carbon dioxide is therefore diffusible, although a small part is apparently combined as a carbamido-derivative of the proteins. S. B. S.

Rate of Regeneration of Anti-substances [Specially Hæmolysin) and Other Constituents of the Blood after Hæmorrhage. R. A. O'BRIEN (*J. Path. Bact.*, 1913, **17**, 425).—The experiments were made on horses. After bleeding, the constituents of the blood are replaced at differing rates; the volume returns to the normal within forty-eight hours; the proteins commence to be reproduced within twenty-four hours, and the red corpuscles and hæmoglobin within two days. The alterations in leucocytes are irregular, and cannot be correlated with any other factor. The production of anti-substances is as rapid as that of the blood-volume, and suggests that the tissues have a long, persistent habit of forming them in the absence of specific antigens. W. D. H.

Can Lipoids Act as Antigens? JAMES RITCHIE and J. MILLER (*J. Path. Bact.*, 1913, **17**, 429—431).—No evidence was found that lipoids can act in this way. W. D. H.

Hydrolysis of Glycogen by Diastatic Enzymes. Comparison of Glycogen from Various Sources. ROLAND VICTOR NORRIS (*Biochem. J.*, 1913, **7**, 26—42).—On hydrolysis with extract of pig's pancreas, the glycogen is rapidly converted into dextrins and

maltose; the further cleavage of the dextrins is slow and incomplete. The optimum temperature for glycogen hydrolysis is 37°, for starch 40°. When excess of glycogen is present the action is a linear one. The concentration of glycogen has little influence on the initial rate of hydrolysis unless very low concentrations are employed. The action is hindered slightly by the products of hydrolysis; it is favoured by traces of acid. Samples of glycogen from different sources are hydrolysed at different rates at the optimum hydrogen ion concentration; thus, taking dog glycogen as 100, the relative rates of hydrolysis are: rabbit glycogen, 94; oyster, 88; and yeast, 84. The degree of opalescence and the coloration with iodine also vary. The difference may be due to differences in constitution, or to variations in colloidal state. If the glycogens are distinct, the enzymes which affect them should be specific; this is to be tested. W. D. H.

The Secretion of Pancreatic Juice. IWAWO MATSUO (*J. Physiol.*, 1913, **45**, 447—458).—In the preparation of secretin from the intestinal mucous membrane, boiling with 0·6% sodium chloride is as effective as 0·4% hydrochloric acid; organic acids give a smaller yield. Injection of salt solution into the duodenum does not, however, cause a flow of pancreatic juice as the injection of acid does. Secretin was not obtained from any other organ. If two dogs are in vascular connexion, injection of acid into the duodenum of one evokes a pancreatic flow from the other. After the introduction of hydrochloric acid into the duodenum, the duodenal contents contain secretin. Secretin, however, is not absorbed from the intestinal contents, nor does it produce its effects when given under the skin. The view that secretin and "vaso-dilatin" are identical is negatived. W. D. H.

The Rôle of the Pituitary in Carbohydrate Metabolism. LEWIS H. WEED, HARVEY CUSHING, and CONRAD JACOBSON (*Proc. Amer. Physiol. Soc.*, 1912; *Amer. J. Physiol.*, **31**, xiii—xiv).—The posterior lobe of the pituitary plays an important part in carbohydrate metabolism, and its action is controlled by fibres in the cervical sympathetic nerve. Stimulation of this nerve, or of the "sugar centre" in the bulb, or of the pituitary body itself, liberates a hormone which causes glycogenolysis and glycosuria, independently of any possible nervous impulse reaching the muscles or abdominal viscera. W. D. H.

Carbohydrate Metabolism in Ducks. G. B. FLEMING (*Proc. physiol. Soc.*, 1913; *J. Physiol.*, **45**, xliii—xliv).—Partial removal of the pancreas in ducks raises the amount of sugar in the blood, but does not produce glycosuria. Complete extirpation of the organ has a more pronounced effect on the blood, and sometimes leads to glycosuria. Subcutaneous injection of adrenaline after partial extirpation lowers the percentage of sugar in the blood, and in half the experiments produced glycosuria. The respiratory quotient after fasting averaged 0·72; after feeding on maize, 0·93; after

adrenaline, 0·88. This suggests that the effect of adrenaline is to mobilise carbohydrates; its effect passes off rapidly. W. D. H.

Nitrogen Retention on Feeding with Urea. EMIL ABDERHALDEN and ARNO ED. LAMPÉ (*Zeitsch. physiol. Chem.*, 1913, **83**, 338—346).—Polemical. A reply to Grafe and Turban (this vol., i, 216). E. F. A.

Protein Metabolism from the Point of View of Blood and Tissue Analyses. VI. Uric Acid, Urea, and Total Non-protein Nitrogen in Blood. OTTO FOLIN and W. DENIS (*J. Biol. Chem.*, 1913, **14**, 29—43).—By the authors' new methods it is possible to measure various degrees of nitrogen retention and urea accumulation due to kidney insufficiency with considerable accuracy. Numerous analyses of the uric acid, urea, and total non-protein nitrogen in the blood are presented both in health and disease. The figures show that there is no relationship between the amount of uric acid and that of urea and non-protein nitrogen. Uric acid may accumulate in the blood, even although urea and other nitrogenous waste products are eliminated quite as well as by normal kidneys; the damage to the kidney in gout may thus affect only its power to eliminate uric acid. Apparently very slight kidney damage may affect its power to excrete uric acid. W. D. H.

The Metabolism of Organic Phosphorus Compounds; Their Hydrolysis by the Action of Enzymes. R. H. ADERS PLIMMER (*Biochem. J.*, 1913, **7**, 43—71).—The action of enzymes is summarised in the following table:

	Pancreas.	Liver.	Intestine.	Castor oil seeds.	Yeast (zymin).	Bran.
Glycero-phosphoric acid	0	0	+	+	+	+
Hexose-phosphoric ,, ...	0		+	+	+	+
Ethyl dihydrogen phosphate .	0		+	+	+	+
Diethyl hydrogen ,,			0	0		
Phytic acid	0	0	0	+	0	+
Nucleic acid (thymus)	0		+		+ ?	+
,, (wheat)			+ ?			
,, (meat)	0		+			
Hydroxymethylphosphinic acid	0		0	0	+ ?	0
Phosphoprotein	+		+		0	0

The most active tissue is the intestinal mucosa. Phytic acid is attacked readily by bran extract only. Phosphoprotein is the only compound hydrolysed by the pancreas. The other compounds in the list are esters; it is evident that the enzyme which attacks them is not lipase. The question whether the phosphatases are single or specific is discussed, and it is suggested that there are mono- and di-phosphatases. Phytase is specific, and if phytin is decomposed in the intestine, this is due to phytase swallowed with the food. It then enters the body as inositol and phosphoric acid. The work of Fingerling and Gregersen is confirmed, that the animal body can and does synthesise its organic phosphorus compounds from inorganic phosphates. W. D. H.

The Rate of Protein Katabolism. E. PROVAN CATHCART and HENRY HAMILTON GREEN (*Biochem. J.*, 1913, **7**, 1—17).—The rise in the output of nitrogen and sulphur after a protein meal is due to katabolism of the actual material ingested, and not to the displacement of "effete" protoplasm from the tissues. This conclusion is based on the ratio of the sulphur and nitrogen in the urine; after ingesting egg albumin the S : N ratio is 1 : 8, which is nearly the same as that in egg-albumin. The ratio in starvation when all the urinary constituents must arise from the tissues is 1 : 15. The sulphur is more rapidly excreted than the nitrogen; this confirms the view of previous investigators that the sulphur-containing moiety of the protein is the more rapidly katabolised. When protein is superimposed on a low protein diet, a retention of part of the nitrogen takes place. The retained material is apparently stored in the tissues (? muscles) as a pabulum of uniform composition. There was no effect on the output of creatinine.

W. D. H.

The Metabolism of Lactating Women. EDWARD MELLANBY (*Proc. Roy. Soc.*, 1913, *B*, **86**, 88—109).—The post-partum excretion of creatine does not depend on the involution of the uterus. After Cæsarian section, involving amputation of the uterus, it may become more marked than in cases in which the uterus is left intact. Rabbits do not excrete creatine at this period; the explanation of this is not obvious. Eating the placenta will not explain the difference, for cows after eating the placenta, excrete large quantities of creatine. The creatine excretion has some relation to the activity of the mammary gland. The rise in the creatine : creatinine ratio in the first few days after delivery corresponds with the increased activity of the milk glands and the development of milk from colostrum. The increase of weight in healthy breast-fed children is roughly proportional to the amount of creatine in the mother's urine. If the activity of the breasts is delayed after childbirth, so also is the excretion of creatine, and later both develop at the same time. Milk suppression from disease is accompanied by a suppression also of creatine excretion. Feeding with caseinogen does not affect the excretion of creatine in parturient women. The post-partum excretion of creatine is dissimilar from that accompanying acidosis and lack of carbohydrates. Lactose and dextrose added to the diet do not affect it. W. D. H.

Nutrition of the Embryonic Chick. I. The Absorption of Egg-white. HUBERT W. BYWATERS (*Proc. physiol. Soc.*, 1913; *J. physiol.*, **45**, xl—xli).—During incubation, the proteins of the white are not absorbed as quickly as the water, and the ratio of coagulable to uncoagulable protein remains constant; the free sugar is rapidly absorbed; there is no cleavage of carbohydrate from the protein. W. D. H.

The Importance of Phosphorus in the Nutrition of Growing Dogs. ERNST DURLACH (*Arch. expt. Path. Pharm.*, 1913, **71**, 210—250).—Young dogs fed on a diet poor in phosphorus stop

growing, waste, and die. This, however, is not wholly attributable to lack of phosphorus. The absence of other unknown constituents of a diet, possibly of lipoid nature, seems to be a factor, as in Stepp's experiments. Inorganic phosphates appear to be as advantageous for nutrition as phosphatides. W. D. H.

Nutritive Value of the Maize Proteins. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL (*Proc. Amer. physiol. Soc.*, 1912; *Amer. J. Physiol.*, **31**, xvi—xvii).—Zein alone produces speedy decline in the growth of rats; it can be made adequate for maintenance by adding tryptophan, or by the addition of another protein. Gliadin suffices for maintenance, but not for growth. Glutelin is adequate for both. W. D. H.

The Influence of Diets upon Growth. F. GOWLAND HOPKINS and ALLEN NEVILLE (*Biochem. J.*, 1913, **7**, 97—99).—A criticism of the work of Osborne and Mendel on the nutrition of young animals on purified proteins (A, 1912, ii, 271). If these workers are correct, the accessory factors in diet (so-called vitamines) are not indispensable. The present experiments do not support this view. On the Osborne-Mendel diet the animals did not grow; but an addition to it daily of 2 c.c. of milk produced growth. W. D. H.

Fasting. PAUL E. HOWE (*Biochem. Bull.*, 1912, **2**, 90—100).—A general discussion of the subject based on the author's work, with special reference to fasting as a therapeutic agent. Long fasts are devoid of benefit, and may be dangerous. Short fasts may be beneficial in certain cases. W. D. H.

A New Method of Drying Tissues and Glands. JACOB ROSENBLOOM (*J. Biol. Chem.*, 1913, **14**, 27—28).—Instead of using anhydrous salts, the employment of calcium carbide is recommended [compare Masson, T., 1910, **97**, 857]. W. D. H.

A New Type of Artificial Cell. E. NEWTON HARVEY (*Biochem. Bull.*, 1912, **2**, 50—52).—The manner of making cells of about the size of those in the body is described; they contain an aqueous solution of lecithin enclosed in a fine protein membrane, and are suitable for permeability and other biochemical studies. W. D. H.

Pigment of the Corpus luteum. HEINRICH H. ESCHER (*Zeitsch. physiol. Chem.*, 1913, **83**, 198—211).—Willstätter and Escher (A., 1912, i, 125) have shown that lutein, the yellow pigment of egg yolk, belongs to the xanthophyll group of pigments soluble in alcohol. It is now proved that the yellow pigment of the *Corpus luteum* belongs to the carrotene group, $C_{40}H_{56}$, soluble in light petroleum. The process of purification adopted in obtaining 0·45 gram of pigment from 146 kilos. (about 10,000 ovaries) is described. The carrotene is indistinguishable from that obtained from carrots or from green leaves. The yellow pigment of fat is considered to belong to the same class of pigments. E. F. A.

The Lipoids of the White and Grey Matter of the Human Brain at Different Ages. J. LORRAIN SMITH and W. MAIR (*J. Path. Bact.*, 1913, **17**, 418—420).—Five brains were analysed by the methods previously described. The results are given in tables. In the adult the percentage of total lipoids is twice as great in the white as in the grey matter, but the cerebroside is higher, and the phosphatide much lower, than in the grey matter. At birth, there is a low percentage of phosphatides, and more of other lipoids, and the composition is nearly the same throughout the brain. By the age of two, the condition in the adult is nearly, but not quite, reached. W. D. H.

Chemical Changes in Nerve During the Passage of a Nerve Impulse. SHIRO TASHIRO (*Proc. Amer. Physiol. Soc.*, 1912; *Amer. J. Physiol.*, **31**, xxii—xxiii).—The author states that he has constructed an apparatus by which he is able to detect and estimate carbon dioxide in amounts as small as 0·0000001 gram. Resting nerve gives off this gas, and the amount is increased when the nerve is stimulated. W. D. H.

The Utilisation of Sugars by the Normal Heart. HUGH MACLEAN and (Miss) IDA SMEDLEY (*J. Physiol.*, 1913, **45**, 462—469). —Locke's method for the isolated heart was employed. The utilisation of sugar by the heart is not confined to dextrose; mannose is also used, and so is lævulose, especially in the dog's heart. Maltose, lactose, and sucrose are not utilised, and galactose very slightly. In the cat, sugar does not disappear from the circulating fluids until about three hours after perfusion commences; it is assumed that the reserves in the heart are utilised first. It was found difficult to secure asepsis during the experiments. W. D. H.

The Behaviour of the Diabetic Heart towards Sugar. HUGH MACLEAN and (Miss) IDA SMEDLEY (*J. Physiol.*, 1913, **45**, 470—472). —The normal power to consume sugar is absent or nearly so in the heart of the depancreatised dogs; the power can be sometimes restored by the addition of pancreatic extract. These experiments confirm those of Knowlton and Starling. W. D. H.

The Storage and Release of Glycogen. KUNIOMI ISHIMORI (*Biochem. Zeitsch.*, 1913, **48**, 332—346).—The methods of experiment were both chemical (estimation of glycogen) and histological (with use of Best's carmine method). Rabbits were employed. It was found that the course of disappearance of glycogen produced by starvation was different from that produced by *piqûre*. In the former case, it disappears from the periphery of the lobe, towards the centre, and glycogen as such could not be detected outside the liver cells. In the latter case, all the liver cells are affected alike, and glycogen could be detected in the lymph spaces and circulation. Intravenous infusion of dextrose and lævulose caused an increase in the glycogen content of the liver. This was not the case with lactose, galactose, and sucrose. S. B. S.

The Character of the Fat Formation in Organs after Phosphorus Poisoning. HANS LEO (*Biochem. Zeitsch.*, 1913, **48**, 297—301).—The author recapitulates the evidence in favour of the new formation of fat in the liver of animals poisoned with phosphorus, which probably exists in this organ in addition to the transported fat. S. B. S.

Fat Formation under the Influence of Phosphorus. HANS LEO and W. TRASCHENNIKOV (*Biochem. Zeitsch.*, 1913, **48**, 302—312). —The majority of the experiments were carried out with the livers of rabbits, part of which were incubated under precautions for strict asepsis in Ringer's fluid alone as a control, and part under the same conditions with the addition of phosphorus. After incubation, the amount of ether-soluble substances, or higher fatty acids, were estimated. In eight experiments the addition of phosphorus caused an increase in fatty substances. In three experiments the results were of a negative character. S. B. S.

Fat Formation in the Surviving Liver. HANS LEO and C. BACHEM (*Biochem. Zeitsch.*, 1913, **48**, 313—327).—The effect produced on the fat content of livers by perfusing both foodstuffs and toxic substances through the surviving organs was investigated. Livers both of cold-blooded and warm-blooded animals were used. and the Langendorff apparatus was employed. In five experiments with foodstuffs (sugar or nutrose in Ringer's fluid), the results indicated fat formation, whereas in four experiments the results were negative. All the experiments with livers of warm-blooded animals yielded a positive result. The addition of alcohol and potassium arsenite showed no fat formation. In four experiments with diphtheria toxin, one gave a negative, one a doubtful result, and two others indicated fat formation in the liver. Out of fourteen experiments with phosphorus water, ten gave negative, and four positive results. The general result indicates that there is no new fat formation in the liver as the result of the action of phosphorus, although two of the experiments with livers of warm-blooded animals indicated an increase in fats. It is suggested that in the case of cold-blooded animals, the rate of fat formation is too slow for it to be possible to obtain an increase in the amount of fat under the conditions of experiment employed. S. B. S.

The Delayed Heat-Production of Muscles Stimulated in Oxygen. ARCHIBALD V. HILL (*Proc. physiol. Soc.*, 1912; *J. Physiol.*, **45**, xxxv—xxxvii).—By improved methods the author's previous conclusion is confirmed that heat-liberation occurs largely (probably 40%) after muscular contraction; oxygen is mainly of use in repair. The action of oxygen is rapid. W. D. H.

The Physico-chemical Basis of Striated Muscle Contraction. II. Surface Tension. WILLIAM N. BERG (*Biochem. Bull.*, 1912, **2**, 101—110. Compare this vol., i, 132).—Bernstein's calculations

of the surface energy changes in contracting muscles are criticised. The energy expended is far greater than any changes in surface tension can furnish. The use of mathematics in biology is regretted, if the treatment, as it so generally does, lacks definiteness; formulæ are often stated with no information as to their use or application to the problem under discussion. W. D. H.

Osmotic and Colloidal Imbibition by Muscle. REINHARD BEUTNER (*Biochem. Zeitsch.*, 1913, **48**, 217—224).—The experiments were carried out with the gastrocnemius muscle of frogs, and the changes after various treatments are measured by estimating the gain or loss of weight of the muscles. It was found that the addition of proteins to salt solutions in which the muscles are immersed has no appreciable effect on the water exchange between the tissues and the surrounding fluid. If the stimulability of muscle is destroyed by treatment with acid, its ordinary osmotic functions can still be detected, even for a long period after the loss of stimulability. If, on the other hand, the stimulability is destroyed by heat coagulation, the osmotic properties are lost. S. B. S.

The Chemical Pathology of Muscle. The Influence of Disuse Atrophy in the Partition of Nitrogen and Phosphorus in the Muscle. GEORGE GRUND (*Arch. expt. Path. Pharm.*, 1913, **71**, 129—141).—Full analytical details of paralysed in comparison with healthy muscle are given. The most important result appears to be an increase of phosphorus in protein union in the paralysed muscles. W. D. H.

The Creatine Content of Normal Muscle and its Relation to Urinary Creatinine. VICTOR C. MYERS and MORRIS S. FINE (*J. Biol. Chem.*, 1913, **14**, 9—26).—The creatine content in muscle is constant in a given animal, but differs in different animals; the percentages are 0·52 for the rabbit, 0·45 for the cat, 0·37 for the dog, and 0·39 for man. The creatinine elimination bears a distinct relation to the muscular creatine content. W. D. H.

Occurrence of Alizarin in the Shell of the Crab. FRIEDRICH KORNFELD (*Chem. Zeit.*, 1913, **37**, 71).—A reply to Grandmougin (this vol., i, 132) describing further experiments which support the view expressed previously (*Chem. Zeit.*, 1912, **36**, 59) that crab-shells contain alizarin. T. A. H.

Normal Presence of Bromine in Human Organs. A. LABAT (*Compt. rend.*, 1913, **156**, 255—258. Compare Pribram, 1907, ii, 111).—The various organs of human beings, who had not taken bromine medicinally for several years, were pulped, dried, and incinerated with calcined magnesia, and the ash examined for bromine by the method of Denigès and Chelle (this vol., ii, 72). Bromine could not be detected in the kidney, spleen, liver, heart, or blood serum or coagulum of the four subjects examined, but in

all cases was found in the brain, thyroid gland, and urine. The amount of bromine present in the thyroid gland is considerably less than the iodine. W. G.

The Presence and Distribution of Manganese in Animal Organs. GABRIEL BERTRAND and FLORENTIN MEDIGRECEANU (*Ann. Inst. Pasteur*, 1913, **27**, 1—11).—Manganese has been found in all the animal products examined with the exception of the white of egg. The variations in amount are only small in a given organ of a given species. There is, as a rule, very little difference in the content of manganese in organs of animals of different species belonging to the same class (birds, fishes, mammals). Amongst functional organs the highest amount of manganese has been found in the uterus of birds (0·786—2·201 mg. per 100 grams). Next in order are the liver, then the kidneys. The organs of birds are richer than those of mammals. Smallest amounts are found in muscular tissue, nervous tissue, and (least of all) the lungs, which only contain 0·006 to 0·023 mg. per 100 grams. The grey nervous matter contains more than the white, and heart muscle more than the muscles of the limbs. The mucous membranes contain more than the underlying muscular tissue. Feathers and nails contain relatively large quantities of manganese (0·111 to 3·214 mg. per 100 grams), whereas the teeth contain little. Milk contains very little manganese, and in the egg the whole of the metal is in the yolk. The general results indicate that manganese plays some physiological rôle as a catalyst. S. B. S.

The Origin of Oxalic Acid in the Animal and Human Organism. LESLAW WEGRZYNOWSKI (*Zeitsch. physiol. Chem.*, 1913, **83**, 112—142).—Proteins have no influence on the formation of oxalic acid in the body, neither have carbohydrates and fats (also glycerol). The ordinary articles of diet have no influence, direct or indirect, on oxalic acid formation. The organism evidently has a very limited capacity to form this acid at all. W. D. H.

Histones and Nucleohistones. Their Detection in the Fluids of the Organism. GEORGES PATEIN (*J. Pharm. Chim.*, 1913, [vii], **7**, 55—60).—A description is first given of the characters of histones and nucleohistones, and by the application of Goubau's method it is shown that these substances do not occur in the blood serum of man or the horse, or in ascitic fluid containing chyle. The conclusion is drawn therefore that histones and nucleohistones, which have only been found in such organs as the thymus and the spleen, are fixed there, and cannot be carried away by the body fluids.

Acetoglobulin tested in the course of these experiments was found to contain only traces of phosphorus, and sometimes none. T. A. H.

Relation of Pulse Pressure to Renal Secretion. ROBERT A. GESELL (*Proc. Amer. physiol. Soc.*, 1912; *Amer. J. Physiol*, **31**, xxviii—xxix).—In dogs alterations of the arterial pressure, espe-

cially if suddenly produced, cause diminution in the secretion of urine, and if albuminuria is present, this is increased. W. D. H.

Excretion of Nitrogen after Ligaturing the Renal Arteries. J. D. PILCHER (*Proc. Amer. physiol. Soc.*, 1912; *Amer. J. Physiol.*, **31**, xii—xiii).—Tying one branch of each renal artery has no effect; but if three-fourths of the arterial supply is cut off, anorexia and loss of weight occur, and the nitrogen output is greater than the intake. The urine secreted contains neither protein nor casts. W. D. H.

Beri-Beri. The Action of Certain Purine and Pyrimidine Derivatives. CASIMIR FUNK (*J. Physiol.*, 1913, **45**, 489—492).—Certain purine and pyrimidine derivatives have marked beneficial effect on pigeons suffering from polyneuritis; no relation, however, between the action and chemical structure can be discovered. Experiments with allantoin suggest that pigeons are not able to convert uric acid into allantoin. W. D. H.

Colloidal Nitrogen in the Urine of a Dog with a Breast Tumour. MAX KAHN and JACOB ROSENBLOOM (*Biochem. Bull.*, 1912, **2**, 87—89).—Töpfer states that the urine of cancer patients is rich in "extractive substance," which includes "colloidal nitrogen." The colloidal nitrogen was more abundant in a dog with a tumour in the breast than in normal dogs. The nature of the tumour was doubtful. W. D. H.

The Comparative Mineralisation of Cancareous and Relatively Healthy Portions of the Liver. ALBERT ROBIN (*Compt. rend.*, 1913, **156**, 334—336).—Cancareous portions of liver are richer in total inorganic matter than healthy parts, and whilst some of the inorganic constituents, namely phosphorus, sodium, potassium, magnesium, and silicon, are in excess, others, namely, calcium and iron, are deficient. A similar deficiency in calcium and iron is found in tuberculous lungs, potassium again being in excess. Whilst in the cancareous liver relatively more sodium than potassium is fixed, the reverse is true in the case of a tuberculous lung. From the experimental results, it seems probable that silicon, phosphorus, sodium, potassium, and magnesium are agents of neoplastic cell construction, not specifically for cancer, whilst iron and calcium are rather agents of organic defence. W. G.

Hæmatogenous Jaundice. GEORGE H. WHIPPLE (*Proc. Amer. physiol. Soc.*, 1912; *Amer. J. Physiol.*, **31**, xi—xii).—If hæmoglobin is given intravenously to a normal dog, it appears in the urine, and one or two hours later bile pigment occurs there also. The same occurs after an Eck fistula, and also when the hepatic artery is tied in addition. This is taken to prove that bile pigments can be formed in the blood, probably by the agency of the endothelial cells. W. D. H.

The Swelling of Connective Tissues. EDWIN HAUBERRISSER and FRITZ SCHÖNFELD (*Arch. expt. Path. Pharm.*, 1913, **71**, 102—128).—Martin Fischer's theory of œdema renders necessary an investigation of the part played by different ions (for example, in Ringer's solution) in causing swelling. A large number of observations on this line are recorded, and the principal conclusion is stated to be that sodium ions do not act differently from the others. The experiments were in the main performed on the ligamentum nuchæ. W. D. H.

Antagonism between Salts and Anæsthetics. III. Parallel Decrease in the Stimulating, Permeability-increasing, and Toxic Actions of Salt Solutions in the Presence of Anæsthetics. RALPH S. LILLIE (*Amer. J. Physiol.*, 1913, **31**, 255—287. Compare A., 1912, ii, 280, 468).—Pure isotonic sodium chloride solutions produce in *Arenicola* larvæ stimulation of the muscles, arrest of ciliary action, and a general toxic action. These results are lessened or prevented by anæsthetics; the stimulating action and permeability increase undergo a parallel diminution. The essential effect of anæsthetics is an alteration in the plasma membranes of the cells affected. The degree of resistance of these membranes is intimately dependent on the state of their lipoid constituents.

W. D. H.

Behaviour of Mercury in the Human and Animal Organism on the Usual Therapeutic Methods of Application. New Method for the Estimation of Mercury in Urine and in the Tissues. HANS BUCHTALA (*Zeitsch. physiol. Chem.*, 1913, **83**, 249—303).—Contains a critical summary of the methods of estimating mercury in urine with a full bibliography. A method is described of destroying the urine by evaporating with potassium chlorate and hydrochloric acid and so converting the mercury into chloride. The solution is filtered and electrolysed in a special apparatus between a cathode of gold foil and a gas carbon anode. The mercury is deposited on the gold, which is rinsed, dried and weighed, and heated to volatilise the mercury, the weight of which is determined by difference.

The skin is equally able to take up volatile and non-volatile mercury ointments; the ointment base has an accelerating influence on the resorption. The separation of mercury in the urine has been studied after internal administration, and also after intramuscular and intravenal injection of mercury salts. In the latter case the separation is materially faster. The addition of potassium iodide to the mercury salt is shown to diminish the excretion of the mercury. E. F. A.

The Influence of Alcohol on Reflex Action in the Frog. IDA H. HYDE, RUTH SPRAY, and IRENE HOWAT (*Amer. J. Physiol.*, 1913, **31**, 309—317).—The reflexes investigated were from certain skin areas. If the dose of alcohol used is sufficient to produce any effect at all, it is always a depressed or slowed response, never the opposite. W. D. H.

Glyconeogenesis. II. The Formation of Dextrose from Valeric and Heptoic Acids. A. I. RINGER and L. JONAS (*J. Biol. Chem.*, 1913, **14**, 43—52).—In phloridzinised dogs, the administration of formic acid leads to no increase in the output of dextrose; butyric and hexoic acids increase the excretion of acetoacetic and β-hydroxybutyric acids, but not that of sugar. Valeric and heptoic acids give rise to dextrose, probably because propionic acid is an intermediate substance in their katabolism, after undergoing β-oxidation. Fatty acids with an uneven number of carbon atoms can therefore give rise to dextrose. W. D. H.

The Fate of Indole-ethylamine [3-β-Aminoethylindole] in the Organism. ARTHUR J. EWINS and PATRICK P. LAIDLAW (*Biochem. J.*, 1913, **7**, 18—25).—If 3-β-aminoethylindole (Ewins, T., 1911, **99**, 270) is perfused through the surviving liver of rabbits and cats, it is converted into indoleacetic acid. If it is given by the mouth to dogs, 30% of it is excreted as *indole-3-acetylglycine*, $\begin{array}{l}C_6H_4\text{---}\\ |\\ NH\cdot CH\end{array}\!\!>\!C\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$ (*picrate*, m. p. 145°) (for which the authors suggest the name *indoleaceturic acid*), which is formed from indoleacetic acid by combination with glycine. Neither 3-β-aminoethylindole nor indoleacetic acid affects the output of kynurenic acid. W. D. H.

Influence of Intraperitonal Injection of Adrenaline on the Partition of Urinary Nitrogen in a Dog. JACOB ROSENBLOOM and WILLIAM WEINBERGER (*Biochem. Bull.*, 1912, **2**, 123—127).—The nitrogen partition was not affected. W. D. H.

Action of Drugs on the Lungs. DENNIS E. JACKSON (*Proc. Amer. physiol. Soc.*, 1912; *Amer. J. Physiol.*, **31**, xxvi—xxvii).—Pilocarpine causes bronchial constriction, which is relieved by adrenaline. The nerve endings are sensitive to the latter drug after atropine. Agaricine slightly depresses the constrictor nerve-endings. In small doses the pilocarpine effect is followed by dilatation, but the second effect does not occur if the suprarenals are tied off. Tyramine also causes dilatation, but this is a secondary adrenaline effect also. Choline hydrochloride acts like adrenaline, so also do trimethylamine hydrochloride and 3:4-dihydroxyphenylethylmethylamine in less degree. W. D. H.

The Pharmacological Susceptibility of the Peripheral Vascular Tonus of the Frog. HANS HANDOVSKY and ERNST P. PICK (*Arch. expt. Path. Pharm.*, 1913, **71**, 89—101).—The Läwen Trendelenburg preparation of the frog was used. Vaso-constrictors fall under three types: (1) adrenaline, which affects post-ganglionic nerve fibres; (2) nicotine, which affects pre-ganglionic and ganglionic structures; and (3) barium, which affects the muscular fibres. The dilators, tyramine, histamine, and Witte's peptone, all

act in the same way. They dilate the vessels after adrenaline is used; tyramine hinders nicotine action. Choline acts as a dilator. W. D. H.

Nicotine and Calcium Salts. W. BURRIDGE (*Proc. physiol. Soc.*, 1912; *J. Physiol.* **45**, xxxvii—xxxix).—Isotonic solutions of sodium oxalate, sulphate, fluoride, pyrophosphate, and citrate produce a slow tonic contraction of the frog's sartorius muscle. This is attributed to the removal of calcium. Nicotine produces, in addition, twitchings, which are largely abolished by curare. W. D. H.

The Effect of Strychnine on Frogs without Heart and Lymph Hearts. SAMUEL J. MELTZER (*Proc. Amer. physiol. Soc.*, 1912; *Amer. J. Physiol.*, **31**, xix—xx).—Abel considers that the effect of drugs in a frog without a heart is brought about by the continued activity of the lymph hearts. This is not so for strychnine. Strychnine convulsions set in after thirty to fifty minutes when the lymph hearts are all destroyed. W. D. H.

Muscle Physiology. Action of Veratrine on Striated Muscles in Warm-blooded Animals. G. QUAGLIARIELLO (*Zeitsch. Biol.*, 1913, **59**, 441—468).—Veratrine causes two contractions, the second of which lasts longer. It also causes fibrillary twitchings in small doses. Variations in the curves obtained with varying doses are illustrated by reproductions of the tracings. W. D. H.

The Action on Man of Vapours of Technical and Hygienic Importance. XXX. Nitric Acid. KARL B. LEHMANN and LUDWIG DIEM (*Arch. Hygiene*, 1913, **77**, 311—322).—The toxic symptoms on animals of air contaminated by nitric acid are not particularly characteristic, and are similar to those produced by other irritant substances, such as hydrogen chloride, sulphur dioxide, etc. Three cats died in the respiration chamber in 35 to 120 minutes in the presence of 0·5 to 0·73 mg. of the acid to 1 litre of air. Two animals recovered after doses of 0·43 to 0·5 mg., and one survived until the next day with a dose of 0·88 mg. after remaining in the presence of the air-acid mixture for 200 minutes. The post-mortem examination showed no marked inflammation of the mucous membrane of the eyes, nose, or mouth, or œdema of the glottis. The bronchial passages were, however, hyperæmic, and the lungs exhibited œdema. S. B. S.

The Action on Man of Vapours of Technical and Hygienic Importance. XXXI. The "Nitrous Gases": Nitric Oxide, Nitrogen Dioxide, Nitrous and Nitric Acids. KARL B. LEHMANN and HASEGAWA (*Arch. Hygiene*, 1913, **77**, 323—368).—A summary is given of a number or cases in the literature describing the toxic symptoms produced in man by the "nitrous gases," which act essentially as a mixture of nitrous and nitric acid. Attention is called to the great differences as regards the susceptibility of

individuals to the poison. Experiments were carried out on animals with gas made by the action of nitric acid on copper. This was diluted with hydrogen, and mixed with air. An apparatus is figured to show how this was accomplished, and how samples of the air to which the animals were exposed could be removed for analysis. The analysis was accomplished by passing the air, first, over hydrogen peroxide, when the nitrous acid was oxidised to nitric acid, and the total nitrate, both preformed and produced by oxidation of the nitrous acid, was precipitated by nitron. The gas unabsorbed in the first absorption apparatus was passed through a second apparatus containing potassium iodide, and the iodine set free was titrated by thiosulphate solution. The general result of the experiments with mixtures of equimolecular proportions of nitrous and nitric acid is to show that the mixture acts as if all the nitrogenous products were in the form of nitric acid (see preceding abstract). In the majority of the animal experiments the toxic symptoms were different from those in man. These were generally only slight inflammatory reactions on the mucous membranes, œdema of lungs, in certain experiments, methæmoglobin formation, and indications of an action on the central nervous system. The temporary recovery after removal from the noxious vapours, with subsequent relapse, as is observed in the case of man, occurred only seldom in the case of animals. Experiments on man (Hasegawa), but carried out only with small doses of the noxious vapours, indicated that the symptoms were similar to those on animals. Various experiments were also carried out on the reduction of nitrate to nitrite by animal tissues, on the distribution of nitrites in tissues after injection into the trachæa, and on the toxic effect of nitrite administration. It was shown that the quantities of nitrite which produced severe symptoms after inhalation were far smaller than the quantities necessary to produce characteristic nitrite poisoning. The injurious effects in the inhalation experiments are to be ascribed to the production of the lung œdema. In man there is a latent period before the injurious effects are observed, which is generally absent in the case of animals.

S. B. S.

The Natural Resistance of the Hedgehog towards Certain Poisons. M. A. Willberg (*Biochem. Zeitsch.*, 1913, **48**, 157—174).—It was found that the hedgehog could tolerate a dose of atropine sulphate 248 times larger (calculated per kilo. of body-weight) than that tolerated by man. The tolerance towards morphine hydrochloride was 245 times as greater; towards nicotine, 29 times; towards potassium arsenite, 10 times; towards curare, 7 times; towards potassium cyanide, 6 times; towards mercuric chloride, 4 times; and towards phenol, twice as grêat. There was no difference in the tolerance towards strychnine nitrate. S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

Bacterial Reduction of Sulphates to Sulphides. ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1913, **83**, 165—169).—Sasaki and Otsuka (A., 1912, ii, 475), working with 21 races of bacteria in pure culture, were unable to reduce sulphate to sulphide, and further state that bacteria produce no hydrogen sulphide from taurine.

Positive evidence is now quoted showing that in a great variety of cases bacteria relatively readily reduce sulphates to hydrogen sulphide. E. F. A.

Bio-chemistry of Micro-organisms. VII. The Fermentation of Formic Acid by Bacillus Kiliense in a Medium of Constant Composition. HARTWIG FRANZEN and F. EGGER (*Zeitsch. physiol. Chem.*, 1913, **83**, 226—228).—The paper consists chiefly of data obtained from experiments carried out on the same lines as those in which *Bacillus prodigiosus* was used (A., 1912, ii, 669). A slight production of formic acid occurs during the early stages of growth, after which fermentation takes place. The results show great divergence in the behaviour of the organism in different series of cultures, and general conclusions cannot be drawn. H. B. H.

Action of Uranium Salts and Metallic Uranium on the Pyocyanic Bacillus. HENRI AGULHON and ROBERT SAZERAC (*Compt. rend.*, 1913, **156**, 162—164. Compare this vol., i, 143).—A study of the influence of uranium salts, soluble and insoluble, on the pyocyanic bacillus, the amount of pyocyanin formed being estimated colorimetrically, the culture medium used being hydrolysed serum. The toxic dose of uranyl acetate is 1 in 500, and of uranyl nitrate, 1 in 200. Doses of from 1 in 50,000 to 1 in 1000 are distinctly favourable, as was shown by the colour test, and also by the thickness of the microbic film produced. With insoluble uranium compounds, potassium or ammonium uranate, doses of 1 in 1000 to 1 in 100 gave an increase of 100% in the yield of pyocyanin, whilst in the case of the metal itself doses of 1% gave a decided growth within twenty-four hours in a medium to which the bacillus was not accustomed. The medium being neutral, this last effect could not be due to any of the uranium passing into solution, and finally favourable action was produced on the microbe in sealed tubes, the uranium being outside, thus pointing to the radioactivity of the uranium as being the cause of the increased growth in this and the previous cases. W. G.

Influence of Salts of Uranium and Thorium on the Development of the Tubercle Bacillus. PAUL BECQUEREL (*Compt. rend.*, 1913, **156**, 164—166).—Radioactive salts of uranium and thorium behave physiologically like many other non-radioactive salts. They each have an optimum dose, which produces the

maximum growth of the bacillus, above which they begin to exert a toxic effect, uranyl nitrate being much more toxic than thorium nitrate. A dose of 1 in 2500 of the former has a marked inhibitory influence, whilst the same dose of the latter seems to be its optimum as regards increased microbic growth. W. G.

Indole Reaction. HUGO ZIPFEL (*Centr. Bakt. Par.*, 1913, i, **67**, 572—584. Compare A., 1912, ii, 793).—The contradictory results often yielded by the indole test may be attributed to unsuitability or variability of the medium. The use of a composite tryptophan medium with or without the addition of glycerol or dextrose is recommended, whereby trustworthy results can be obtained in twenty-four to forty-eight hours. Comparative tests of a large number of strains of certain pathogenic and non-pathogenic bacteria were made, and consistent results obtained with the various strains of each species of organism. The *p*-dimethylaminobenzaldehyde test for indole was found to be the most trustworthy. H. B. H.

Mechanism of Alcoholic Fermentation. S. KOSTYTSCHEV (*Ber.*, 1913, **46**, 339. Compare Kostytschev, A., 1912, ii, 589; Kostytschev and Hübbenet, *ibid.*, 1912, ii, 860).—A claim for priority against von Lebedev (this vol., i, 144), in demonstrating that acetaldehyde is formed during the fermentation of sugar in the presence of zinc chloride, and, further, that acetaldehyde is reduced to ethyl alcohol by living yeast and various yeast preparations. H. W.

Alcoholic Fermentation. III. Conditions Regulating the Formation of Acetaldehyde during the Fermentation of Hefanol (Yeast). S. KOSTYTSCHEV (*Zeitsch. physiol. Chem.*, 1912, **83**, 93—104. Compare A., 1912, ii, 589; also Kostytschev and Hübbenet, A., 1912, ii, 860).—A reply to the criticisms of Neuberg and Kerb (A., 1912, ii, 973). Paracetaldehyde is very easily decomposed into acetaldehyde on distillation with traces of acid.

Autofermentation of yeast is a true alcoholic fermentation of the yeast glycogen; acetaldehyde is one of the products of the change. When fermentation of hefanol is effected in presence of sufficient methylene-blue to render the active reducing agent inoperative, acetaldehyde is formed as the normal reduction of acetaldehyde to ethyl alcohol is restricted. E. F. A.

Biochemical Synthesis of Alkylglucosides (α-Glucosides) by means of a Ferment (α-Glucosidase) contained in Air-dried Bottom Yeast. α-Ethylglucoside. ÉMILE BOURQUELOT, HENRI HÉRISSEY, and MARC BRIDEL (*Compt. rend.*, 1913, **156**, 168—170).—The authors have obtained α-ethylglucoside in a crystalline form, $[\alpha]_D$ +150·64°, by the action of a ferment, extracted from bottom yeast by water, on a dilute alcoholic solution of dextrose containing at least 65% of water by volume. The yield with respect to the dextrose used was 33%, and the glucoside was readily hydrolysed in aqueous solution by the same ferment, which they name α-glucosidase. W. G.

Assimilation of Nitrate and Nitrite. V. OSKAR BAUDISCH and ERWIN MAYER (*Ber.*, 1913, **46**, 115—125. Compare A, 1911, ii, 523; 1912, ii, 286, 1202).—When a dilute formaldehyde–potassium nitrate solution is exposed to sunlight a mixture of nitrous oxide and hydrogen, together with some carbon dioxide and monoxide, is evolved. In a formaldehyde–potassium nitrite solution, in addition, small quantities of nitric oxide are also formed. This originates from the decomposed nitroxyl NOH, a substance which does not exist as gas.

Angeli's salt, ONa·N:NO·ONa, decomposes on warming in aqueous solution into nitrous and nitric oxides and ammonia.

Solutions of potassium nitrite in either formaldehyde or methyl alcohol which have been exposed to light contain methylamine and, further, formic acid, hyponitrous acid, and hydroxylamine. In addition an alkaloidal compound similar to nicotine and containing a pyrrole ring is formed. Whereas in the assimilation of carbon the carbonic acid is reduced to carboxylic acid by the yellow and red rays of the spectrum, in the assimilation of nitrogen the blue, violet, and ultra-violet rays cause the reduction of nitrates to nitroxyl. E. F. A.

The Influence of Uranium and Lead on Vegetation. JULIUS STOKLASA (*Compt. rend.*, 1913, **156**, 153—155).—Uranyl nitrate added in small amounts to pot cultures of *Melilotus albus* already supplied with suitable fertilisers, had a favourable effect on the total yield of dry matter, the optimum quantity being 2·5 kilos. of uranium per hectare of soil. With 20 kilos. per hectare there was no indication of any toxic effect. The results with lead nitrate on oats and on *Polygonum fagopyrum* are of the same order, but the amount of lead which has an injurious effect is much less than in the case of uranium, the addition of lead nitrate at the rate of 8 kilos. per hectare being detrimental to the total crop in each case. W. G.

The Cause of Growth in Plants. I. G. A. BOROVIKOV (*Biochem. Zeitsch.*, 1913, **48**, 230—246).—The author reviews M. Fischer's experiments on the influence of acids, bases, and salts on various imbibition processes, for example, in gelatin and muscle. The view has been expressed by Fischer and others, that the phenomena of growth are determined, not so much by the osmotic properties of the cell, as by the capacity of the various colloids to imbibe water. The capacity is affected differently by various ions contained in the solution. The method of experiment employed by the author to investigate the various factors was as follows. Seedlings (six days old) of *Helianthus annuus* were placed in tubes which hung vertically in cylinders containing various solutions, and after intervals of three, six, and twelve hours and longer, removed, and the rate of growth was measured and compared with the rate of growth in pure water. The influence of various acids, bases, and salts on the rate of growth during short intervals was thus ascertained. It was found that acids accelerate the growth during the

first period, and if salts are present at the same time, the growth in the presence of both acid and salt is diminished as compared with that in acid alone. The effect of the various ions and cations was studied in some detail, and attention is drawn to the parallelism between their influence on the rate of growth and their general effect on imbibition processes. The experiments, generally, confirm the conception of the relationship between imbibition processes and growth. S. B. S.

Presence of Formaldehyde in the Sap of Green Plants. FRANCESCO ANGELICO and G. CATALANO (*Gazzetta*, 1913, **43**, i, 38—43). —The formaldehyde which is supposed to be an intermediate product in the photosynthesis of starch in green plants has never been demonstrated in the sap with certainty. The test for formaldehyde with atractylin (compare Angelico, A., 1910, i, 403) is not only very sensitive, but also specific. The leaf-sap and its distillate of eleven species of green plants tested in this way showed the presence of formaldehyde, whilst the same products from six species previously kept for twenty-four hours in the dark gave no reaction. Three non-chlorophyllic, parasitic plants were also tested, and formaldehyde was found to be absent. The results are therefore in complete agreement with the usual theory of photosynthesis.

R. V. S.

The Function of the Carboxylase in Plants. W. ZALESKI and ELIZABETH MARX (*Biochem. Zeitsch.*, 1913, **48**, 175—180).—The seeds employed were sterilised with mercuric chloride, then dried and powdered. The seeds of *Lupinus luteus* decompose free pyruvic acid as readily as they do its sodium salt. Pea seeds, on the other hand, decompose the free acid less readily than its salt, a fact due probably to the alkalinity of the powder. Seeds of *Vicia faba* only weakly attack the free acid, although they readily attack the sodium salt. Lupine seeds can also attack pyruvic acid in a vacuum. Both pyruvic acid and its sodium salts inhibit the carbon dioxide production of the immature seeds. Acetaldehyde could be detected in the experiments with both lupine and pea seeds when pyruvic acid was present. It could be also detected, but in very much smaller quantities in the control experiments, in which the acid was absent. The authors call attention to the parallelism of the actions of the seed carboxylase and of zymase, and discuss the rôle played by pyruvic acid in degradation of sugars and the production of ethyl alcohol. S. B. S.

Rôle of Oxydases in the Formation of the Anthocyan Pigments of Plants. FREDERICK KEEBLE and EDWARD FRANKLAND ARMSTRONG (*J. of Genetics*, 1912, **2**, 277—311. Compare A, 1912, ii, 673).—The methods previously described for the localisation of oxydases have been extended to a variety of plants. Peroxydase is shown to be more widely distributed than the organic peroxide which activates it. The very general phenomenon of browning presented by dried plants is regarded as an indication of the presence

of a complete oxydase. Exposure of plants to darkness leads to the formation of peroxide and to an increase of peroxydase. The bearing of these facts on the general metabolism in the plant is discussed.
E. F. A.

Colloidal Chlorophyll and the Shifting of the Absorption Bands in the Leaves of Living Plants. D. IVANOVSKI (*Biochem. Zeitsch.*, 1913, **48**, 328—331).—Herlitza has drawn the conclusion, from spectroscopic observations, that chlorophyll exists in the colloidal form in living plants. The author gives a table of extinction coefficients, and shows that those of the chlorophyll of the leaf fall between those of colloidal chlorophyll and of an alcoholic solution of the pigment. He draws attention to the fact that the chlorophyll in leaves exists, not evenly distributed, but in the chloroplasts, and that the absorption spectrum of the leaf combines the characters of an absorption and reflection spectrum. He shows that the absorption spectrum of the leaf can be closely imitated by the addition of electrolytes to colloidal chlorophyll. According to the size of the granula thus produced, the absorption band is shifted thereby towards the ultra-red. S. B. S.

Plant Fats. CARL THOMAE (*J. pr. Chem.*, 1913, [ii], **87**, 144).—The fatty and waxy constituents of yeast, rose blossoms, and the skins of apples, grapes, peaches, potatoes, lemons, gherkins, and other parts of plants may be readily isolated in a state of purity by heating under diminished pressure. F. B.

The Non-Specificity of Zinc as a Biological Catalyst for the Culture of Aspergillus niger. CHARLES LEPIERRE (*Compt. rend.*, 1913, **156**, 258—261).—The author has tried the effect of replacing the zinc in Raulin's solution by cadmium on the cultivation of *Sterigmatocystis nigra*, and his results are not in accord with those recently put forward by Javillier (compare this vol., i, 235). On the contrary, he finds that cadmium replaces zinc perfectly in Raulin's solution, and, like it, plays a very energetic part in the rapid growth of the plant, being fixed by the plant. Further, he finds that zinc is not a specific catalyst for this culture, but can be replaced by other elements chemically analogous to it.
W. G.

Attempts to Substitute Glucinum for Magnesium and Zinc in the Culture of Sterigmatocystis nigra (Aspergillus niger). MAURICE JAVILLIER (*Compt. rend.*, 1913, **156**, 406—409. Compare this vol., i, 235).—A reply to Lepierre (preceding abstract). From further experiments the author maintains that glucinum cannot replace magnesium or zinc in the culture medium for *Aspergillus niger*, the magnesium being necessary as a nutrient and the zinc as a catalyst. He suggests that the difference between his and Lepierre's results may be due to the conditions of their culture media, or hereditary influences on the cultures. W. G.

Replacement of Zinc by Glucinum in the Culture of Aspergillus niger. CHARLES LEPIERRE (*Compt. rend.*, 1913, **156**, 409—411. Compare this vol., i, 235; preceding abstracts).—The results obtained are in direct opposition to those of Javillier (previous abstract). The author finds that the zinc in Raulin's liquid can be replaced by glucinum without affecting the weight of crop finally obtained from the culture of *Aspergillus niger* thereon, except that the maximum is somewhat retarded. This retardation is, however, only relative, and diminishes as the plant adapts itself to the new medium. Time, adaptation, and easy access of air play an important part in these cultures. The glucinum is fixed by the plant. W. G.

Formation of Urea by Two Moulds. ROBERT FOSSE (*Compt. rend.*, 1913, **156**, 263—265. Compare A., 1912, ii, 1203).—The author has isolated urea in small quantities in the form of its xanthhydrol derivative from the expressed juice of mycelium gathered from the surface of Raulin's liquid and also from *Aspergillus niger* grown on a solution in which ammonium nitrate has replaced the chloride in Raulin's liquid. *Penicillium glaucum* similarly contains small quantities of urea in its cells. From his results the author draws the conclusion that the principal factor in ureogenesis is a process of oxidation, and not, as at present supposed, a diastatic oxidation. W. G.

The Nitrogenous Constituents of Lime Juice. CASIMIR FUNK (*Biochem. J.*, 1913, **7**, 81—86).—In view of work on beri-beri, in which the physiological importance of certain substances (probably pyrimidine derivatives) has been shown, lime juice was examined in reference to scurvy. Lime juice cures scurvy, and also contains an antineuritic substance. Pyrimidine substances in general prolong life in birds with polyneuritis. No anti-scorbutic substance, however, was separated out from lime juice. The investigation was hampered by the guinea-pigs refusing to take oats, a diet which leads to scurvy in these animals. Milk prevents oats from causing scurvy, even though the proteins are removed. The anti-scorbutic material in milk is destroyed by a high temperature. Its unstable character may have led to the negative results with lime juice. Several new compounds were, however, separated from lime juice; one, $C_{13}H_{24}O_3$, needles, m. p. 97—100°, apparently belongs to the terpene group; one, $C_6H_7O_2N_5$, crystalline plates, m. p. 282° (corr.), to the purine group; one, $C_9H_{18}O_6N_2$, microscopic spherolites, m. p. 188—189° (decomp.), to the pyrimidine group; and a fourth to the choline group; the latter crystallised in cubes, and gave a platinichloride, $(C_8H_{15}O_2N)_2H_2PtCl_6$, m. p. 220°. The phosphotungstic and silver nitrate precipitates were mainly examined. W. D. H.

Constituents of Apples. CARL THOMAE (*J. pr. Chem.*, 1913, [ii], **87**, 142—144).—The substance, m. p. above 200°, previously isolated by the author (A., 1911, ii, 920) from apple-skins may be separated

by treatment with ether into an insoluble substance of high melting point, and a waxy substance crystallising in needles, m. p. 68·5°. On distillation under diminished pressure, the oil obtained by extracting the skins with ether yields a crystalline substance of low melting point having an odour of apples and a yellow oil which readily solidifies. The behaviour of the skins on distillation is also described. F. B.

Leaves of Barosma venusta. HAROLD R. JENSEN (*Pharm. J.*, 1913, [iv], **36**, 60—61).—This material from Cape Province, South Africa, yielded 1·1% of volatile oil, $D_{15\cdot5}^{15\cdot5}$ 0·8839, a_D^{20} + 0°30′, n_D^{20} 1·4967, of greenish-yellow colour, and having acid value 2·4 and saponification value 13·4. On treatment with potassium hydroxide solution, 16% of the oil dissolved, and a further 4% was absorbed by a solution of neutral sodium sulphite. The oil was separated into nine fractions by distillation under reduced pressure, and the physical constants, ultimate composition, and reactions with bromine, sodium, and phenylhydrazine of each fraction are recorded. From a consideration of these data the following composition is tentatively suggested for the oil: myrcene, 35; chavicol, 16; myrcenol and sesquiterpene alcohols, 15; methylchavicol and anethole, 15; sesquiterpenes, esters, ketones, aldehydes, and acids, 19%. The leaves also contain oleoresin, acid resins, colourless glucosides, fat, carbohydrates, and a little tannin. The results show that these leaves do not contain the same constituents as the commercial buchus derived from *B. betulina* and *B. serratifolia*, and that they cannot be used in medicine in place of these. T. A. H.

Constituents of Lycoperdon bovista. JAN J. BLANKSMA (*Chem. Weekblad*, 1913, **10**, 96—100).—Fresh specimens of the edible mushroom, *Lycoperdon bovista*, contain trehalose, tyrosine, a substance with m. p. 165°, chitin, and leucine, all previously isolated (compare Bourquelot, *J. Pharm. Chim.*, 1907, [vi], **25**, 382; Bamberger and Landsiedl, A., 1903, ii, 567; 1905, ii, 852). The trehalose is converted by trehalase, invertase, and diastase into reducing sugars, these ferments being present in the mushrooms. The darkening in colour of mushrooms is explained by the conversion of tyrosine into melanin, a black substance, under the influence of tyrosinase. It is possible that leucine is converted into *iso*amylamine, and the tyrosine into *p*-hydroxylphenylethylamine, a substance of very poisonous character. It is known that old specimens of *Lycoperdon bovista* are poisonous. The author recommends the preparation of glucosamine hydrochloride by boiling mushrooms with dilute hydrochloric acid after elimination of proteins, fats, and calcium salts. A. J. W.

Organic Chemistry.

Notes on Mine Gas Problems. GEORGE A. BURRELL (*J. Ind. Eng. Chem.*, 1913, 5, 181—186).—The author gives an account of the various problems met with in connexion with mine gases, interpolating from time to time some of the data accumulated by the Bureau of Mines with respect to the explosibility and physiological effects of mine atmospheres, and to flame extinction and after-damp.

The lower explosive limit of mixtures of air and methane is confirmed to be 5·5% methane. The presence of carbon dioxide alters this explosive limit, but even 10% of carbon dioxide raises it only to 6·6%. Reduction in the volume percentage of oxygen also raises the explosive limit. Harger has suggested that a small reduction in the oxygen percentage and a small increase in the carbon dioxide percentage in mine air will suffice to produce an atmosphere incapable of supporting combustion, and consequently an atmosphere in which explosions and gob fires cannot occur, but the data obtained by the Bureau of Mines indicate that the figures given by Harger are much too low, both with respect to the increase in carbon dioxide and diminution in oxygen.

When acetylene is used in the miner's lamp, the flame resembles the ordinary wick flame burning in pure air, when the oxygen content of the air decreases to 16—16·5%; this behaviour of the flame can be used as a guide to men venturing into workings containing black damp and less oxygen than the percentage given. The ordinary miner's lamp is extinguished when the oxygen falls to about 16·5—17%; the extinguishing of the flame is shown to be due to deficiency in oxygen and not to the presence of carbon dioxide.

Reference is made to the following subjects: Effect of vitiated air on the luminosity of miner's lamps (compare Haldane, *Colliery Guardian*, Oct. 25th, 1912); high velocity of air currents in mines; distribution of after-damp; intrusion of natural gas into mines, etc. Analyses are also given of mine-gas mixtures containing explosive and other proportions of methane, and of samples of after-damp atmospheres which show the large amount of carbon monoxide (white-damp) present shortly after an explosion. T. S. P.

Solvents for Acetylene. JOSEPH H. JAMES (*J. Ind. Eng. Chem.*, 1913, 5, 115—120).—An investigation of the solvent powers for acetylene of a number of organic liquids shows that those containing the carbonyl group are generally the best solvents. Organc acids must be excluded, however, the hydroxyl in the carboxyl group seeming to inhibit the solvent action of the carbonyl. The presence of the carbonyl group is not sufficient, of itself, to account for the solubility, since methylal and acetal are very good solvents.

It is found that acetaldehyde fulfils all the industrial requirements for an acetylene solvent. T. S. P.

Preparation of Dimethylacetylene [Crotonylene] and Ethylacetylene from Carbides. CARL WILLI SCHLECHTER (D.R.-P. 253802).—When methyl alcohol is heated with an alkaline earth carbide during four days at 60—120° under a pressure of 50 atmospheres, or during six days in a closed tube at 200° it yields a mixture of crotonylene (Δ^{β}-butinene), CMe⋮CMe, b. p. 28°, and ethylacetylene [Δ^{a}-butinene], CEt⋮CH, b. p. 18°. F. M. G. M.

$\Delta^{a\gamma\epsilon}$-Heptatriene and Related Substances. CORNELIS J. ENKLAAR (*Chem. Weekblad*, 1913, **10**, 187—189. Compare this vol., i, 243).—A discussion of the influence of structure on the possibility of solidifying unsaturated hydrocarbons. By cooling with liquid air several butadienes and related substances have been converted into the solid state. A. J. W.

Vinylacetylene. RICHARD WILLSTÄTTER aud THEODOR WIRTH (*Ber.*, 1913, **46**, 535—538).—By the action of dimethylamine in benzene solution on the dibromide of butadiene, $a\delta$-tetramethyldiamino-Δ^{β}-butylene, $NMe_2\cdot CH_2\cdot CH{:}CH\cdot CH_2\cdot NMe_2$, is obtained. The use of an indifferent solvent, such as benzene, is essential; with alcohol numerous secondary reactions take place.

When the corresponding diquaternary ammonium base is distilled in a vacuum it is decomposed, and vinylacetylene, $CH{⋮}C\cdot CH{:}CH_2$, is obtained.

$a\delta$-Tetramethyldiaminobutylene is a colourless oil with a narcotic odour, b. p. 171—172°/723 mm., 65—65·5°/17 mm., D_4^0 0·8198. The *picrate* forms needles, m. p. 222—223°; the *aurichloride* separates in crystalline needles, m. p. 201° (decomp.); the *platinichloride*, $2H_2O$, crystallises in long, rhombohedric prisms, m. p. 227—228°, whilst the *dimethiodide* forms prisms, decomp. 270°.

Vinylacetylene [*$\Delta^{a\gamma}$-buteninene*] melts to a colourless liquid, b. p. 2—3°/729 mm., and has an odour like acetylene. It forms a greenish-yellow copper salt and a colourless, crystalline silver salt, which explodes when heated. E. F. A.

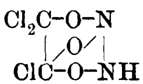
A Catalytic Method of Isomerisation of Alkyl Chlorides and Bromides. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1913, **156**, 658—659. Compare A., 1905, i, 677).—Barium chloride or thorium chloride at 250° causes the decomposition of primary alkyl chlorides or bromides into ethylene hydrocarbons and hydrogen chloride or bromide. These then recombine, when passed over pumice stone at 200°, giving, not the original haloid, but the isomeric chloride or bromide. The resulting liquid is submitted to fractional distillation, thus separating any of the original unchanged substance. W. G.

Trichloroethylene and Some of its Derivatives. JACOB BÖESEKEN [with C. E. KLAMER and J. G. DE VOOGT] (*Rec. trav. chim.*, 1913, **32**, 15—22).—Unsuccessful attempts have been made to bring trichloroethylene and tetrachloroethylene into reaction with benzoyl chloride, sulphur chloride, phosphorus chloride, thionyl chloride, and

sulphuryl chloride respectively in the presence of aluminium chloride. Charred products were obtained, except in the case of tetrachloroethylene and sulphuryl chloride, when hexachloroethane was isolated, owing to the decomposition of sulphuryl chloride into sulphur dioxide and chlorine and union of the latter with tetrachloroethylene.

Barium monochlorosulphoacetate, C_2HO_5ClSBa, was isolated from the product of the action of fuming sulphuric acid (containing 10% SO_3) on trichloroethylene at 88°.

When trichloroethylene was added drop by drop to a mixture of nitric acid (D 1·5) and concentrated sulphuric acid, cooled by a freezing mixture of salt and ice, and the action interrupted as soon as the temperature of the product rose but slowly when removed from the freezing mixture, dichloroacetic acid was obtained, together with a *substance*, $C_2HO_3N_2Cl_3$, b. p. 32°/36 mm., which, when preserved, became converted into colourless, very hygroscopic needles, which were insoluble in, or decomposed by, the ordinary solvents, and had mol. wt. 194 in nitrobenzene solution. When heated with hydrochloric acid, this substance yielded small amounts of nitric oxide and carbon dioxide, but neither hydroxylamine nor oxalic acid could be detected. Alcoholic potassium hydroxide decomposed it according to the equation: $C_2HO_3N_2Cl_3 + 7KOH = 3KCl + 2K_2CO_3 + 4H_2O + N_2$. With zinc and cold dilute sulphuric acid it gave a quantitative yield of ammonia. It did not give Liebermann's reaction. In view of the above properties, the annexed formula is tentatively proposed for it.



H. W.

Elimination of Water from Pinacolyl Alcohol. Tertiary Butylethylene. W. Fomin and N. Sochanski (*Ber.*, 1913, **46**, 244—248).—Pinacolyl alcohol was converted by Couturier (A., 1893, i, 245) into a bromide, which, when treated with solid potassium hydroxide, gave a mixture of $\beta\gamma$-dimethyl-Δ^{β}-butylene (compare Zelinsky and Zelikov, A., 1902, i, 2) with a small quantity of a hydrocarbon, b. p. 56—59°, which was described as *tert.*-butyl ethylene. The latter compound has now been prepared from pinacolyl alcohol by Tschugaev's method and has other properties.

The potassium derivative is prepared by adding the alcohol to potassium *tert.*-amyloxide (compare Tschugaev, A., 1905, i, 167) and then treated with carbon disulphide and methyl iodide. The *methyl pinacolyl xanthate*, $C_6H_{13}\cdot O\cdot CS\cdot SMe$, b. p. 100°/12 mm., D_4^{18} 1·0228, decomposes at 160—175°, and the purified tert.-*butylethylene* [$\gamma\gamma$-*dimethyl*-Δ^{α}-*butylene*], $CMe_3\cdot CH{:}CH_2$, is a colourless liquid, having b. p. 41·2°/760 mm., D_4^{18} 0·6549, and n_D 1·37667. On oxidation with permanganate, acetone is not obtained, the chief product being $\alpha\alpha$-dimethylpropionic acid, whilst reduction with hydrogen in presence of platinum black results in the formation of $\beta\beta$-dimethylbutane.

J. C. W.

Decomposition of Heptyl Alcohol at 220° in the Presence of Finely Divided Nickel. Jacob Böeseken and G. H. van Senden (*Rec. trav. chim.*, 1913, **32**, 23—38).—The authors have repeated the

experiments described by van Beresteyn (A., 1911, i, 761), who obtained heptyl alcohol and a substance which he regarded as *n*-hexylene, by the reduction of heptaldehyde according to the general method of Sabatier and Senderens. Heptyl alcohol, under similar circumstances, was found to yield *n*-hexylene, carbon monoxide, and hydrogen, the course of the actions being represented by the equations: $C_6H_{13}\cdot CHO + H_2 = C_7H_{15}\cdot OH$. $C_7H_{15}\cdot OH = C_6H_{12} + CH_3\cdot OH$. $CH_3\cdot OH = CO + 2H_2$. On theoretical grounds, the authors consider this interpretation to be improbable, and are led to the conclusions: (1) that heptyl alcohol, in the presence of finely divided nickel at 220°, is decomposed into heptaldehyde and hydrogen; (2) that, particularly in the presence of an inert gas, the heptaldehyde is converted into *n*-hexylene, hydrogen, and carbon monoxide; (3) that *n*-hexylene combines with a considerable proportion of the liberated hydrogen to form *n*-hexane, and that, in the presence of an excess of hydrogen, all the *n*-hexylene undergoes reduction; (4) that heptaldehyde is not reduced in the presence of carbon dioxide, and only slightly reduced in an atmosphere of hydrogen; (5) that *n*-hexylene (mixed with *n*-hexane) is best obtained by the decomposition of heptaldehyde by nickel at 220° in a current of carbon dioxide, and (6) that *n*-hexane is obtained by the catalytic decomposition of heptyl alcohol or heptaldehyde by nickel at 220° in a current of hydrogen.

Heptyl alcohol was obtained by the reduction of heptaldehyde dissolved in glacial acetic acid by means of sodium amalgam. Small quantities of s-*di*-n-*hexylethyleneglycol* [n-*tetradecane*-$\eta\theta$-*diol*], b. p. 218°/14 mm., m. p. 69—70°, were obtained as by-product.

Heptyl alcohol, when passed over nickel at 220° in a current of hydrogen, yielded about 62% *n*-hexane, 17% of a mixture of heptyl alcohol and heptaldehyde, and carbon monoxide. In a current of carbon dioxide, however, it yielded about 14·5% *n*-hexylene, 31% *n*-hexane, 24% of a mixture of heptyl alcohol with a little heptaldehyde, carbon monoxide, and hydrogen, the change being represented by the equation: $3C_7H_{15}\cdot OH = 2C_6H_{14} + C_6H_{12} + 3CO + 4H_2$.

Heptaldehyde, at 220° in a current of carbon dioxide, gave about 24% *n*-hexylene, 29% *n*-hexane, 16% unchanged heptaldehyde, carbon monoxide, hydrogen, and possibly a trace of formaldehyde. The quantities of the products obtained agreed with the equation: $100C_6H_{13}\cdot CHO = 45C_6H_{12} + 55C_6H_{14} + 100CO + 45H_2$. At 180°, the course of the reaction was similar.

n-Hexane was not affected when passed over nickel at 220° in a current of carbon dioxide. H. W.

$\alpha\delta$-Oxide from Undecyl Alcohol. N. A. LOGGINOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 136—145).—The action of zinc chloride or 50% sulphuric acid on undecyl alcohol results in displacement of the double linking of the alcohol and formation of the $\alpha\delta$-*oxide*, $CH_3\cdot[CH_2]_6\cdot CH<\begin{matrix}CH:CH\\ O\text{---}CH_2\end{matrix}$, b. p. 219—222°, D_0^0 0·8641 (or 0·8667), D_0^{17} 0·8522, D_0^{18} 0·8538.

When zinc chloride is used, the oxide is accompanied by an unsaturated *alcohol*, $C_{11}H_{22}O$, b. p. 243—246°, which forms a crystalline *phenylurethane*, $C_{18}H_{27}O_2N$, m. p. 49·5°, and is being further investigated. T. H. P.

Action of αβ-Dichloroethyl Ether on Mixed Magnesium Derivatives. ROBERT LESPIEAU and BRESCH (*Compt. rend.*, 1913, **156**, 710—712).—αβ-Dichloroethyl ether condenses readily with magnesium derivatives of ethyl and allyl bromides and acetylene, giving products somewhat difficult to purify. The *compound*,

$$C_{10}H_{16}O_2Cl_2,$$

obtained from the acetylene derivative is a colourless liquid, b. p. 136—137°/12 mm., and is probably a mixture of two *cis*- and *trans*-isomerides (compare Dupont, A., 1910, i, 85). On bromination in chloroform, it yields two *dibromides*, $C_{10}H_{16}O_2Cl_2Br_2$, separable by their varying solubility, the less soluble one having m. p. 107—108°, and the other m. p. 71—72°. These are also probably *cis*- and *trans*-isomerides. W. G.

Compounds of Ethyl Phosphite with Silver Haloids. ALEXANDER E. ARBUZOV and A. V. KARTASCHOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 79—81).—Derivatives of tervalent phosphorus of the form PR_3 or $P(OR)_3$ form compounds with cuprous and platinous haloids, and the authors find that ethyl phosphite forms similar compounds with silver haloids. These compounds form colourless, ribbon-like crystals, their melting points being: $P(OEt)_3,AgCl$, 4·5—5·5°; $P(OEt)_3,AgBr$, 40—40·5°; $P(OEt)_3,AgI$, 81—83°. T. H. P.

Uranium Formate. WILLIAM ŒCHSNER DE CONINCK and ALBERT RAYNAUD (*Bull. Soc. chim.*, 1913, [iv], **13**, 221—223).—Uranium formate is a deliquescent, yellow salt, readily soluble in water. Attempts to estimate the water of crystallisation were unsuccessful, owing to the ready loss of formic acid from the salt on prolonged desiccation. When calcined in a closed vessel, the salt leaves a residue of pure uranous oxide, but, if an open vessel is used, traces of a higher oxide are formed. Similar results were previously obtained with uranium oxalate (A., 1912, i, 535).

When boiled with a large quantity of water, uranium formate is hydrolysed, hydrated uranium trioxide, $UO_3,2H_2O$, separating as a yellow precipitate, which is converted by calcination into the green oxide, U_3O_8.

Uranium formate was exposed to diffused daylight during three months in the presence of methyl alcohol. A brown deposit of uranium oxide was thereby obtained, and the strongly acid methyl alcoholic solution was found to contain methyl formate.

Very little decomposition occurred in similar circumstances in the presence of ethyl alcohol. Very little formic acid was liberated, whilst the residue contained only small amounts of mono- and di-hydrated uranium trioxide mixed with unchanged uranium formate. H. W.

Preparation of Halogen Formic Esters. EMANUEL MERCK (D.R.-P. 254471).—The following halogen formic esters in addition to those previously described (this vol., i, 5) have now been prepared. *Dimethylethylcarbinyl chloro-formate*, a liquid which decomposes at 20° and cannot be distilled in a vacuum; the homologous *methyldiethylcarbinyl chloro-formate* has similar properties. F. M. G. M.

Distillation and Sublimation of Ammonium Salts under Diminished Pressure. RICHARD ESCALES and HANS KOEPKE (*J. pr. Chem.*, 1913, [ii], **87**, 258—279).—Of the normal salts examined the formate (*s*, 90—140°), acetate (*s*, 90°), thiocyanate (*d*, 165°), cyanate (*s*, 160—190°), nitrite (*s*, 70°), and sulphite (*s*, 70—120°) distil or sublime under a pressure of 10 mm. without decomposition, whilst the propionate (*d*, 70—75°), butyrate (*d*, 70—80°), glycollate (*d*, 160°), lactate (*d*, 140—150°), benzoate (*s*, 60—130°), and salicylate (*s*, 90—150°) are converted into the corresponding acid salts, NH_4HX_2; the temperatures at which distillation or sublimation occurs are given in brackets (*s* denotes sublimation; *d*, distillation). When heated to 300°/10 mm., ammonium sulphate and persulphate lose ammonia, yielding the acid salts; ammonium thiosulphate sublimes at 70°/10 mm., the sublimate consisting of ammonium sulphite. Ammonium carbonate undergoes complete dissociation, whilst carbamide and thiocarbamide sublime in the form of ammonium cyanate and thiocyanate respectively. Of the acid salts, NH_4HX_2, the acetate (*d*, 67°), propionate (*d*, 73°), butyrate (*d*, 78°), glycollate (*d*, 160°), lactate (*d*, 145°), benzoate (*s*, 60—130°), salicylate (*s*, 90—150°), and hydrogen carbonate distil or sublime unchanged at 10 mm.

A mixture of normal or acid ammonium acetate and propionic acid in molecular proportions distils at 66—68°/10 mm., yielding the acid *ammonium* salt, $CH_3\cdot CO_2\cdot NH_4,C_2H_5\cdot CO_2H$, which forms very deliquescent crystals, m. p. 42—43°, and is converted by distillation with butyric acid into the *ammonium* salt, $CH_3\cdot CO_2\cdot NH_4,C_3H_7\cdot CO_2H$. This has m. p. 41°, b. p. 72—74°/10 mm., and is also obtained by distilling normal or acid ammonium acetate with butyric acid. F. B.

Decomposition of Certain Acid Chlorides by Aluminium Chloride. JACOB BÖESEKEN (*Rec. trav. chim.*, 1913, **32**, 1—14).—In continuation of the work of Böeseken and Prins (A., 1910, i, 152; 1911, i, 173), the action of aluminium chloride on the chlorides or sulphonyl chlorides of a number of halogenated acids has been investigated. Normal results were obtained with acid chlorides which did not contain hydrogen or a benzene group, but, in the presence of the latter, the reaction appeared to be complex, giving resinous products from which no definite compound could be isolated.

[With P. HASSELBACH.]—Monochloroacetyl chloride and aluminium chloride yielded a hygroscopic, crystalline *compound*,

$$CH_2Cl\cdot COCl,AlCl_3,$$

which, when heated alone or with carbon tetrachloride, evolved hydrogen chloride, leaving a charred residue. Carbon monoxide could not be detected in the gas evolved. When heated in chloroform solution at 80°, a small quantity of a *substance*, m. p. about 175°, was obtained, to

which no definite composition could be assigned. Similarly, aluminium chloride and chlorofumaryl chloride or $\alpha:\beta:\beta:\beta$-tetrachloropropionyl chloride yielded only charred or resinous products, from which a definite compound could not be separated.

[With (Mlle.) S. VAN DER TAS.]—*p*-Chlorobenzenesulphonyl chloride and aluminium chloride gave resinous products. The gases evolved contained hydrogen chloride and, generally, sulphur dioxide.

[With W. J. P. PELLE.]—*p*-Bromobenzenesulphonyl chloride and aluminium chloride yielded a crystalline additive product,

$$C_6H_4Br\cdot SO_2Cl,AlCl_3,$$

which, when heated at 150—200°, evolved sulphur dioxide and hydrogen chloride, and left a brown resin.

[With P. HASSELBACH.]—*Trichloroacrylyl chloride*, b. p. 158°/760 mm., was obtained by the action of thionyl chloride on trichloroacrylic acid. When mixed with aluminium chloride in carbon disulphide solution, it yielded the *compound*, $CCl_2{:}CCl\cdot COCl,AlCl_3$, which, when heated in a current of dry air, gave only trichloroacrylyl chloride mixed with a little aluminium chloride, but no carbon monoxide. In the presence of aluminium chloride, trichloroacrylyl chloride reacted with benzene and its homologues to form quantitative yields of ketones of the type $R\cdot CO\cdot CCl{:}CCl_2$, only the chlorine atom attached to the carbonyl group being replaced.

Pentachloropropionyl chloride, m. p. 42°, obtained from the preceding chloride by the action of chlorine in sunlight, when heated with aluminium chloride at 60° evolved carbon monoxide and carbonyl chloride, leaving a residue from which hexachloroethane and tetrachloroethylene were isolated, decomposition occurring according to the equations: (I) $CCl_3\cdot CCl_2\cdot COCl = CO + C_2Cl_6$. (II) $CCl_3\cdot CCl_2\cdot COCl = COCl_2 + C_2Cl_4$. When treated with aluminium chloride in the presence of benzene, *pentachloropropiophenone*, $COPh\cdot CCl_2\cdot CCl_3$, m. p. 83°, was obtained when the reaction was continued until one molecule of hydrogen chloride had been evolved. When, however, reaction was continued until two molecules of hydrogen chloride had been evolved, tetrachloroethylene and benzophenone were formed. The presence of the latter may be due to dissociation of pentachloropropionyl chloride into tetrachloroethylene and carbonyl chloride, and condensation of the latter with benzene, or pentachloropropiophenone may be decomposed by aluminium chloride into tetrachloroethylene and benzoyl chloride. The odour of the latter is perceptible when pentachloropropiophenone is warmed with a little aluminium chloride. H. W.

Montanic Acid and its Derivatives. HUGH RYAN and JOSEPH ALGAR (*Proc. Roy. Irish Acad.*, 1913, **30**, 97—105. Compare A., 1909, i, 629).—The authors have prepared a series of derivatives of montanic acid, the formulæ of which are in agreement with the formula, $C_{28}H_{56}O_2$, for montanic acid itself, thus confirming the previous work of Ryan and Dillon (A., 1909, i, 629), and Easterfield and Taylor (T., 1911, **99**, 2302), in contrast to that of Hell (*Zeitsch angew. Chem.*, 1900, **13**, 556), von Boyen (A., 1902, i, 72), and Eisenreich.

Methyl montanate, prepared by boiling montanic acid with methyl

alcohol in the presence of sulphuric acid, crystallises in white, curved needles, m. p. 66°. The similarly crystallised *ethyl* and *n-propyl* esters have m. p. 64—65° and 63·5° respectively.

Dimethylheptacosylcarbinol, $C_{27}H_{55}\cdot CMe_2\cdot OH$, obtained from methyl montanate and magnesium methyl iodide, has m. p. 63—64°, whilst the corresponding *diethyl* and *diphenyl* derivatives melt respectively at 59—60° and 58°. When ethyl montanate is treated with *p*-bromotoluene and the resulting product subjected to steam distillation, the residue is found to consist of the unsaturated *hydrocarbon*, $C_{27}H_{54}\colon C(C_6H_4Me)_2$, m. p. 47°. When, however, the steam distillation is omitted and the product purified by repeated crystallisation from alcohol, it can be separated into two portions, the major part consisting of the above hydrocarbon, the minor part of *di-p-tolylheptacosylcarbinol*, m. p. 51—52°. The action of an ethereal solution of magnesium α-naphthyl bromide on ethyl montanate appears to yield a mixture of *di-α-naphthylheptacosylcarbinol*, m. p. 57—58°, and, probably, *α-naphthylheptacosyl ketone*, $C_{27}H_{55}\cdot CO\cdot C_{10}H_7$, m. p. 51—53°. These substances can be readily separated, since the former dissolves very sparingly in hot methyl alcohol, in which the latter is readily soluble.

Unsuccessful attempts were made to isolate *montanyl chloride* in the pure state by the action of phosphorus tri- or penta-chloride on montanic acid. The product obtained had m. p. 63—65°. It was transformed by concentrated aqueous ammonia into *montanamide*, m. p. 109°, small quantities of a *substance*, probably montanonitrile, m. p. 60—65°, being simultaneously formed.

Attempts to prepare ceryl alcohol from montanic acid were unsuccessful, owing to the difficulty of isolating *heptacosylmethylurethane* from the product of the successive action of bromine and sodium methoxide on montanamide. The converse operation (the preparation of montanic acid from ceryl alcohol by the malonic ester synthesis) could not be effected, since cerylmalonic ester could not be obtained from ceryl iodide and sodiomalonic ester under the most varied conditions. *Ceryl iodide*, $C_{26}H_{53}I$, m. p. 55—56°, was obtained by the action of iodine and red phosphorus on ceryl alcohol. H. W.

Action of Thionyl Chloride on Certain Lactones. PHILIPPE BARBIER and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1913, [iv], **13**, 223—229).—A critical survey of the action of thionyl chloride on organic substances is given. The authors have investigated the effect of boiling certain γ-lactones (1 mol.) in benzene solution with thionyl chloride (1·1 mol.). The product of the reaction was poured into excess of methyl or ethyl alcohol and subsequently examined in the form of its methyl or ethyl ester. In these circumstances, thionyl chloride transforms the γ-lactones employed (except coumarin) into esters of γ-hydroxy-acids according to the scheme:

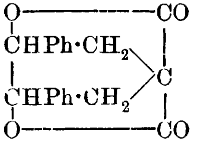
$$\begin{array}{l}R\cdot CH\cdot CH_2\cdot CH_2 \\ O\text{———}CO\end{array} \xrightarrow{SOCl_2} \begin{array}{l}R\cdot CH\cdot CH_2\cdot CH_2\cdot COCl \\ O\cdot SOCl\end{array} \xrightarrow{2C_2H_5OH}$$

$$\begin{array}{l}R\cdot CH\cdot CH_2\cdot CH_2\cdot CO_2Et \\ OH\end{array} + SO{<}\begin{array}{l}OEt \\ Cl\end{array} + HCl.$$

γ-Valerolactone was transformed into ethyl γ-hydroxyvalerate,

b. p. 80—81°/12 mm. (compare Neugebauer, A., 1885, 651), from which a phenylurethane could not be obtained.

γ-Phenyl-γ-butyrolactone, m. p. 37—38°, b. p. 175—176°/11 mm. (Jayne, A., 1883, 472; Fittig and Leoni, A., 1898, i, 196), was prepared by the condensation of bromoacetophenone with ethyl sodiomalonate and saponification of the crude product with alcoholic sodium hydroxide at 160°. At the high temperature employed, the latter substance probably acted as a reducing agent. In addition, small quantities of benzoylpropionic acid and of a neutral *substance*, m. p. 190—192°, probably a dilactone (annexed formula), were obtained. When acted on successively by thionyl chloride and ethyl alcohol, γ-phenyl-γ-butyrolactone yielded *ethyl γ-hydroxy-γ-phenylbutyrate*, b. p. 158—160°/17 mm.



Coumarin did not react with thionyl chloride under the conditions employed. H. W.

Action of Thionyl Chloride on Certain Lactonic Acids.

PHILIPPE BARBIER and RENÉ LOCQUIN (*Bull. Soc. chim.*, 1913, [iv], **13**, 229—236. Compare preceding abstract).—The experimental conditions chosen were the same as those previously described (*loc. cit.*). In these circumstances, thionyl chloride does not cause a rupture of the lactonic grouping, the product of the reaction being the lactonic acid chloride. This result is not influenced by the use of an excess of thionyl chloride.

Methylparaconyl chloride, b. p. about 142°/10 mm., obtained by the action of thionyl chloride on methylparaconic acid, was converted by methyl alcohol into *methyl methylparaconate*, b. p. 145—146°/11 mm.

In similar circumstances, terebic acid slowly yielded the corresponding chloride, b. p. 143°/12 mm., from which *methyl terebate*, b. p. 148—149°/17 mm., was obtained.

ββ-Dimethylbutyrolactone-γ-carboxylic acid (Perkin and Thorpe, T., 1899, **75**, 56) gave the corresponding chloride, which, when treated with methyl alcohol, yielded the *methyl* ester, b. p. 149—150°/12 mm.

Similarly, terpenylic acid formed terpenyl chloride, methyl terpenylate, b. p. 145—147°/15 mm., and ethyl terpenylate, m. p. 37·5°, b. p. 174—177°/15 mm. Fittig and Levy (A., 1890, 873) give b. p. 305°/ordinary pressure, whereas Simonsen (T., 1907, **91**, 187) found 169—171°/15 mm.

Phenylparaconyl chloride, prepared by the action of thionyl chloride on anhydrous phenylparaconic acid, m. p. 106°, 115°, or 121° (compare Jayne, A., 1883, 473; Fittig and Röders, A., 1890, 621) yielded, when decomposed by water, the acid, m. p. 99°. With methyl alcohol it yielded *methyl phenylparaconate*, m. p. 69—70°, b. p. 211°/14 mm. In the case of phenylparaconic acid, small quantities of polyphenylcrotonic acid, m. p. 179°, were also isolated.

The authors have attempted unsuccessfully to repeat the previously recorded transformation of terebic and phenylparaconic acids into the

anhydrides of *cis*-3 : 3-dimethyl*cyclo*propane-1 : 2-dicarboxylic acid and *cis*-3-phenyl*cyclo*propane-1 : 2-dicarboxylic acid (A., 1911, i, 722) under the action of thionyl chloride. They now attribute this result to the presence of some impurity in the specimen of thionyl chloride used, and point out that the substance is frequently contaminated with phosphoryl chloride, stannic chloride, sulphur trioxide, etc., to the presence of which the irregular results frequently obtained by the application of the reagent are ascribed. H. W.

$\gamma\gamma\gamma$-Trichloro-β-hydroxybutyric Acid and $\gamma\gamma\gamma$-Trichlorocrotonic Acid. KARL VON AUWERS and M. SCHMIDT (*Ber.*, 1913, **46**, 487—494. See following abstract).—$\gamma\gamma\gamma$-Trichloro-β-hydroxybutyric acid, m. p. 118—119° (von Thurnlackh, A., 1892, 429), is best obtained by gently boiling a mixture of malonic acid, chloral, and acetic acid for several hours; a certain specimen of malonic acid, although apparently normal in all other respects, always failed to give this reaction. The substance can be distilled almost undecomposed in small quantities, b. p. 181—188°/17 mm.; methyl ester, rhombohedral crystals, m. p. 61—62°, b. p. 135—136°/13 mm.; *ethyl* ester, silky needles, m. p. 56—57°, b. p. 143—144°/12 mm.; the *acetyl* derivative, needles, m. p. 97—99°, gives an oily *methyl* ester, b. p. 130°/13 mm., $D_4^{14\cdot3}$ 1·3937, $n_D^{14\cdot5}$ 1·46815, and an oily *ethyl* ester, b. p. 134°/10 mm., $D_4^{14\cdot1}$ 1·3395, $n_D^{14\cdot1}$ 1·46458. All endeavours to produce a substance, $\begin{matrix}OH\cdot CH\cdot CCl_2 \\ \mid \\ CH_2\text{-}CO\end{matrix}\!\!>\!O$, by elimination of hydrogen chloride from the trichlorohydroxybutyric acid were fruitless.

The method described by Kötz (A., 1907, i, 707) for the preparation of $\gamma\gamma\gamma$-trichlorocrotonic acid is found to yield the above trichlorohydroxybutyric acid, and the m. p. given for the substance (*loc. cit.*) agrees with that of this acid. It is now found that the elements of water can be eliminated from trichlorohydroxybutyric acid by heating with acetic anhydride and sodium acetate; the resultant *$\gamma\gamma\gamma$-trichlorocrotonic acid* forms needles, m. p. 113—114°, b. p. 143—146°/18 mm.; it immediately reduces potassium permanganate in the cold, and is rapidly decomposed by hot water with formation of hydrochloric acid. The *potassium* and *silver* salts were prepared, the latter of which when heated in benzene on the water-bath eliminates silver chloride with the formation of a mixture of substances mainly complex, but possibly containing a little of the *lactone*, $\begin{matrix}CH\text{-}CCl_2 \\ \| \\ CH\text{--}CO\end{matrix}\!\!>\!O$. The acid forms an oily *methyl* ester, b. p. 85·4°/12 mm., $D_4^{21\cdot4}$ 1·3968, $n_D^{21\cdot2}$ 1·48975, and an oily *ethyl* ester, b. p. 100·5°/13 mm., $D_4^{14\cdot2}$ 1·3375, $n_D^{14\cdot2}$ 1·48693.

From the above results it follows that the group $-CCl_3$ exerts no special spectrochemical influence. D. F. T.

The Constitution of the Chlorides of 1 : 2- and 1 : 3-Dicarboxylic Acids. KARL VON AUWERS and M. SCHMIDT (*Ber.*, 1913, **46**, 457—487).—The consideration of the spectrochemical effect of chlorine in organic substances (von Auwers, A., 1912, ii, 1015) is extended to the question of the structure of such acid dichlorides

as succinyl and phthalyl chlorides (compare Scheiber, A., 1912, i, 559; Scheiber and Knothe, A., 1912, i, 701; Bredt, A., 1912, i, 411; Ott, A., 1912, i, 828). The decision of Brühl as to the symmetrical structure of phthalyl chloride (*Ber.*, 1907, **40**, 884, 896) is based on too little experimental evidence to be entirely satisfactory; an investigation of the specific exaltations of the refractivity and dispersive power of various acid chlorides nevertheless indicates the correctness of this view.

A comparison of the chlorides and ethyl esters of crotonic, benzoic, and cinnamic acid shows that the exaltations in specific refractivity stand in the order acid > chloride > ester, whilst for the dispersion the exaltation is least for the ester, the free acid and the chloride being approximately equal. Phthalyl chloride shows no exceptional exaltation when compared with ethyl phthalate, the values in fact being in good agreement with those for the corresponding derivatives of benzoic acid; the results, however, when compared with those calculated for the unsymmetrical formula $C_6H_4<\genfrac{}{}{0pt}{}{CCl_2}{CO-}>O$ would indicate an improbably large exaltation.

The ethyl ester and chloride of fumaric acid exhibit exaltations approximately equal to those of the corresponding phthalic acid compounds; *iso*phthalic ester and chloride have exaltations appreciably higher, but this is probably to be attributed to the effects of structure isomerism. Maleyl chloride could not be obtained sufficiently pure for spectrochemical investigation.

In order to throw further light on this question, most of the chlorides of the oxalic series of acids were examined from oxalic to sebacic acid, and no exaltation was observed except a trace in the case of oxalyl chloride which may be attributed to the -CO·CO- group. Succinyl and glutaryl chloride must therefore be entirely of the symmetrical dichloride structure.

In the absence of pure, simple derivatives of the dichlorolactone molecule $\genfrac{}{}{0pt}{}{CH\cdot CCl_2}{CH{-}{-}CO}>O$, $\alpha\delta$-dichloro-γ-valerolactone,

$$\genfrac{}{}{0pt}{}{CHCl\cdot CO{-}{-}{-}{-}{-}{-}}{CH_2\cdot CH(CH_2Cl)}>O$$

(Leuchs and Giua, A., 1912, i, 603, 604), was investigated and compared with the lactones of δ-methoxy- and δ-ethoxy-γ-hydroxyvaleric acids, and with methyl $\alpha\beta$-butyleneoxide-δ-carboxylate. All were found to be optically normal. It is therefore probable that the hypothetical dichlorolactonic structure for succinyl and phthalyl chlorides would also be optically normal.

d-cis-Camphoryl, *l-trans*-camphoryl, *d*-chlorocamphoryl, and dehydrocamphoryl chlorides from their spectrochemical behaviour are probably all normal acid chlorides. The first and third named certainly exhibit a certain negative exaltation, but as this is also to be observed with the corresponding esters it probably arises from the *gem*-dimethyl groups (see this vol., ii, 261).

A comparison of the chlorides and esters of chlorofumaric and fumaric acids shows a similar exaltation in the chloride and ester

of each acid, thus indicating the normal symmetrical structure of the chlorides. With chloromaleyl chloride, however, the molecular refraction is below that of the isomeric chlorofumaryl chloride, and is in agreement with that calculated on theoretical grounds for the structure $\begin{matrix} CH\cdot CCl_2 \\ \| \\ CCl-CO \end{matrix}\!\!>\!O$; the lactonic formula is also favoured by a consideration of the molecular volume (Ott, *loc. cit.*). The structure of phthalyl chloride, on the other hand, is almost certainly the symmetrical one, as is indicated by recent chemical and physicochemical investigations (Scheiber, *loc. cit.*; Ott, *loc. cit.*) and by the present confirmation of Brühl's results. The constitution of the chlorides of the isomeric camphoric acids, chlorocamphoric acid, and dehydrocamphoric acid is also decided in favour of the symmetrical acid chloride form (compare Scheiber and Knothe, *loc. cit.*).

Succinyl chloride gave curiously variable results for density, refraction, and dispersion, probably due to some difficultly removable impurity; a specimen regarded as pure, indicated a true acid chloride structure, as already suggested by Ott.

The following substances were examined, but only the refraction for sodium light is quoted below; the original paper gives the values for the α-, β-, and γ-lines also.

Acetyl chloride, b. p. 51—52°, $D_4^{20\cdot6}$ 1·1039, $n_D^{20\cdot8}$ 1·38831; *iso*valeryl chloride, b. p. 114·5—115·5°/771 mm., $D_4^{24\cdot3}$ 0·9854, $n_D^{24\cdot3}$ 1·41361; crotonyl chloride, b. p. 117—120°/754 mm., $D_4^{17\cdot4}$ 1·0822, $n_D^{17\cdot9}$ 1·46001; methyl αβ-butyleneoxide-δ-carboxylate [γδ-oxidovalerate],

$$\begin{matrix} CH_2 \\ | \\ O \end{matrix}\!\!>\!CH\cdot CH_2\cdot CH_2\cdot CO_2Me,$$

$D_4^{24\cdot1}$ 1·0731, $n_D^{24\cdot7}$ 1·42589; δ-methoxy-γ-valerolactone, $D_4^{22\cdot6}$ 1·1205, $n_D^{23\cdot2}$ 1·44533; δ-ethoxy-γ-valerolactone, $D_4^{24\cdot5}$ 1·0718, $n_D^{24\cdot9}$ 1·44082; αδ-dichloro-γ-valerolactone, $D_4^{24\cdot2}$ 1·4367, $n_D^{24\cdot6}$ 1·49624; oxalyl chloride, b. p. 60—61°, $D_4^{13\cdot4}$ 1·4884, $n_D^{12\cdot9}$ 1·43395; malonyl chloride, b. p. 58°/26 mm., $D_4^{22\cdot9}$ 1·4505, $n_D^{23\cdot4}$ 1·45973; succinyl chloride, b. p. 88·8°/19 mm., $D_4^{15\cdot2}$ 1·3948, $n_D^{15\cdot2}$ 1·47348; glutaryl chloride, b. p. 107—108°/16 mm., $D_4^{21\cdot8}$ 1·3221, $n_D^{20\cdot2}$ 1·47281; suberyl chloride, b. p. 149—150°/12 mm., $D_4^{20\cdot8}$ 1·1718, $n_D^{20\cdot6}$ 1·46847; sebacyl chloride, b. p. 168—170°/16 mm., $n_D^{18\cdot3}$ 1·46836; fumaryl chloride, b. p. 158—160°, $D_4^{16\cdot8}$ 1·4117, $n_D^{18\cdot1}$ 1·50038; chlorofumaryl chloride, b. p. 87—87·5°/28 mm., $D_4^{18\cdot2}$ 1·5653, $n_D^{17\cdot6}$ 1·52172; ethyl chlorofumarate, b. p. 135—136°/17 mm., $D_4^{18\cdot7}$ 1·1886, $n_D^{18\cdot3}$ 1·45782; *uns* chloromaleyl chloride $\left(\begin{matrix} CH\cdot CCl_2 \\ \| \\ CCl-CO \end{matrix}\!\!>\!O\text{, Ott, } \textit{loc. cit.}\right)$, b. p. 82·2—82·5°/26 mm., $D_4^{17\cdot7}$ 1·6055, $n_D^{18\cdot1}$ 1·51362.

Benzoyl chloride, $D_4^{20\cdot9}$ 1·2105, $n_D^{20\cdot9}$ 1·55376; cinnamoyl chloride, b. p. 131°/20 mm., $D_4^{45\cdot3}$ 1·1617, $n_D^{42\cdot5}$ 1·61364; phthalyl chloride, b. p. 156—157°/23 mm., $D_4^{15\cdot2}$ 1·4081, $n_D^{15\cdot5}$ 1·57099; ethyl phthalate, b. p. 162—163°/7 mm., $D_4^{17\cdot8}$ 1·1202, $n_D^{17\cdot7}$ 1·50293; *iso*phthalyl chloride, m. p. 40—41°, $D_4^{47\cdot3}$ 1·3880, $n_D^{46\cdot9}$ 1·56999; ethyl *iso*phthalate, b. p. 170—170·5°/24 mm., $D_4^{16\cdot7}$ 1·1239, $n_D^{17\cdot5}$ 1·50815; *d-cis*-camphoryl chloride, b. p. 144·5—145·5°/17 mm., $D_4^{20\cdot2}$ 1·2446, $n_D^{19\cdot9}$ 1·50133; ethyl *d-cis*-camphorate, b. p. 150—152°/8 mm., $D_4^{19\cdot2}$ 1·0318, $n_D^{19\cdot1}$ 1·45613;

l-trans-camphoryl chloride, b. p. 153—154°/24 mm., $D_4^{20\cdot6}$ 1·2270, $n_D^{20\cdot7}$ 1·49880; ethyl *l-trans*-camphorate, b. p. 155—157°/20 mm., D_4^{22} 1·0282, $n_D^{21\cdot6}$ 1·45454; *d*-chlorocamphoryl chloride, b. p. 152—152·5°/17 mm., $D_4^{31\cdot5}$ 1·3219, $n_D^{31\cdot3}$ 1·50797; *d*-dehydrocamphoryl chloride, b. p. 160—161°/32 mm., $D_4^{49\cdot3}$ 1·2176, n_D^{48} 1 50433. D. F. T.

Preparation of Terpenylic and Terebic Acids. RÉNÉ LOCQUIN (*Bull. Soc. chim.*, 1913, [iv], **13**, 166—169).—Tiemann and his collaborators (A., 1895, i, 548; 1896, i, 385; 1897, i, 81) have suggested that methoethylheptanonolide yields terpenylic acid on oxidation by chromic acid, and terebic acid when oxidised by nitric acid, and may be used as a source of these two acids. The author finds that on oxidation by nitric acid, terpenylic acid is the chief product (58·2% of the theoretical), the yield of terebic acid (18·6% of the theoretical) being small. The preparation and separation of the two acids are described. T. A. H.

Attempts to Synthesise Monosubstituted Paraconic Acids. PHILIPPE BARBIER and RÉNÉ LOCQUIN (*Bull. Soc. chim.*, 1913, [iv], **13**, 161—166. Compare A., 1911, i, 708)—The only method hitherto available for the preparation of these acids is that of Fittig (A., 1890, i, 583), which gives poor yields when aliphatic aldehydes are used. The authors have modified Reformatsky's reaction for the production of *β*-hydroxy-acids (A., 1896, i, 128) with a view to preparing monosubstituted paraconic acids by this means, but the yields are poor, only 7% of the theoretical yield of *iso*propylparaconic acid being obtained, and 12% of the calculated yield of hexylparaconic acid. The latter acid had m. p. 79—80°, which is 10° below that recorded by Schneegans. T. A. H.

Preparation of Strontium Cholate. KNOLL & Co. (D.R.-P. 254530).—*Strontium cholate*, $(C_{24}H_{39}O_5)_2Sr,10H_2O$, colourless, hair-like tufts is readily obtained when an alcoholic solution of cholic acid is heated with an aqueous solution (or suspension) of strontium hydroxide; it has an important therapeutic action. F. M. G. M.

Oxidation of Aldehydes by an Aqueous Solution of Bromine. ERNEST ANDERSON (*Amer. Chem. J.*, 1913, **49**, 179—184).—It is usually supposed that the method used for converting aldoses into the corresponding acids by oxidation with aqueous solution of bromine is not applicable to the ordinary aldehydes. In order to test this question, several aldehydes have been subjected to the action of bromine, and the oxidation products isolated. The results show that whilst benzaldehyde, acetaldehyde, paraldehyde, and formic acid give good yields of the corresponding acids, namely, benzoic, acetic, and carbonic, formaldehyde and aldol are oxidised to only a small extent, and salicylaldehyde and chloral not at all.

Acetaldehyde was found to give 71% of the theoretical yield of acetic acid; benzaldehyde, 80% of benzoic acid; paracetaldehyde, 86% of acetic acid; and formic acid, 80% of carbonic acid. E. G.

Glyoxal. CARL D. HARRIES (*Ber.*, 1913, **46**, 294—296. Compare A., 1907, i, 183).—Polymerisation of glyoxal is accelerated by the presence of moisture. When technical glyoxal which has been dried over phosphoric oxide at 95° is distilled alone, the unimolecular compound is obtained. It is claimed that Meisenheimer's depolymerisation of methylglyoxal (A., 1912, i, 831) was foreshadowed in the above-mentioned paper. J. C. W.

Catalytic Preparation of Ketones. JEAN B. SENDERENS (*Ann. Chim. Phys.*, 1913, [viii], **28**, 243—344).—A résumé of work already published (A., 1909, i, 286, 627; 1910, i, 11, 179, 489; 1911, i, 134, 302; 1912, i, 537). H. W.

The Synthesis of Sugars by means of Radioactive Emanations. JULIUS STOKLASA, JOHANN ŠEBOR, and WENZEL ZDOBNICKÝ (*Compt. rend.*, 1913, **156**, 646—648. Compare A., 1911, i, 178, 769).—As with ultra-violet rays, so under the influence of radium emanation hydrogen and carbon dioxide react in the presence of potassium hydrogen carbonate, giving formaldehyde, which in the presence of potassium hydroxide polymerises and gives reducing sugars. No formates could be detected during the reaction. The sugars formed are a mixture of hexoses giving phenylosazones, separable into two fractions, one, m. p. 198—199°, and the other, m. p. 178°. Unlike the sugars obtained in the photochemical synthesis under the influence of ultra-violet rays (compare A., 1912, i, 606), these sugars are optically active and have $[\alpha]_D$ +17·58°. By distillation with hydrochloric acid indications of the presence of a pentose were obtained. W. G.

Preparation of δ-Dimethylamino-Δ^{α}-*iso*amylene and δ-Dimethylamino-Δ^{α}-butylene. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 254529. Compare A., 1912, i, 742, 781; and Euler, A., 1897, i, 585).—*δ-Dimethylamino-Δ^{α}-*isoamylene*,*

$$CH_2{:}CH{\cdot}CHMe{\cdot}CH_2{\cdot}NMe_2,$$

a colourless liquid, b. p. 113—116°, and identical with the so-called "β-methyldimethylpyrrolidine" (Euler, *loc. cit.*), can be prepared by heating γ-hydroxy-β-methylbutyldimethylamine with concentrated sulphuric acid (3 parts) during three to four hours at 100°, or with 50% sulphuric acid (5—10 parts) during ten hours at 150—160°.

δ-Dimethylamino-Δ^{α}-butylene, $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_2$, a colourless liquid, b. p. 94—96°, is obtained in a similar manner from γ-hydroxybutyldimethylamine with 20—30% sulphuric acid (5 parts) at 200° during ten hours.

These compounds have an odour of coniine, and find employment in the preparation of isoprene and erythene. F. M. G. M.

Preparation of δ-Dimethylamino-γ-dimethylbutan-β-ol. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 254713).—When methyl tetramethyldiamino*iso*propyl ketone (following abstract) is boiled during one hour with 20% sulphuric acid (4—6 parts), it furnishes *dimethylamino-β-acetylallylene*, $CH_2{:}CAc{\cdot}CH_2{\cdot}NMe_2$, which

on reduction gives rise to δ-dimethylamino-γ-methylbutan-β-ol (A., 1911, i, 598), a colourless oil, b. p. 67—69°/17 mm. F. M. G. M.

Preparation of Amino- and Diamino-ketones of the Aliphatic Series. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 254714. Compare A., 1911, i, 598, and preceding abstract). —When dimethylaminomethyl alcohol, $OH\cdot CH_2\cdot NMe_2$, or tetramethyldiaminomethane, $Me_2N\cdot CH_2\cdot NMe_2$, are condensed with acetone (or its homologues), the following reactions take place (R = hydrogen or alkyl).

1. $CH_3\cdot CO\cdot CH_2R + OH\cdot CH_2\cdot NMe_2 = CH_3\cdot CO\cdot CHR\cdot CH_2\cdot NMe_2 + H_2O.$
2. $CH_3\cdot CO\cdot CH_2R + NMe_2\cdot CH_2\cdot NMe_2 = NHMe_2 + CH_3\cdot CO\cdot CHR\cdot CH_2\cdot NMe_2.$

The following compounds are described: dimethyl-β-acetylpropylamine (*loc. cit.*), b. p. 51—51·5°/13 mm.

ββ-Acetylmethyltrimethylenetetramethyldiamine [*methyl tetramethyldiamino*tert.-*butyl ketone*], $CH_3\cdot CO\cdot CMe(CH_2\cdot NMe_2)_2$, a colourless, viscous oil, b. p. 110—112°/18 mm., from methyl ethyl ketone and dimethylaminomethyl alcohol.

β-Acetylethyldimethylamine [*methyl dimethylaminoethyl ketone*], $CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot NMe_2$, a colourless oil with a strong ammoniacal odour, b. p. 57—58°/18 mm.; and *β-acetyltrimethylenetetramethyldiamine* [*methyl tetramethyldiamino*iso*propyl ketone*], $CH_3\cdot CO\cdot CH(CH_2\cdot NMe_2)_2$, a colourless, odourless, viscous oil, b. p. 96—98°/16 mm.

These compounds are employed in the preparation of erythrene and isoprene. F. M. G. M.

Preparation of Urethanes of Tertiary Alcohols. EMANUEL MERCK (D.R.-P. 254472. Compare this vol., i, 5).—It is found that the halogen formyl esters described previously can be readily converted by the action of ammonia or substituted ammonias into urethanes of tertiary alcohols:

$$OR\cdot CO\cdot Cl + 2NHR_1R_2 \longrightarrow OR\cdot CO\cdot NR_1R_2 + NHR_1R_2,HCl,$$

where RO is a tertiary alcoholic group, and R_1 and R_2 hydrogen, alkyl or aryl groups.

Dimethylethylcarbinyl chloro-formate with alcoholic ammonia furnishes a *urethane*, colourless needles, m. p. 85—87°; an *ethyl urethane*, a colourless oil, b. p. 89°/13 mm., and 86°/11 mm.; a *phenylurethane*, colourless crystals, m. p. 44—47°, b. p. 146°/9 mm.; a *methylphenylurethane*, a colourless oil, b. p. 133°/13 mm., and with *p*-phenetidine a p-*ethoxyphenylurethane*, colourless needles, m. p. 88—90°, whilst methyldiethylcarbinol gives rise to a *urethane*, colourless needles, m. p. 61°, and a *phenylurethane*. F. M. G. M.

Behaviour of Formamide Under the Influence of the Silent Electric Discharge. The Question of Nitrogen Assimilation. WALTHER LÖB (*Ber.*, 1913, **46**, 684—697).—In the course of some experiments on the influence of the silent electric discharge on various combinations of moist carbon dioxide, carbon monoxide,

alcohol and ammonia, with or without oxygen or air, the only compound obtained which could be regarded as of interest to the problem of nitrogen assimilation was hexamethylenetetramine (A., 1909, i, 769). Further investigations on the behaviour of this compound towards oxidising and reducing agents, and towards living yeast, showed that it had no relation to the amino-acids, and, therefore, throws no light on the general question. The discovery of Losanitsch and Jovitschitsch (A., 1897, i, 179) that ammonia and carbon monoxide produce formamide led the author to regard this compound as an intermediate stage, and to try the effect of the silent discharge on the dry substance and on an aqueous solution, both boiling under reduced pressure. In the former case, oxamide was deposited on the sides of the discharge tube, and in the latter, as would be expected, ammonium oxamate. Some reduction was therefore necessary in order to arrive at glycine. Previous experience had shown that water itself is a reducing agent under these conditions (A., 1906, ii, 324), whilst the reaction $CO + H_2O = CO_2 + H_2$ had also to be considered. The resolution of some formamide into carbon monoxide and ammonia was to be expected, and, indeed, an examination of the gases liberated during the experiment proved the presence of these substances. The existence of glycine in the product, after the removal of ammonia, was unquestionably demonstrated by the formaldehyde test of Sörensen, the "deaminising" method of van Slyke, the reaction with triketohydrindene hydrate, and the formation of the naphthalenesulphonyl compound (E. Fischer and Bergell, A., 1903, i, 24).

The presence of glycine could also be observed on repeating the experiment with moist carbon monoxide and ammonia. The formation of glycine from carbon dioxide (which breaks down into carbon monoxide under the influence of the silent discharge), ammonia, and water is therefore a process of reduction, and the oxidation of glycine should lead to these or intermediate products. Halsey has shown that the products of the action of permanganate do, indeed, include formamide and oxamic acid (A., 1898, ii, 529).

The reactions may be formulated thus:

$$\text{(I)}\quad 2CO_2 + 2NH_3 + H_2O \longrightarrow 2H\cdot CO\cdot NH_2 + H_2O + O_2.$$

$$\text{(II)}\quad 2H\cdot CO\cdot NH_2 + H_2O \longrightarrow NH_2\cdot CO\cdot COONH_4 + H_2.$$

$$\downarrow$$

$$NH_2\cdot CH_2\cdot COONH_4 + O.$$

Reference must be made to the original paper for the experimental details, but it may be said that the amount of oxamide accumulated during twenty hours from 20 grams of dry formamide, boiling at 110°/15 mm., was about 0·05—0·08 gram, whilst about 0·01 gram of ammonium oxamate was obtained from a 5—10% solution during the same time, the glycine present being comparable with a 0·01% solution.

J. C. W.

The Diamide of Sulpho*iso*butyric Acid. Jacob Moll van Charante (*Rec. trav. chim.*, 1913, **32**, 90—96. Compare A., 1905, i, 16).—Sulpho*iso*butyrodiamide, $NH_2\cdot SO_2\cdot CMe_2\cdot CO\cdot NH_2$, was obtained by passing ammonia into a cold methyl-alcoholic solution of methyl

chlorosulpho*iso*butyrate. It decomposed without melting at about 340°. At 17°, one part of diamide dissolved in 201·8 parts of water, whilst at 100° the solubility was one part in 24·9. It was insoluble in the other usual solvents. Attempts to condense it with carbonyl chloride, in the presence or absence of a catalyst, were unsuccessful. Similarly, oxalyl chloride, alone or in benzene solution, was without action on it.

To determine whether it was possible to cause a sulphonamide to react with oxalyl chloride, a solution of benzenesulphonamide and oxalyl chloride in benzene was boiled during two and a-half days. Hydrogen chloride was slowly evolved, and *diphenylsulphonoxamide*, $C_2O_2(NH{\cdot}SO_2Ph)_2$, formed. It had m. p. 256° (corr., slight decomp.).

H. W.

Extraction of Glutamic Acid Hydrochloride and Betaine Hydrochloride from Molasses Residue. HUGO STOLTZENBERG (*Ber.*, 1913, **46**, 557—566. Compare A., 1912, i, 680).—Molasses residue is mixed with hydrochloric acid and subsequently saturated with hydrogen chloride. The crude hydrochlorides which are precipitated are treated with alcohol and hydrogen chloride, whereby glutamic acid hydrochloride is converted into the readily soluble ester hydrochloride. The solution of the latter is concentrated to a syrup, the residue boiled with water, the solution filtered from humin, decolorised, and concentrated until crystallisation begins, when it is again saturated with hydrogen chloride, whereby glutamic acid hydrochloride is precipitated. This has m. p. 213° when rapidly heated, and is shown to be partly racemised, the highest observed value for $[\alpha]_D^{15}$ being $+26{\cdot}15°$ in 10% hydrochloric acid solution, whereas Siegfried and Schutt (A., 1912, i, 952) observed $+34{\cdot}89°$. Purification by transformation into the barium salt and subsequent reprecipitation of the hydrochloride effected no improvement. The filtrates obtained after removal of glutamic acid hydrochloride deposited, on evaporation, betaine hydrochloride, and contained also a strongly acid *substance*, which could not be obtained in the crystalline state.

The remainder of the paper consists of a reply to the criticisms brought by Ehrlich (A., 1912, i, 835) against the previous work of the author (*loc. cit.*). Stoltzenberg's process of isolating betaine hydrochloride from molasses differs essentially from that of Ehrlich (1904, D.R.-P. 157173), in that hydrochloric acid and alcohol are employed in the given order in the former process, in the inverse order in the latter. In the second method, the chemical nature of the residue is not affected by agitation with alcohol, and the hydrogen chloride is only used to precipitate the hygroscopic betaine. In the first method, however, the composition of the residue itself is greatly altered by the action of the hydrogen chloride. Ehrlich's statement that the alcohol consumption is less in his process than in that of the author is incorrect.

The paper concludes with a critical survey of the historical development of the subject as described by Ehrlich. H. W.

Action of Sodium Hypobromite on Semicarbazide. ROBERT STOLLÉ (*Ber.*, 1913, **46**, 260. Compare Linch, T., 1912, **101**, 1755).

—The product of the action of sodium hypobromite on semicarbazide is hydrazodicarbonamide, and not *p*-urazine as described by Linch. The compound obtained on oxidation with chromic acid is therefore azodicarbonamide (Thiele, A., 1892, 1295 and 1430), and not a stable tetrazine. J. C. W.

Salt- and Complex Salt-Formation with Amino- and Hydroxy-acetohydroxamic Acids. HEINRICH LEY and F. MÄNNCHEN (*Ber.*, 1913, **46**, 751—758).—On account of the similarity in structure between the carboxylic and hydroxamic acids, the authors have investigated certain derivatives of the latter in which the formation of complex salts was to be expected. It is found that internally complex salts are obtainable from amino- and hydroxy-hydroxamic acids somewhat analogous to those obtained from the simple amino-acids. To the normal copper salts is attributed the structure $R\cdot C{<}^{NO}_{-O-}{>}Cu$; acid salts could be obtained only from substituted hydroxamic acids, and the constitution suggested is

$$CH_2{<}^{\quad\quad NH_2}_{C(:NOH)\cdot O}{>}M{<}^{NH_2\quad\quad}_{O\cdot C(:NOH)}{>}CH_2$$

(compare Ley, A., 1909, i, 138), where M represents a bivalent metal atom. Complex salts containing a bivalent metal together with an alkali metal could be obtained both from the unsubstituted and substituted acids; the heavy metal is present as part of a complex ion, but from the colour of the salts of the amino- and hydroxy-substituted acids the conclusion is drawn that this atom is also linked with the anion complex by supplementary partial valencies.

Aminoacetohydroxamic acid, $NH_2\cdot CH_2\cdot C(OH){:}N\cdot OH$, was obtained by the interaction of equimolecular quantities of hydroxylamine, ethyl aminoacetate, and sodium ethoxide in alcoholic solution; it was precipitated as the copper salt and recovered by the action of hydrogen sulphide; it is a colourless, crystalline solid, m. p. 107° (approx.); normal *copper* salt, green, amorphous powder, obtained by mixing aqueous solutions of the acid and copper acetate; *acid copper* salt, obtained by adding copper acetate to a solution of the *sodium* salt, separates in violet crystals; *acid nickel* salt, prepared by the addition of dilute sodium hydroxide solution to a solution of nickel acetate with a bimolecular quantity of the acid, forms deep red crystals; the complex *sodium nickel* salt, $(C_2H_4O_2N_2)_2NiNaH,H_2O$, yellowish-red, rhombic tablets, was obtained by treating a solution of the sodium salt with nickel acetate and sodium hydroxide.

Anilinoacetohydroxamic acid, $NHPh\cdot CH_2\cdot C(OH){:}N\cdot OH$, colourless needles, m. p. 126° (decomp.), separates in the form of the *sodium* salt when ethyl anilinoacetate is treated in alcoholic solution with an equimolecular quantity of hydroxylamine; *copper* salt, green, amorphous solid.

Phenylglycollohydroxamic acid, $OH\cdot CHPh\cdot C(OH){:}N\cdot OH$, colourless, rhombic leaflets, m. p. 132°, was prepared in a similar manner to the last; *sodium* salt, needles; the green *copper* salt, like that of the last acid, gives a violet solution in aqueous sodium hydroxide; the *nickel sodium* salt could be obtained only as a reddish-yellow solution.

The free acid soon decomposes in solution with the formation of benzaldehyde.

Phenoxyacetohydroxamic acid, OPh·CH$_2$·C(OH):N·OH, prepared in an analogous manner from ethyl phenoxyacetate, forms colourless leaves, m. p. 114°; the addition of copper acetate and sodium hydroxide solution to the solution of the *sodium* salt causes the formation of the crystalline, bluish-violet *copper sodium* salt,

$$(C_8H_7O_3N)_2CuNa_2,2H_2O,$$

which is converted by water into the green *copper* salt.

The interaction of equimolecular quantities of hydroxylamine, ethyl lactate, and sodium ethoxide in alcoholic solution produces unstable *sodium lactohydroxamate*, CH$_3$·CH(OH)·C(ONa):NOH.

An aqueous solution of acetohydroxamic acid (Miolati, A., 1892, 699) when treated with copper acetate and sodium hydroxide, after some days, deposits blue crystals of a complex *copper sodium* salt,

$$(C_2H_3O_2N)_2CuNa_2,7H_2O,$$

which is converted by water into the ordinary green copper salt.

D. F. T.

New Method of Preparing Nitriles of the Aliphatic Series. ALEXANDER E. ARBUZOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 74—79).—Catalytic decomposition of the hydrazones of aliphatic aldehydes in presence of cuprous chloride, platinous chloride, or zinc chloride always yields nitriles to some extent, although the yield varies considerably. In general, hydrazones containing small radicles give very small proportions of nitriles, the decomposition then yielding principally substituted indoles and other compounds (see this vol., i, 388). On the other hand, hydrazones containing large radicles, such as *iso*valeraldehydephenylhydrazone, undergo nitrilic decomposition almost exclusively: $C_5H_{10}N·NHPh = NH_2Ph + C_5H_9N$.

*iso*Valeronitrile, thus obtained in 56% yield, is a colourless, mobile liquid, b. p. 128·5°, or 52·5—53°/50 mm., D_0^0 0·7884, D_0^{20} 0·8054 (compare Erlenmeyer, *Annalen*, 1871, **160**, 266).

*iso*Butyronitrile is similarly obtained from *iso*butaldehydephenylhydrazone in 37% yield, and *n*-heptonitrile, b. p. 183·5°, D_0^{20} 0·8107 (compare Henry, A., 1905, i, 561), from *n*-heptaldehydephenylhydrazone.

T. H. P.

Chromates and Mercuric Cyanide. DANIEL STRÖMHOLM (*Zeitsch. anorg. Chem.*, 1913, **80**, 155—160. Compare A., 1912, ii, 648).—The following compounds have been obtained:

$$(NH_4)_6Cr_2O_7Cl_4,6Hg(CN)_2,4H_2O,$$

long, reddish-yellow crystals, with only a narrow range of stability; $2K_2CrO_4,3Hg(CN)_2,2H_2O$. A chloride-chromate salt has not been obtained in the case of potassium.

C. H. D.

Potassium β-Ferricyanide. HORACE L. WELLS (*Amer. Chem. J.*, 1913, **49**, 205—206).—Hauser and Biesalski (this vol., i, 26) have stated that the potassium β-ferricyanide described by Locke and Edwards (A., 1899, i, 407) is merely the ordinary salt, contaminated with colloidal Prussian-blue. It is now shown that this view is incorrect, and that Hauser and Biesalski have overlooked the fact that the

β-ferricyanide does not yield a precipitate with bismuth nitrate, and is thus readily distinguished from the ordinary salt. E. G.

Crystalline Form of Two Scandium Platinocyanides. PETR N. TSCHIRVINSKI (*Zeitsch. Kryst. Min.*, 1913, **52**, 44—47).—The crystalline form, as observed under the microscope, is described for the yellow salt, $Sc_2[Pt(CN)_4]_3,18H_2O$, and for the red salt,

$$Sc_2[Pt(CN)_4]_3,21H_2O.$$

New observations are also given for the yttrium salt,

$$Y_2[Pt(CN)_4]_3,21H_2O.$$

L. J. S.

Magnesium Methyl Iodide. PIERRE JOLIBOIS (*Compt. rend.*, 1913, **156**, 712—714. Compare A., 1912, i, 675, 753).—The action of methyl iodide on magnesium in dry ether is a simple one, there being practically no secondary reaction under any conditions. The magnesium methyl iodide, so obtained, when heated in a vacuum, first loses its ether of constitution at 130°, and at 240° methane is evolved, according to the equation: $2MgMe_2,MgI_2 = 3CH_4 + Mg_2C,2MgI_2$.

By raising the temperature to 600° no more gas is evolved. The residue is a voluminous, yellow mass, from which only a definite portion of the iodine can be extracted in the form of magnesium iodide by dry ether, leaving a *compound*, having the definite composition Mg_2C,MgI_2, which is violently decomposed by water with development of light and heat, and, on controlled decomposition by moist ether, yields practically pure methane. W. G.

The Catalytic Hydrogenation of Camphorone. Some New *cyclo*Pentane Hydrocarbons. MARCEL GODCHOT and FÉLIX TABOURY (*Compt. rend.*, 1913, **156**, 470—473).—Camphorone on hydrogenation in the presence of reduced nickel at 130° yields dihydrocamphorone (compare Semmler, A., 1904, i, 260). If the reduction is carried out at 280°, the product obtained is 1-*methyl*-3-iso*propyl*cyclo*pentane*, $C_5H_8MePr^\beta$, a liquid with a terpene-like odour, b. p. 132—134°, D^{19} 0·773, n_D^{19} 1·4250. The same compound is obtained by dehydrating 1-methyl-3-*iso*propyl*cyclo*pentane-2-ol with zinc chloride, which furnishes a mixture of two isomeric unsaturated hydrocarbons, b. p. 143—145°, D^{18} 0·786, n_D^{18} 1·4465, non-separable, but which on hydrogenation at 170° are converted into the pentane hydrocarbon.

Dihydrocamphorone reacts with magnesium methyl iodide, giving a mixture of 1 : 2-*dimethyl*-3-iso*propyl*-Δ^1- and -Δ^2-cyclo*pentenes*, b. p. 150—155°, D^{17} 0·812, n_D^{17} 1·4500, which on hydrogenation at 180° are transformed into 1 : 2-*dimethyl*-3-iso*propyl*cyclo*pentane*, b. p. 146—148°, D^{16} 0·786, n_D^{16} 1·4337. Similarly by using magnesium *iso*propyl iodide a mixture of 1-*dimethyl*-2 : 3-*di*iso*propyl*-Δ^1- and -Δ^2-cyclo*pentene*, b. p. 160—168°, D^{18} 0·812, n_D^{18} 1·4509, is obtained, yielding on hydrogenation at 180°, 1-*methyl*-2 : 3-*di*iso*propyl*cyclo*pentane*, b. p. 150—152°, D^{17} 0·781, n_D^{17} 1·4318. W. G.

The *cyclo*Octane Series. VI. *cyclo*Octatetraene. RICHARD WILLSTÄTTER and MICHAEL HEIDELBERGER (*Ber.*, 1913, **46**, 517—527. Compare Willstätter and Waser, A., 1912, i, 17).—The previous

observations with *cyclo*octatetraene have been repeated and extended. The quaternary ammonium base is now distilled in a still lower vacuum and at a correspondingly lower temperature (30—45°). On cooling, the hydrocarbon solidifies to a pale yellow, crystalline mass, m. p. −27°. It forms an additive compound with bromine, taking up two atoms only. The *dibromide*, $C_8H_8Br_2$, crystallises in lustrous, snow-white needles, m. p. 70—71·5° (corr.). It decolorises permanganate instantaneously and tends to take up more bromine, but hydrogen bromide is then eliminated, and a *substance*, $C_8H_7Br_3$, m. p. 53—55°, is obtained instead of the tetrabromide.

The tetraene reacts immediately with chlorine, and hydrogen chloride is eliminated; an oily *chloride* is obtained, and can be separated into two fractions, both of which have the composition $C_8H_7Cl_3$.

With hydrogen bromide in acetic acid solution the tetraene forms a *hydrobromide*, C_8H_9Br, which is an almost colourless oil with a sweet odour, b. p. 85—87°/12·5 mm. It slowly decomposes in presence of oxygen, and gives an orange coloration with concentrated sulphuric acid.

The molecular refraction of *cyclo*octatetraene shows little or no exaltation. Similarly, the molecular dispersion (β—α) shows no marked exaltation, although in consequence of the greater dispersion in the ultra-violet the molecular dispersion, M_γ—M_α, shows a larger exaltation.

The tetraene behaves, like benzene, optically normal in regions where it is free from absorption; the dispersion is, however, abnormal in the region where selective absorption takes place.

Such selective exaltation of the molecular dispersion is even more marked in the case of the yellow fulvenes; data are quoted for methylethylfulvene and dimethylfulvene, as well as *cyclo*octatriene.

When *cyclo*octatetraene is hydrogenated by the platinum method the yellow colour disappears after the addition of 1·5 molecules of hydrogen. The first three molecules appeared to be absorbed in approximately equal times and the fourth more slowly, the actual figures being 35, 40, 40, and 95 minutes respectively.

Methylethylfulvene does not lose the yellow colour until reduction is nearly complete. The three molecules of hydrogen were absorbed in 7, 7, and 10 minutes.

The product, sec.-*butyl*cyclo*pentane*, is a mobile liquid, with an odour like limonene, b. p. 152—154°/725 mm., D_4^0 0·810.

The *cyclo*octane formed even from pure *cyclo*octatetraene is not pure, and probably contains an isomeride.

Pure *cyclo*octatetraene may be kept for several months without decomposition. E. F. A.

[Preparation of *cyclo*Hexene.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 254473. Compare A., 1899, i, 22; 1902, i, 2, and T., 1898, **73**, 941).—When the vapour of chloro*cyclo*hexane at 350—450°/15—20 mm. is conducted over a catalytic agent (such as barium chloride, aluminium oxide, or nickel chloride), it gives rise to *cyclo*hexene. F. M. G. M.

Rational Preparation of Some Benzene Homologues. II. FRANZ KUNCKELL and GEORG ULEX (*J. pr. Chem.*, 1913, [ii], **87**, 227—236).—A continuation of previous work (this vol., i, 29) on the preparation of benzene homologues by the interaction of alkyl esters of chloro-formic acid with aromatic hydrocarbons in the presence of aluminium chloride.

Methyl chloro-formate reacts with benzene to form toluene and *m*-xylene; with toluene it yields *p*-xylene and ψ-cumene.

The interaction of ethyl chloro-formate with benzene and toluene yields respectively *p*-diethylbenzene and 1-*methyl*-3 : 4-*diethylbenzene*, b. p. 200—203°, the constitution of which has been established by its oxidation to 4-methylphthalic acid.

m-Xylene reacts with ethyl chloro-formate, yielding 1 : 3-*dimethyl*-5-*ethylbenzene*, b. p. 182—188°, and with *p*-xylene to form 1 : 4-*dimethyl*-2-*ethylbenzene*, b. p. 183—185°.

The interaction of cumene with methyl and ethyl carbonates yields *dimethyl*iso*propylbenzene*, b. p. 195—210°, and *diethyl*iso*propylbenzene*, b. p. 250—256° respectively.

The addition of *iso*butyl chloro-formate to a mixture of aluminium chloride and benzene gives rise to *tert.*-butylbenzene, whilst the addition of aluminium chloride to a mixture of the ester with benzene yields *di*-(tert. ?)-*butylbenzene*, b. p. 225—235°, and *tri*-(tert. ?)-*butylbenzene*.

The preparation of a *p*(?)-methylbutylbenzene, b. p. 190—195°, and a *methyldibutylbenzene*, b. p. 241—247°, from toluene and *iso*butyl chloro-formate, and p-*methylamylbenzene*, b. p. 205—210°, from amyl chloro-formate and toluene is also described. F. B.

Chemical Action of Light. XXV. Autoxidations. III. GIACOMO L. CIAMICIAN and PAUL SILBER (*Ber.*, 1913, **46**, 417—422*).—A continuation of the investigation of the autoxidation of aromatic hydrocarbons (A., 1912, i, 174, 645). The results are in accordance with those of Suida (A., 1912, i, 957), but as the present authors gave prolonged exposure to light and investigated only the final products, indications of peroxides were but rarely observed.

Benzene in contact with water and oxygen is completely unaltered after several months' exposure to sunlight (compare Suida, *loc. cit.*).

Ethylbenzene under similar conditions gives a yellow aqueous layer, and after neutralisation with sodium carbonate, ether extracts acetophenone with some unchanged ethylbenzene; the former was characterised by its semicarbazone; this, it was observed, separates from methyl alcohol with one molecule of alcohol of crystallisation, which is lost on drying over sulphuric acid. The alkaline solution, which had been extracted with ether, was found to contain formic and benzoic acids.

Mesitylene, when treated similarly, gave a strongly acidic mixture, which after neutralisation yielded an ethereal extract containing mainly unchanged hydrocarbon, together with a small quantity of a non-volatile *substance* and a trace of an aldehyde. The aqueous liquid on acidification gave formic acid, mesitylenic acid, a substance probably

* and *Atti. R. Accad. Lincei*, 1913, [v], **22**, i, 127—132.

a polycarboxylic acid which sublimed near 300°, and some resinous matter.

The oxidation product of ψ-cumene contained as its neutral constituents only unchanged hydrocarbon and a trace of an aldehydic substance; the acidic constituents comprised formic acid, together with 3:4-dimethylbenzoic acid, 2:4-dimethylbenzoic acid, and a difficultly volatile, crystalline *substance*; the presence of 2:5-dimethylbenzoic acid could not be detected.

Indene was practically completely changed, and the reaction mixture slowly gave the reaction for a peroxide. A relatively large amount of resinous matter was produced which was partly soluble in ether, the soluble portion being separable by boiling water into a colourless *substance*, crystallising in leaflets, m. p. 72°, and a yellow, amorphous substance, m. p. 123° (approx.). The acidic portion of the reaction product contained formic and phthalic acids, together with a third substance, m. p. 174°, probably homophthalic acid.

Naphthalene proved quite resistant to autoxidation, but tetrahydronaphthalene (Bamberger and Kitschelt, A., 1890, 1146) is readily oxidised, giving much resinous matter and a little phthalic acid.

D. F. T.

Influence of Substituents in Benzene on the Binary Systems. Substituted Benzene–Antimony Trihaloids. Boris N. Menschutkin (*J. Chim. phys.*, 1912, **10**, 598—611. Compare A., 1912, i, 98, 99, 100, 177).—The compounds of benzene with antimony trichloride and tribromide are of the type $2SbCl_3,C_6H_6$, but some substituted benzenes give in addition compounds of the type $SbCl_3,PhR$. Methyl-, ethyl-, propyl- and *iso*amyl-benzenes exhibit a decreasing stability in the compounds $2SbCl_3,PhR$, whereas the stability of the compounds $SbCl_3,PhR$ attains a maximum in ethylbenzene.

Antimony tribromide has less affinity for the phenyl nucleus than the chloride. Toluene gives compounds of both types, but ethyl-, propyl- and *iso*amyl-benzenes of the type $SbBr_3,PhR$ only, the ethyl compound again having the maximum stability.

Diphenyl forms the compounds $2SbCl_3,PhPh$ (stable) and $2SbBr_3,PhPh$ (unstable), and diphenylmethane gives two stable compounds of the same types. Triphenylmethane, however, does not combine with antimony tribromide, and with the chloride gives only an unstable compound of the formula $SbCl_3,CHPh_3$.

The xylenes form with antimony trichloride compounds of both types, which are intermediate in stability between those of toluene and ethylbenzene. *p*-Xylene gives the most, and *m*-xylene the least, stable. With antimony tribromide, *p*-xylene gives only the compound $2SbBr_3,C_6H_4Me_2$, which is intermediate in stability between those of benzene and toluene, whilst *m*- and *o*-xylene give also compounds, $SbBr_3,C_6H_4Me_2$, which are less stable than that of toluene.

The compounds of antimony trichloride and tribromide with cymene are analogous in composition and inferior in stability to those of *p*-xylene. The unfavourable influence of the *iso*propyl group is thus manifest in presence of the methyl group.

Mesitylene and ψ-cumene form compounds of both types with antimony trihaloids, those of ψ-cumene being less and those of mesitylene more stable than the toluene compounds. Apparently the three methyl groups in mesitylene neutralise each other's effects on the phenyl nucleus. R. J. C.

Influence of Substituents in Benzene on the Properties of the Binary Systems Formed by Substituted Benzenes and Antimony Trichloride or Tribromide. BORIS N. MENSCHUTKIN (*J. Chim. phys.*, 1912, **10**, 612—623. Compare A., 1912, i, 193).—The compounds of monosubstituted benzenes with antimony trichloride are all of the two types $2SbCl_3,PhR$ and $SbCl_3,PhR$. When R is H, OH, Me, OMe, Et, Pr^{α} or $C_5H_{11}{}^{\beta}$, both compounds are formed. When R is OEt, Bz, Ph, COH, COMe, COPh, CN, compounds of the second type only are produced. When R is NO_2, F, Cl, Br, I, $CHPh_2$, compounds of the second type are also produced, which, however, decompose on melting, and when R is SO_3H, CO_2H, or COCl no combination occurs.

From the behaviour of phenol and anisole it is argued that oxygen has very little influence, although in phenetole the cumulative effect of the oxygen and the ethyl group prevents the formation of the compound $2SbCl_3,PhOEt$. Neither anisole nor ethylbenzene forms compounds of this type with antimony tribromide. Nitro-, fluoro-, chloro-, bromo-, and iodo-benzene do not combine with the tribromide at all.

m-Dinitrobenzene gives an unstable compound, $SbCl_3,C_6H_4(NO_2)_2$, which, like the compound $SbCl_3,PhI$, does not invariably crystallise out, so that complete f.p. diagrams of these systems are obtainable showing only one eutectic point. The nitro-group diminishes the affinity of the phenyl nucleus for antimony less than the halogens. *p*-Dichloro- and *p*-dibromo-benzene do not combine with antimony trichloride.

p-Chlorotoluene gives no compounds, but *o*- and *m*-chlorotoluene give compounds, $SbCl_3,C_6H_4MeCl$, which decompose on melting. No corresponding compounds of antimony tribromide exist.

The three nitrotoluenes form compounds of the formula

$$SbCl_3,C_6H_4Me{\cdot}NO_2,$$

the most stable being given by *o*-nitrotoluene, which also combines with antimony tribromide.

Benzene has more affinity for antimony haloids than any of its derivatives, but *cyclo*hexane does not combine at all. The degree of saturation of the phenyl nucleus varies with the nature of the substituting atoms or groups. This variation is not expressible by ordinary structural formulæ, but such formulæ as have been proposed recently by Kaufmann and by Stark are capable of giving some explanation of it.

The compounds of aniline containing 1, 2, 3, 4, and 6 molecules of aniline per molecule of antimony trichloride are in a class by themselves, and are to be attributed to the residual affinity of the amino-group. R. J. C.

The Catalytic Action of Mercury in Nitrations. Richard Wolffenstein and Oskar Böters (*Ber.*, 1913, **46**, 586—589).—Mercury has no catalytic action on the nitration of benzene when concentrated nitric acid or a nitric acid-sulphuric acid mixture is used, nitrobenzene being formed as usual (compare Holdermann, A., 1906, i, 439). When, however, a more dilute nitric acid (D = 1·31) is used, nitro-phenols are produced. The reaction is first one of oxidation to phenol, and then nitration, since when nitrobenzene is used instead of benzene, no trace of a nitrophenol is produced. Similar reactions take place with toluene, and ethyl- and propyl-benzenes.

To prepare dinitro- or trinitro-phenol, a mixture of benzene (100 grams), nitric acid (800 grams; D = 1·31), and mercuric nitrate (15 grams) is heated on the water-bath under reflux, stirring vigorously meanwhile. At the end of the reaction, the flask contains a mass of crystals of 2 : 4-dinitrophenol and of picric acid. Additive mercury compounds are formed as intermediate products.

Instead of using nitric acid, nitrous acid, nitrogen dioxide or tetroxide, and nitrogen pentoxide may be used. For example, a mixture of 120 grams of benzene, 20 grams of mercuric nitrate, and 270 grams of nitrogen tetroxide is kept at the ordinary temperature for a few days, after which a crystalline mass of almost pure 2 : 4-dinitrophenol is obtained. T. S. P.

Hydrogenation of Aromatic Compounds by means of Platinum and Hydrogen. II. Dihydronaphthalene. Richard Willstätter and Victor L. King (*Ber.*, 1913, **46**, 527—535. Compare Willstätter and Hatt, A., 1912, i, 545).—Dihydronaphthalene has not previously been prepared free from contamination with naphthalene or tetrahydronaphthalene. It may be obtained pure by distilling the quaternary hydroxide of tetrahydro-β-naphthylamine in a vacuum, or more conveniently by reducing naphthalene dibromide by means of zinc powder and alcohol at 60°. Pure dihydronaphthalene is a colourless oil with a sweet odour, b. p. 84·5°/16 mm., D_4^{20} 0·9974; it crystallises in large plates, m. p. −9°.

When hydrogenated by means of platinum and hydrogen, the first stage is the formation of tetrahydronaphthalene, the one nucleus only being saturated. The further reduction to a completely saturated perhydronaphthalene takes place very slowly.

Naphthalene under similar conditions yields no tetrahydronaphthalene at any stage of the process, but a mixture of naphthalene and perhydronaphthalene, $C_{10}H_{16}$, is always obtained. This behaviour is not in accord with an aromatic-olefinic structure for naphthalene, such as proposed by Willstätter and Waser (A., 1912, i, 18). E. F. A.

Derivatives of *p*-Xylene. Jan J. Blanksma (*Chem. Weekblad*, 1913, **10**, 136—141. Compare A., 1910, i, 661).—The melting-point curve of mixtures of 2 : 3-dinitro-*p*-xylene and 2 : 6-dinitro-*p*-xylene has been plotted, and a number of derivatives of *p*-xylene have been prepared. The curve indicates the formation of an additive product containing equimolecular proportions of the two substances.

Reduction of 2 : 5-dinitro-*p*-xylene with ammonium sulphide yields

5-nitro-*p*-2-xylidine, m. p. 142°, converted by Sandmeyer's reaction into 2-bromo-5-nitro-*p*-xylene, colourless crystals, m. p. 70°, which is reduced by iron powder and sulphuric acid to 5-bromo-*p*-2-xylidine, colourless crystals, m. p. 96°. Acetic anhydride converts this substance into *5-bromo-2-aceto-*p*-2-xylidide*, colourless crystals, m. p. 180°, also formed by the action of a solution of bromine in glacial acetic acid on 2-aceto-*p*-2-xylidide. On saponification it yields 5-bromo-*p*-2-xylidine, already mentioned. On substituting bromine for the amino-group by Sandmeyer's reaction, there is formed 2 : 5-dibromo-*p*-xylene, m. p. 75°, also produced by bromination of *p*-xylene.

Bromine dissolved in glacial acetic acid transforms 5-nitro-*p*-2-xylidine into *3-bromo-5-nitro-*p*-2-xylidine*, pale yellow crystals, m. p. 125°, converted by acetic anhydride and a trace of concentrated sulphuric acid into 3-bromo-5-nitro-2-aceto-*p*-2-xylidide, colourless crystals, m. p. 208°. Replacement of the amino-group in 3-bromo-5-nitro-*p*-2-xylidine produces 2 : *3-dibromo-5-nitro-*p*-xylene*, colourless crystals, m. p. 99°.

Bromine in glacial acetic acid reacts with *p*-2-xylidine, forming 3 : 5-dibromo-*p*-2-xylidine, m. p. 65°, converted by diazotisation and the action of boiling alcohol into 2 : *6-dibromo-*p*-xylene*, colourless plates of mother-of-pearl lustre, m. p. 32°, also obtained in an impure liquid form by the bromination of *p*-xylene. Nitration in presence of sulphuric acid converts 2 : 6-dibromo-*p*-xylene into 2 : *6-dibromo-3 : 5-dinitro-*p*-xylene*, colourless crystals, m. p. 190°.

3 : 5-Dibromo-*p*-2-xylidine is converted by acetic anhydride and concentrated sulphuric acid into 3 : 5-dibromo-2-aceto-*p*-2-xylidide, colourless crystals, m. p. 192° (not 165°, as stated in *Rec. trav. chim.*, 1906, **25**, 362). This substance is transformed by nitric and sulphuric acid into 3 : *5-dibromo-6-nitro-2-aceto-*p*-2-xylidide*, colourless crystals, m. p. 256°, which is hydrolysed to 3 : *5-dibromo-6-nitro-*p*-2-xylidine*, yellow crystals, m. p. 176°, also formed by bromination of 6-nitro-*p*-2-xylidine. By diazotisation and the action of boiling alcohol, this substance yields 3 : *5-dibromo-2-nitro-*p*-xylene*, colourless crystals, m. p. 83°, which is converted by nitric and sulphuric acid into 3 : 5-dibromo-2 : 6-dinitro-*p*-xylene, already mentioned.

Replacement of the amino-group in 6-nitro-*p*-2-xylidine by bromine by the Sandmeyer reaction produces *2-bromo-6-nitro-*p*-xylene*, pale yellow crystals, m. p. 38°. A. J. W.

Kinetics of Ammonium Salts. EDGAR WEDEKIND and F. PASCHKE (*Zeitsch. physikal. Chem.*, 1913, **82**, 314—324).—Polemical. an answer to von Halban (A., 1911, i, 852; compare also A., 1909, ii, 722; 1908, i, 723; 1911, i, 628). Several new preliminary experiments are given. It is shown that the addition of an inactive non-decomposable salt to a chloroform solution of an active iodide does not decrease the dissociation of the active iodide, but brings about a double decomposition, thus:

$$d\text{-NMePrPh}(C_7H_7)I + r\text{-NMePrPh}(C_7H_7)\cdot NO_3 \rightleftarrows r\text{-NMePrPh}(C_7H_7)I + d\text{-NMePrPh}(C_7H_7)\cdot NO_3,$$

and of these four substances the iodides alone can dissociate, so that the decrease in the rate of dissociation, which is determined polari-

metrically, is explained. The remaining and unchangeable activity is due to the active nitrate which exists together with inactive nitrate in the solution. The latter can be precipitated by ether, and the amount of active nitrate determined, which is always found to be equal in concentration to that of the inactive nitrate added. Preliminary experiments are given on the rate of formation of phenylbenzylmethylpropylammonium bromide in chloroform solution at various temperatures from methylpropylaniline and benzyl bromide. J. F. S.

The Kinetics of Ammonium Salts. HANS VON HALBAN (*Zeitsch. physikal. Chem.*, 1913, **82**, 510—512).—Polemical, an answer to Wedekind and Paschke's criticism (preceding abstract) of Halban's paper (A., 1911, i, 852). J. F. S.

Nitro-derivatives of Cresyl Oxides [Tolyl Ethers]. ALPHONSE MAILHE (*Bull. Soc. chim.*, 1913, [iv], **13**, 169—173).—Most of this work has been published already (this vol., i, 173, 261). *p*-Tolyl ether on nitration yields only a *tetranitro*-derivative, m. p. 84°, crystallising in yellow needles, and furnishing on boiling with a dilute solution of potassium hydroxide an amorphous, red powder which does not melt at 300°. T. A. H.

Nitro-derivatives of Cresylene Oxides [Tolylene Oxides]. ALPHONSE MAILHE (*Bull. Soc. chim.*, 1913, [iv], **13**, 173—176. Compare this vol., i, 261).—Part of this work has been published already (*loc. cit.*). *p*-Tolylene oxide, m. p. 166°, on nitration in acetic acid solution at 80° yields a mixture of the *mono*- and *dinitro*-derivatives. The former has m. p. 197°, and is sparingly soluble in boiling alcohol. The dinitro-derivative has m. p. 136°, and is readily soluble in boiling alcohol; it alone is formed when the nitration is effected in sulphuric acid solution in the cold. No higher nitro-derivative of the para-ether could be obtained, whence the author considers that the union of the two nuclei is in the ortho-position to the ether linking, whilst in *o*-tolylene oxide (*loc. cit.*) it is in the meta-position. T. A. H.

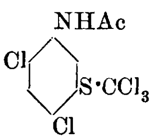
Preparation of Halogenated Aminonaphtholsulphonic Acids. FARBENFABRIKEN VORM FRIEDR. BAYER & CO. (D.R.-P. 254715).—Substituted aminonaphtholsulphonic acids can be readily prepared by the halogenation of the *ON*-diacyl derivatives of 2-aminonaphtholsulphonic acids with subsequent elimination of the acyl groups. 5-*Chloro*-6-*amino*-1-*naphthol*-3-*sulphonic acid* crystallises from water as a colourless powder. 5-*Bromo-di*-p-*tolylsulphonyl*-6-*amino*-1-*naphthol*-3-*sulphonic acid* is a yellow, crystalline powder. The preparation of 8-*bromo*-6-*amino*-1-*naphthol*-3-*sulphonic acid* is also described.
F. M. G. M.

3-Aminophenyl Mercaptan. THEODOR ZINCKE and JOH. MÜLLER (*Ber.*, 1913, **46**, 775—786).—The preparation of 3-*aminophenyl mercaptan* and of 3-*aminophenyl methyl sulphide* is described. A number of derivatives of the latter have been investigated.

Acetylaniline-m-*sulphonyl chloride*, $NHAc\cdot C_6H_4\cdot SO_2Cl$, is formed by

the action of phosphorus pentachloride on the corresponding sodium salt. It forms white needles, m. p. 88°, and is readily converted into the *amide*, m. p. 217°, and the *anilide*, m. p. 179°. Reduction of an alcoholic solution of the chloride by means of zinc dust transforms it into 3 : 3′-*diacetylaminodiphenyl disulphide*, $S_2(C_6H_4{\cdot}NHAc)_2$, m. p. 210°, from which 3 : 3′-*diaminodiphenyl disulphide*, colourless needles, m. p. 52°, is obtained by hydrolysis. The corresponding *hydrochloride* dissolves freely in water, whilst the *nitrate* and *sulphate* are sparingly soluble. When an alcoholic solution of the hydrochloride is boiled with sodium sulphide in the presence of a small quantity of sodium hydroxide, 3-aminophenyl mercaptan, b. p. 180—190°/16 mm., is formed as a pale yellow oil, which, when pure, is fairly stable towards air, but is readily oxidised when impure. Ferric chloride converts it into the disulphide. The *hydrochloride* and *sulphate* were examined. It forms a *diacetyl* derivative, m. p. 97°. With alcoholic benzaldehyde, it yields a *benzylidene* derivative, $CHPh(S{\cdot}C_6H_4{\cdot}N{:}CHPh)_2$, yellow powder, m. p. 59° (compare A., 1912, i, 257).

3-*Acetylaminophenyl methyl sulphide*, $NHAc{\cdot}C_6H_4{\cdot}SMe$, needles, m. p. 75°, is obtained by reducing 3 : 3′-diacetylaminodiphenyl disulphide in alcoholic solution by means of sodium sulphide in the presence of sodium hydroxide and treatment of the product so obtained with methyl sulphate. Bromine converts it into a *perbromide*, which is readily transformed into a dibromo-substitution *product*. When a solution of it in chloroform is cooled in ice and saturated with chlorine, a pentachloro-*compound*, needles, m. p. 160°, probably having annexed formula, is obtained, which, when heated with aniline, yields triphenylguanidine and *dichloro*-3-*acetylaminophenyl mercaptan*, m. p. 152°. Hydrolysis of 3-acetylaminophenyl methyl sulphide by means of hydrochloric acid in aqueous alcoholic solution yields the *hydrochloride* of 3-aminophenyl methyl sulphide, from which the free *base*, pale yellow oil, b. p. 163—165°/16 mm., is obtained by means of ammonia. The *sulphate* was examined.



3-*Methylthiolphenyltrimethylammonium iodide*, $SMe{\cdot}C_6H_4{\cdot}NMe_3I$, m. p. 183—185° (decomp.), is obtained by the action of excess of methyl iodide on a methyl-alcoholic solution of 3-acetylaminophenyl methyl sulphide. It forms a di-iodo- and a tetra-iodo-additive product. The free *base* is obtained by evaporation of its solution in a vacuum as yellowish-white, hygroscopic crystals.

3-*Methylthiolphenyltrimethylammonium chloride*, obtained from the corresponding iodide and silver chloride, forms white, hygroscopic needles. It yields a pale yellow, stable *platinichloride*, and an orange-yellow *dichromate*.

3-*Dimethylaminophenyl methyl sulphide*, pale yellow oil, b. p. 165—167°/16 mm., is obtained when the above iodide is heated above its m. p. under diminished pressure. It forms a readily soluble *hydrochloride* and *sulphate*.

3-Acetylaminophenyl methyl sulphide is oxidised by hydrogen peroxide in glacial acetic acid solution to the corresponding *sulphoxide*, $NHAc{\cdot}C_6H_4{\cdot}SO{\cdot}CH_3$, needles, m. p. 112°; this is converted by

hydrogen bromide into a *perbromide*, which readily passes into a monobromo-substitution *product*. When heated with aqueous alcoholic potassium hydroxide the above acetyl derivative is transformed into 3-*aminophenylmethylsulphoxide*, colourless, rhombic leaflets, m. p. 115°. The *hydrochloride*, white needles, is readily soluble in water.

3-*Acetylaminophenylmethylsulphone*, $NHAc \cdot C_6H_4 \cdot SO_2Me$, obtained by the action of a larger quantity of hydrogen peroxide on a solution of 3-acetylaminophenyl methyl sulphide in glacial acetic acid (compare above), forms small, white needles, m. p. 137°, and is converted by aqueous alcoholic hydrogen chloride into 3-*aminophenylmethylsulphone*, m. p. 72°.

3-*Methylthiolbenzenediazonium chloride*, $SMe \cdot C_6H_4 \cdot N_2Cl$, is obtained in moderately stable, yellow leaflets by the addition of amyl nitrite to an alcoholic solution of the hydrochloride of 3-aminophenyl methyl sulphide in the presence of alcoholic hydrogen chloride. It couples with dimethylaniline and with β-naphthol, yielding dyes which crystallise in red needles. It decomposes when heated with water, but a phenol could not be isolated from the product of the reaction. It was transformed by the usual methods into 3-*methylthiolbenzonitrile*, white needles, m. p. 40° (3-*methylthiolbenzoic* acid, leaflets, has m. p. 129°), and 3-*methylthiolphenyl iodide*, almost colourless oil, b. p. 157°/16 mm.

3 : 3′-Diacetylaminodiphenyl disulphide is converted into the corresponding ammonium *iodide*, $S_2(C_6H_4 \cdot NMe_3I)_2$, m. p. 185—186° (decomp.), when heated with methyl alcohol and methyl iodide; this substance, when heated under diminished pressure, yields 3 : 3′-*dimethylaminodiphenyl disulphide*, $S_2(C_6H_4 \cdot NMe_2)_2$, colourless oil, b. p. 162—166°/16 mm. A solution of the latter in formic acid is converted by amyl nitrite in the presence of a little hydrochloric acid into 6 : 6′-*dinitroso*-3 : 3′-*dimethylaminodiphenyl disulphide*,

$$S_2(C_6H_3[NO] \cdot NMe_2)_2,$$

dark green needles, m. p. 130°, which is reduced by hydrogen sulphide in ammoniacal solution to 6-*amino*-2-*dimethylaminophenyl mercaptan*. The *hydrochloride* of the latter, white needles, m. p. 235° (decomp.), was investigated. It forms a colourless double *salt* with mercuric chloride. With potassium ferricyanide, it yields a dark green *precipitate*, the colour of which deepens on addition of alkali. Ferric chloride converts it into a dark red oxidation *product*, which yields a dark violet double *salt* with mercuric chloride. Hydrogen sulphide decomposes the latter, the original mercaptan being regenerated.

H. W.

Basic Properties of Sulphoxides and their Position Among the Organo-metallic Bases. EMIL FROMM (*Annalen*, 1913, **396**, 75—103).—The similarities in behaviour between bases of the type $R_{n+1}Md \cdot OH$ (where Md represents a metalloid element such as N, P, As, Sb, O, S, Se, Te, or I, and n the number of atoms of hydrogen with which it can unite, and R an organic radicle) have frequently been emphasised. Compounds of the type MdR_n may be regarded as the anhydrides of $R_{n+1}Md \cdot OH$. All these bases are monoacidic.

The anhydrides, R_nMdO, of a second series of bases of the type $R_nMd(OH)_2$ are known. In the anhydrides, Md may be any one of the elements given above, but in the hydroxides hitherto Md has been only N, P, As, Sb, or Te. All these bases and their anhydrides are diacidic, and the anhydrides or their salts are characterised by the three equilibrium reactions: (i) $R_nMdO \rightleftarrows R_nMd + O$; (ii) $R_nMdX_2 \rightleftarrows R_nMd + X_2$ (where X is halogen); (iii) $R_nMdCl_2 + H_2O \rightleftarrows R_nMdCl{\cdot}OH + HCl \rightleftarrows R_nMdO + 2HCl$.

In the present communication the author deals with substances in which Md is sulphur, and, therefore, $n = 2$. Sulphoxides can be prepared by reaction (i), the oxygen being supplied by nitric acid, hydrogen peroxide, or chromic acid, and also by reactions (ii) and (iii). The dichlorides of diaryl sulphides have been prepared by Fries and Vogt (A., 1911, i. 538), and are converted into sulphoxides by water; di-iodides of dialkyl sulphides, which have long been known, are, it is now shown, converted into sulphoxides by silver acetate.

It is also shown that sulphoxides can combine with one equivalent of hydrogen chloride to form hydrogen salts, $OH{\cdot}SR_2Cl$, and with two equivalents of hydrogen bromide or iodide to form normal salts, R_2SX_2, which are identical with the dibromides or di-iodides produced by reaction (ii). The hydrogen salts and the normal salts are both hydrolysed more or less rapidly by water, reproducing the sulphoxide. In addition to hydrolysis, the normal salts can also dissociate according to reaction (ii), and it depends on the relative velocities of dissociation and of hydrolysis whether a normal salt yields the sulphoxide or the sulphide by treatment with aqueous alkali hydroxide or silver acetate. The parent substance, H_2SO, of the sulphoxides, and its tautomeric form, $HS{\cdot}OH$, are unknown; anthraquinone derivatives of both have been described by Fries (A., 1912, i, 1005).

The relations between disulphides and disulphoxides and the basic properties of the latter can be represented by equations similar to (i), (ii), and (iii).

[With FRITZ SCHÄFER, AQUILA FORSTER, and BORIS VON SCHERSCHEWITZKI.]—*o*-Nitrophenyl benzyl sulphide and the para-isomeride, 2 : 4-dinitrophenyl benzyl sulphide, dinitrophenyl methyl sulphide, and *s*-di-*o*-nitrophenylthiolethane, resemble di-*p*-tolyl sulphide (Fromm and Raiziss, A., 1910, i, 554) in not forming additive compounds with bromine; 2 : 4-dinitrophenyl benzyl sulphide in cold chloroform yields *bromodinitrophenyl benzyl sulphide*, $C_6H_2Br(NO_2)_2{\cdot}S{\cdot}CH_2Ph$, m. p. 104°, yellow needles. Also the dibromides cannot be obtained from the sulphoxides and hydrogen bromide. Both reactions proceed, however, when the nitro-groups are reduced to amino-groups and the latter acetylated; thus di-*o*-acetylaminophenylthiolethane and bromine in cold chloroform yield the *tetrabromide*, $C_2H_4(SBr_2{\cdot}C_6H_4{\cdot}NHAc)_2$, m. p. 60—61°, unstable, orange crystals, which is converted by water into *di-o-acetylaminophenylsulphoxyethane*, $C_2H_4(SO{\cdot}C_6H_4{\cdot}NHAc)_2$, m. p. 214°, colourless needles; the latter and hydrogen bromide in chloroform regenerate the tetrabromide.

Dibenzyl sulphide and chlorine in petroleum at 0° yield the very unstable *dichloride*, $SCl_2(CH_2Ph)_2$, which is converted into the sulphoxide by water. The dibromide is more stable (Fromm and

Raiziss, *loc. cit.*). The *di-iodide*, $SI_2(CH_2Ph)_2$, m. p. 64—65°, violet crystals, prepared from the sulphide and iodine in glacial acetic acid on the water-bath, is extremely stable. It is decomposed, without hydrolysis, by dilute sodium hydroxide, dibenzyl sulphide being regenerated; the hydrolysis is effected by silver acetate in dilute acetic acid, whereby dibenzylsulphoxide is produced.

Dibenzylsulphoxide and hydrogen iodide in chloroform at 0° yield the preceding dibenzyl sulphide di-iodide. The sulphoxide and hydrogen chloride in benzene form *dibenzylsulphoxide hydrochloride*,

$$OH\cdot SCl(CH_2Ph)_2,$$

m. p. 90°, colourless crystals, which does not further react with hydrogen chloride, and is decomposed into the sulphoxide by water or in a vacuum.

s-Dibenzylthiolethane reacts with chlorine in cold petroleum to form the unstable *tetrachloride*, $C_2H_4(SCl_2\cdot CH_2Ph)_2$, white crystals, with bromine in cold chloroform to form the moderately stable *tetrabromide*, m. p. 84°, orange-red crystals, and with iodine in boiling glacial acetic acid to form the *tetraiodide*, m. p. 94°, red needles. The tetrachloride and the tetrabromide are very rapidly converted into the disulphoxide by water. On the contrary, the disulphoxide suspended in cold petroleum or chloroform is converted into the tetrabromide by hydrogen bromide, and into a comparatively stable *dihydrochloride*,

$$C_2H_4[SCl(OH)\cdot CH_2Ph]_2,$$

by hydrogen chloride.

p-*Tolyl benzyl sulphide*, $C_6H_4Me\cdot S\cdot CH_2Ph$, m. p. 44°, prepared from *p*-tolyl mercaptan and benzyl chloride, yields the *sulphoxide*, m. p. 136—137°, by oxidation with 30% hydrogen peroxide in glacial acetic acid or with nitric acid, and reacts with chlorine or bromine in cold petroleum to form respectively the very unstable *dichloride*, $C_6H_4Me\cdot SCl_2\cdot CH_2Ph$, and comparatively unstable *dibromide*, and with iodine in hot glacial acetic acid to form the stable *di-iodide*, m. p. 72°, dark blue plates. The dichloride and the dibromide by treatment with water, and the di-iodide by treatment with silver acetate, are converted into *p*-tolylbenzylsulphoxide; the di-iodide and aqueous sodium hydroxide yield *p*-tolyl benzyl sulphide. The dibromide and the di-iodide are obtained from the sulphoxide and hydrogen bromide or iodide in chloroform. p-*Tolyl methyl sulphide di-iodide*, $C_6H_4Me\cdot SMeI_2$, m. p. 40°, prepared from its components in petroleum, crystallises in dark blue needles.

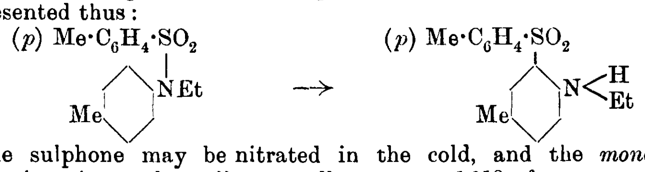
Formaldehyde-*p*-tolylmercaptal (this vol., i, 176) forms a *tetraiodide*, $CH_2(SI_2\cdot C_6H_4Me)_2$, m. p. 68—70°, which can also be obtained from the disulphoxide and hydrogen iodide in chloroform, and is not converted into the disulphoxide by silver acetate. Formaldehydebenzylmercaptal also forms a *tetraiodide*, $CH_2(SI_2\cdot CH_2Ph)_2$, decomp. 110—140°, which is converted by silver acetate, not into the sulphoxide as usual, but into formaldehydebenzylmercaptal.

In boiling glacial acetic acid, benzyl disulphide and iodine form the *tetraiodide*, $S_2(CH_2Ph)_2I_4$, decomp. 113—120°, green crystals, which is converted into the disulphoxide by silver acetate in hot glacial acetic acid; from the latter the tetraiodide is regenerated by hydrogen iodide at −5° in carbon tetrachloride. *Benzyl disulphide tetrachloride* is

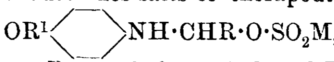
extremely unstable, and the *tetrabromide* has m. p. 2° (decomp.); the latter and silver acetate yield the disulphoxide. C. S.

Substituted Aryl Sulphonamides. OTTO N. WITT and D. UERMÉNYI (*Ber.*, 1913, **46**, 296—308).—Hinsberg's method for the preparation of secondary bases (A., 1891, 49) has not yet received general application, owing to the difficulty which has been experienced in hydrolysing the sulphonamides. For this purpose Schroeter and Eisleb (A., 1909, i, 575) dissolved the substances in cold concentrated sulphuric acid, but obtained in the case of benzenesulphonanilide, not aniline but sulphanilic acid. It is now shown that good results may be obtained with 80% sulphuric acid. The toluene-*p*-sulphonamide is suspended in this acid and heated to 135—150°, when solution and hydrolysis take place. On cooling, *p*-toluenesulphonic acid separates, and is removed by filtration, whilst the base is liberated from the diluted filtrate and distilled in steam. The yields are somewhat impoverished by the formation of non-volatile by-products, which occur to a preponderating extent in the case of ethyl-*p*-toluidine, and consist of a sulphone, being due to the displacement of the *p*-toluenesulphonic acid residue into the ring.

Toluene-*p*-sulphon-*p*-toluidide and also its *acetyl* derivative, m. p. 133·5°, give *p*-toluidine-*m*-sulphonic acid with concentrated sulphuric acid, but sulphonation of the base does not occur with 80% acid at 150°. Crude methyl- and ethyl-aniline and also methyl-*o*-toluidine (*toluene*-p-*sulphonmethyl*-o-*toluidide*, $C_{15}H_{17}O_2NS$, has m. p. 119—120°) may be conveniently purified by this process. *Toluene*-p-*sulphonethyl*-o-*toluidide*, $C_{16}H_{19}O_2NS$, forms long needles, m. p. 75°, but the ethyl-*o*-toluidine is accompanied by a small quantity of the rearranged *sulphone*, white needles, m. p. 134°. The hydrolysis of *toluene*-p-*sulphonethyl*-p-*toluidide*, colourless needles, m. p. 71—72°, gives less than a 50% yield of ethyl-*p*-toluidine, the chief product being precipitated on adding water, in colourless needles, m. p. 113°. It is formed in still greater quantity when concentrated acid is used, and is a secondary base, since it gives an *acetyl* compound, $C_{16}H_{18}O_2NS{\cdot}C_2H_3O$, in silky, white needles, m. p. 143—144°. When the base is heated at 275° in a current of hydrogen chloride, ethyl chloride is removed and the resulting primary *aminoditolylsulphone*, $C_{14}H_{15}O_2NS$, colourless crystals, m. p. 169°, may be diazotised and deprived of the amino-group. The resulting compound forms colourless needles, m. p. 116°, and can be synthesised by condensing the chloride of *m*-toluenesulphonic acid with toluene by means of aluminium chloride. It is, therefore, mp-*ditolylsulphone*, and the rearrangement of the sulphonamide into a sulphone is to be represented thus:



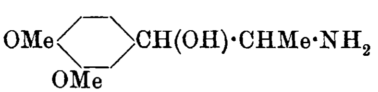
The sulphone may be nitrated in the cold, and the *mononitro*-derivative, intensely yellow needles, m. p. 161°, forms an *acetyl* compound, $NO_2{\cdot}C_{16}H_{17}O_2NS{\cdot}C_2H_3O$, in colourless crystals, m. p. 159—160°. J. C. W.

Preparation of *p*-Alkyloxyphenylaminoalkyl Sulphites. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 255305).—When acetaldehyde (or its higher homologues) is condensed with *p*-alkyloxyaminobenzenes in the presence of an alkali (or ammonium) hydrogen sulphite it furnishes salts of therapeutic value, and having the general formula , where M is an alkali metal or ammonium, R = methyl or ethyl, and R^1 an alkyl group.

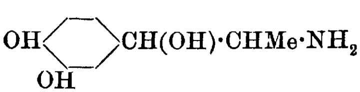
Sodium p-*phenetidinoethyl sulphite*, needles, is obtained when a cooled aqueous solution of 40% sodium hydrogen sulphite (110 parts) is treated with acetaldehyde (20 parts) and *p*-phenetidine (55 parts), and subsequently gently heated until a clear solution is obtained; on cooling, the solution sets to a crystalline mass.

The *p*-phenetidine can be replaced by *p*-anisidine, and the acetaldehyde by propaldehyde. F. M. G. M.

Preparation of Aromatic Amino-alcohols. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 254438).—The reduction of aromatic ketones to the corresponding alcohols has previously been described, and is now found to proceed quantitatively if hydrogen is employed in the presence of colloidal metals of the platinum group.



3 : 4-*Dimethoxyphenyl-α-propanolamine* (annexed formula), hard, colourless crystals, m. p. 138°, is obtained when 100 parts of α-aminopropionylveratrole (A., 1910, i, 313) in 300 parts of water with palladous chloride (5 parts), gum arabic (10 parts), and hydrazine hydrate are submitted to the action of hydrogen during two days at 20° and under a pressure of 1·5 atmospheres; the *hydrochloride*, colourless leaflets, has m. p. 212°; whilst the reduction in a similar manner of 4-*α-aminopropionylcatechol* (A., 1910, i, 313) gives rise to a 95% yield of



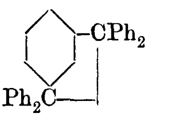
3 : 4-*dihydroxyphenyl-α-propanolamine* (annexed formula), m. p. 188°; the *hydrochloride*, a colourless powder, has m. p. 95°. F. M. G. M.

Preparation of Esters of Nitroanthraquinonylanthranilic Acid. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 254475).—When nitroaminoanthraquinones are treated with the esters of *o*-halogenated benzoic acids in the presence of copper (or a salt of copper), they give rise to nitroanthraquinonylanthranilic acid esters.

Methyl 4-*nitro*-1-*anthraquinonylanthranilate*, reddish-brown needles, m. p. 234—240°, is thus obtained from 1-nitro-4-aminoanthraquinone and methyl *o*-chlorobenzoate. On hydrolysis and subsequent reduction, these compounds furnish the corresponding aminoanthraquinonylanthranilic acids, which are of technical value. F. M. G. M.

Metaquinonoids. OTTO STARK and O. GARBEN (*Ber.*, 1913, **46**, 659—666).—The method by which Thiele and Balhorn obtained yellow

tetraphenyl-*p*-xylylene from methyl terephthalate (A., 1901, i, 491) has been applied to methyl *iso*phthalate, and a yellow tetraphenyl-*m*-xylylene of the annexed formula has been prepared.



Tetraphenyl-m-*xylylene glycol*, $C_{32}H_{26}O_2$, is obtained by the action of magnesium phenyl bromide on methyl *iso*phthalate in a boiling mixture of benzene and anisole. It crystallises from glacial acetic acid with one molecule of the solvent in light yellow prisms, m. p. 88°, and from light petroleum in the free state, m. p. 112—113°. Hydrogen chloride precipitates from an acetic acid solution the *dichloride*, $C_{32}H_{24}Cl_2$, which crystallises from petroleum in white needles, m. p. 137°, and like the *dibromide*, m. p. 167—168°, can be titrated with alkali in alcoholic solution. When heated with zinc dust and Devarda's alloy in benzene (compare Schmidlin, A., 1908, i, 150), a golden-yellow solution with red fluorescence is obtained, from which petroleum precipitates *tetraphenyl*-m-*xylylene*, in yellow needles, m. p. 210—220° (decomp.). It gives the above dichloride with chlorine, but is stable towards oxygen.

When hydrogen chloride is passed into the acetic acid mother liquors of the glycol, a *dichloride* is obtained, which is insoluble in hot petroleum, and has m. p. 236—238°. It may be hydrolysed and converted into a *dimethyl ether*, $C_{34}H_{30}O_2$, m. p. 187—188°, from which the *dibromide*, m. p. 242°, is obtained. It is supposed that the $-C(OH)Ph_2$ group has wandered into the *para*-position and that the compounds are isomeric, according to Schmidlin's isomerism (A., 1912, i, 32), with tetraphenyl-*p*-xylylene glycol dimethyl ether, m. p. 181—182·5°, and tetraphenyl-*p*-xylylene dibromide, m. p. 270—272° (Thiele and Balhorn, *loc. cit.*). J. C. W.

Direct Hydrogenation of the Phenylacetic Esters. Preparation of *cyclo*Hexylacetic Acid. PAUL SABATIER and MARCEL MURAT (*Compt. rend.*, 1913, **156**, 424—427. Compare A., 1912, i, 353).—The esters of phenylacetic acid are readily hydrogenated by excess of hydrogen in the presence of very active nickel at 180°. By this means the following esters have been prepared.

Methyl cyclo*hexylacetate*, b. p. 200—202° (corr.), D_0^0 0·9961, D_0^{14} 0·9896, n_D^{14} 1·459. Ethyl *cyclo*hexylacetate, b. p. 211—212° (corr.), D_0^0 0·9626, D_0^{14} 0·9537, n_D^{14} 1·451 (compare Freundler, A., 1905, i, 890). *Propyl* cyclo*hexylacetate*, b. p. 228—229° (corr.), D_0^0 0·9560, D_0^{15} 0·9431, n_D^{15} 1·450. iso*Butyl* cyclo*hexylacetate*, b. p. 240—241° (corr.), D_0^0 0·9445, D_0^{14} 0·9307, n_D^{14} 1·452. iso*Amyl* cyclo*hexylacetate*, b. p. 250—251° (corr.), D_0^0 0·9388, D_0^{16} 0·9267, n_D^{16} 1·454.

The refractive indices are practically constant throughout, but the density diminishes regularly with increase in molecular weight. All these esters are readily saponified by alcoholic potassium hydroxide, giving the free acid, m. p. 32°.

The phenylpropionic esters undergo similar hydrogenation.

It is of interest to note that benzyl acetate, the isomeride of methyl phenylacetate, submitted to similar hydrogenation is decomposed, giving

toluene and acetic acid, at the same time destroying the activity of the nickel. W. G.

Esters of Cellulose with Benzoic Acid and its Derivatives. OTTO HAUSER and H. MUSCHNER (*Zeitsch. angew. Chem.*, 1913, **26**, 137—139).—In the preparation of the esters the authors used hydrocellulose, which was made according to the method of Girard. The hydrocellulose is treated, under cooling, with a large excess of benzoyl chloride and sodium hydroxide, and the resulting product washed with hot water to remove alkali, and finally with alcohol and ether. The results show that the product obtained is always cellulose monobenzoate; no dibenzoate is formed, whatever may be the concentration of the sodium hydroxide (compare Cross and Bevan, A., 1901, i, 452). The only effect of the concentration of the sodium hydroxide is on the time of reaction, the stronger the alkali the shorter the time. The best concentration is 20%, and the temperature should be kept at 20° by appropriate cooling.

Cellulose mono-p-*chlorobenzoate*, $C_{19}H_{23}O_{11}Cl$, was prepared similarly from hydrocellulose and *p*-chlorobenzoyl chloride. It is an amorphous, white powder, insoluble in all solvents, non-hygroscopic and non-fusible. Esters could not be obtained from *m*-nitrobenzoyl chloride and *p*-bromobenzoyl chloride, owing to the fact that the high temperature necessary to melt the chloride resulted in its saponification by the sodium hydroxide before the cellulose entered into reaction. *p*-Toluoyl chloride gave a product corresponding with the formula $C_{18}H_{26}O_{11}$, instead of the expected formula $C_{20}H_{26}O_{11}$. T. S. P.

An Interesting Case of Dimorphism. ALEXIS DUFFOUR (*Compt. rend.*, 1913, **156**, 473—475).—Vanillyl benzoate is obtained in two distinct crystalline forms, monoclinic or triclinic, accordingly as it is prepared by the hydrogenation of vanillin benzoate in the cold in the presence of platinum black (compare Vavon, A., 1912, i, 260), or by the condensation of benzoyl chloride and sodium vanillyloxide. These two forms are both stable at the ordinary temperature, having been kept for a year unaltered. The triclinic crystals

$$[a:b:c=0{\cdot}8697:1:0{\cdot}5283;\ \alpha=90°20';\ \beta=72°22';\ \gamma=72°44']$$

have m. p. 99°, whilst the monoclinic

$$[a:b:c=0{\cdot}7814:1:1{\cdot}3460;\ \beta=111°9'],$$

observed under a microscope, begin to melt at 90°, and in the liquid obtained, triclinic crystals begin to form, transforming the whole into a friable mass only melting at 99°. This transformation of the monoclinic into the triclinic form when the two are in contact is retarded by diminution in temperature and becomes inappreciable at 30°.
W. G.

Nitration of Benzoic Acid in the Presence of Mercury RICHARD WOLFFENSTEIN and W. PAAR (*Ber.*, 1913, **46**, 589—599).—When benzoic acid (50 grams) is nitrated with nitric acid (300 grams; D = 1·35) in the presence of mercuric nitrate, 2 : 4 : 6-trinitro-*m*-hydroxybenzoic acid is obtained. The mixture is heated on the brine-bath at

105° for twenty hours, after which it is filtered from unchanged benzoic acid, the filtrate made alkaline to remove the mercury, acidified, and then extracted with ether to dissolve out any *m*-nitrobenzoic acid formed. The aqueous solution is then concentrated in order to obtain crystals of the readily soluble 2 : 4 : 6-trinitro-*m*-hydroxybenzoic acid. Various trinitrohydroxybenzoic acids have been described in the literature, and in order to compare them with the above acid they have been again prepared by the authors. Shardinger (A., 1876, 584) obtained an acid by the nitration of anthraflavone. Since anthraflavone is a mixture of the two isomerides, anthraflavic acid and 1 : 7-dihydroxyanthraquinone, the authors have nitrated each of these substances. In each case a tetranitro-derivative is first obtained, which undergoes fission, on further action of nitric acid, with the formation of the above-mentioned 2 : 4 : 6-trinitro-*m*-hydroxybenzoic acid. The third isomeride of anthraflavic acid is anthrarufin, the tetranitro-derivative of which has been prepared by Liebermann (A., 1879, 537). This on boiling with nitric acid undergoes fission with the formation of the above acid. Tetranitroanthrarufin is therefore 3 : 4 : 6 : 8-tetranitro-1 : 5-dihydroxyanthraquinone. Beilstein and Geitner (*Annalen*, 1866, **139**, 12) obtained a trinitrohydroxy-acid by the action of fuming nitric acid on *m*-aminobenzoic acid, and this the authors prove to be identical with their acid.

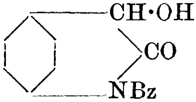
2 : 4 : 6-Trinitro-*m*-hydroxybenzoic acid, $C_7H_3O_9N_3$, crystallises with one molecule of water of crystallisation, in rhombic tablets; m. p. 180°. It forms a series of salts, characterised by their water of crystallisation. The *sodium*, *potassium*, *barium*, and *silver* salts have $2H_2O$, and the *copper* salt, $5H_2O$. Its constitution was proved by its conversion into picric acid when heated in small quantities (0·2 gram) at a time at 195°. The simplest method of preparation is from *m*-hydroxybenzoic acid. Five grams of this acid are dissolved in 30 grams of fuming nitric acid (D = 1·52), and the solution heated on the water-bath. The nitric acid is expelled on the water-bath, the residue again evaporated down with nitric acid, then with water, and finally extracted with benzene, leaving the pure acid. T. S. P.

2 : 4 : 6-Trinitro-*m*-hydroxybenzoic Acid. RICHARD WOLFFENSTEIN and W. PAAR (*Ber.*, 1913, **46**, 680—682. Compare preceding abstract).—E. F. Smith (*Proc. Amer. Phil. Soc.*, **25**) described a compound, which he obtained by treating ethyl *m*-hydroxybenzoate with nitrous acid and then with an excess of potassium hydroxide, as a trinitro-*m*-hydroxybenzoic acid, basing his formula on an estimation of potassium in the monopotassium salt. It might be expected that the hydroxyl hydrogen should also have been replaced by potassium and that the acid might be identical with Wolffenstein and Paar's compound. These authors have repeated Smith's experiment, and find that the product is in reality an ester which cannot be hydrolysed by prolonged boiling with alcoholic or aqueous potash, and is therefore, according to Victor Meyer's rule that ortho-substituents protect a carboxyl or ester group, *ethyl* 2 : 6-*dinitro*-m-*hydroxybenzoate*. It has m. p. 117°.

J. C. W.

Action of Hydrogen Cyanide on *p*-Nitrobenzaldehyde. GUSTAV HELLER [with OTTO FRITSCH] (*Ber.*, 1913, **46**, 280—294). —When *p*-nitrobenzaldehyde is suspended in glacial acetic acid and shaken with a concentrated aqueous solution of potassium cyanide until dissolved, it is converted into *p*-nitromandelonitrile, which may be precipitated by water. The behaviour of this substance towards various reagents, its conversion into nitro- and amino-mandelic acid, and attempts to form anhydrides of the latter acid are described.

p-*Nitromandelonitrile*, $NO_2\cdot C_6H_4\cdot CH(OH)\cdot CN$, crystallises from benzene in faintly yellow needles, m. p. 109—110°, which on hydrolysis with hydrochloric acid readily yield *p*-nitromandelic acid. Towards sodium hydroxide it is very sensitive, and from the product of the reaction, *p*-nitroso-, *p*-nitro-, and *p*-azoxy-benzoic acids have been isolated. *a-Benzoyloxy-*p*-nitrophenylacetic* acid, $NO_2\cdot C_6H_4\cdot CH(OBz)\cdot CO_2H$, is obtained by benzoylating the acid in pyridine solution, in yellowish-white prisms, m. p. 185—186°. It is easily hydrolysed, and all attempts to reduce it resulted in the production of benzoic acid. The reduction of *p*-nitromandelic acid itself follows different courses; with zinc and acetic acid it results in p-*azoxymandelic acid*, $C_{18}H_{14}O_7N_2$, in yellow needles, which darken at 190°; with stannous chloride the product is *p*-aminophenylacetic acid; ferrous sulphate and ammonia lead to p-*aminomandelic* acid, $NH_2\cdot C_6H_4\cdot CH(OH)\cdot CO_2H$, which forms faintly yellow needles from warm water, and a colourless *hydrochloride*. When warmed for a long time in water, it gradually deposits a yellow *anhydride*, $(C_8H_7O_2H)_x$, m. p. 210° (decomp.), which is insoluble in organic solvents. *p*-Aminomandelic acid yields a normal *benzoyl* derivative in sodium carbonate solution as a crystalline powder, m. p. 218°, which does not lose water when heated with acetic anhydride, but when benzoylated in pyridine in the cold, the product is 3-*hydroxy*-1-*benzoylindole* (annexed formula).



This substance could only be obtained as a colourless, amorphous powder, which was not readily attacked by warm aqueous alkali, but was hydrolysed by cold alcoholic potash to *p*-benzoylamino-mandelic acid.

If the solution of *p*-nitrobenzaldehyde in concentrated potassium cyanide and acetic acid is not immediately precipitated by water, but is left for a day, pp'-*dinitrodeoxybenzoin cyanide*,

$$NO_2\cdot C_6H_4\cdot CO\cdot CH(CN)\cdot C_6H_4\cdot NO_2,$$

is deposited. This crystallises in pale yellow needles, m. p. 267—268°, cannot be acetylated, and gives no reaction with ferric chloride. On reduction it yields *p*-aminobenzoic acid, and when dissolved in hot sodium hydroxide it deposits *p*-azoxybenzoic acid. When the red solution in cold sodium hydroxide is at once filtered into hydrochloric acid, however, 4-*nitro*-4'-*nitrosostilbene*-*aβ*-*diol*,

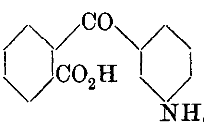
$$NO_2\cdot C_6H_4\cdot C(OH)\colon C(OH)\cdot C_6H_4\cdot NO,$$

can be extracted by means of boiling water from the precipitate. It forms colourless leaflets, m. p. 225° (decomp.), which give an intense, dark red colour with ferric chloride, and form acetyl and benzoyl derivatives which could not be obtained pure. J. C. W.

Preparation of Carboxydiarylhydrols. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 254122).—*6-Hydroxy-2 : 4-dimethylbenzoic acid*, m. p. 66°, is prepared by the action of carbon dioxide on *s*-xylenol; when it is slowly added to a cooled solution of *p*-diethylaminobenzaldehyde (1 mol.) in concentrated sulphuric acid, it gives rise to a *hydrol*, which can be further condensed with *o*-hydroxytoluic acid to yield *compounds*, which dye wool in violet shades.

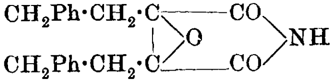
Similar *compounds* are also described from *o*-chloro-*p*-diethylaminobenzaldehyde with *m*-hydroxytoluic acid, and its further condensation with *o*-hydroxytoluic acid; from *o*-chlorobenzaldehyde with 6-hydroxy-2:4-dimethylbenzoic acid, followed by condensation with *o*-hydroxytoluic acid, whilst the tinctorial properties of other similar compounds are tabulated in the original. F. M. G. M.

Preparation of 2-Halogen-5-acylaminobenzoylbenzoic Acid. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 254091).—3-Aminobenzoylbenzoic acid (annexed formula) and its homologues can be readily acetylated by ordinary methods, and on subsequent halogenation (in the same solution) yield 2-halogen-5-acetylaminobenzoylbenzoic acid.



The following compounds are described: *6-Bromo-3-acetylaminobenzoylbenzoic acid*, hard crystals, m. p. 218°; *6-bromo-3-acetylamino*-p-*toluoylbenzoic acid* (prepared from 3-amino-*p*-toluoylbenzoic acid), colourless needles, m. p. 226°; *2-bromo-5-acetylamino-4-carboxybenzoylbenzoic acid* (from 3-amino-4-carboxybenzoylbenzoic acid, m. p. 265°), short, colourless, rod-like crystals, m. p. 264—266°, and *2-chloro-5*-p-*toluenesulphonyl*-p-*toluoylbenzoic acid*, colourless rods, m. p. 135°. F. M. G. M.

α-Hydroxy-γ-phenylcrotonic Acid. An Example of an Ether of a Ketone Hydrate. J. BOUGAULT (*Compt. rend.*, 1913, **156**, 555—556).—The acid amide, $C_{20}H_{23}O_6N$, obtained by the hydrolysis of α-hydroxy-γ-phenylcrotonamide (compare this vol., i, 269) on treatment with potassium permanganate in dilute acid solution gives a *compound*, $C_{20}H_{19}O_3N$, m. p. 120°, to which the author assigns the annexed constitution.



The presence of the imide group in the compound is shown (1) by its pseudo-acid properties; (2) by its transformation into an *acid amide*, $C_{20}H_{21}O_4N$, m. p. 171°, and finally to the dibasic *acid*, $C_{20}H_{20}O_5$, m. p. 204°, by the action of dilute alkali hydroxides; (3) by the formation of a N-*methyl* derivative, m. p. 86°, which liberates methylamine on treatment with alkali. The compound, unlike the acid amide from which it is prepared (*loc. cit.*), is not readily decomposed by alkalis to give benzylpyruvic acid. Its preparation by the elimination of two tertiary hydroxyl groups appears to be the reverse of Wagner's action. W. G.

Preparation of Esters of Acetylsalicylic [*o*-Acetoxybenzoic] Acid. RICHARD WOLFFENSTEIN and JOSEF ZELTNER (*Ber.*, 1913, **46**, 582—586).—Attempts to prepare ethyl *o*-acetoxybenzoate by the action of *o*-acetoxybenzoyl chloride on ethyl alcohol led to the isolation of ethyl salicylate, ethyl acetate, salicylic acid, and salicylic anhydride, the primarily formed ethyl *o*-acetoxybenzoate being decomposed by the hydrogen chloride liberated during the reactions. Satisfactory results were, however, obtained when the reaction was carried out in the presence of a substance capable of absorbing hydrogen chloride, for example, quinoline.

*Trichloro*iso*propyl* o-*acetoxybenzoate* was obtained by heating a a mixture of *o*-acetoxybenzoyl chloride, trichloro*iso*propyl alcohol, and dimethylaniline on the water-bath during two hours. It had m. p. about 65°, and could not be distilled without decomposition. Occasionally this ester was obtained in an oily form, which could not be caused to crystallise, but which, according to analysis, was pure.

Trichloro-tert.-*butyl* o-*acetoxybenzoate*, m. p. 55—57°, after previous softening, b. p. about 180°/16 mm. (slight decomp.), was obtained by heating *o*-acetoxybenzoyl chloride and *tert*.-trichlorobutyl alcohol at 140° in the presence of barium carbonate. H. W.

Preparation of Chloroanthraquinonecarboxylic Acids. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P., 255121).—The method previously described (A., 1911, i, 466), in which anthraquinone was chlorinated in sulphuric acid solution in the presence of iodine, has now been extended to the anthraquinone-α- and β-carboxylic acids.

When anthraquinone-β-carboxylic acid dissolved in fuming sulphuric acid (in the presence of iodine) is chlorinated at 125°, it gives rise to a *dichloroanthraquinonecarboxylic acid*, yellow crystals, m. p. above 300°, which when heated with *p*-toluidine furnishes an intensely green quinazarin-like derivative, thus indicating that the chlorine atoms are in the para-position with regard to each other.

The analogous compound from anthraquinone-α-carboxylic acid crystallises from acetic acid, and has m. p. 240—241°. The anthraquinonedicarboxylic acids can also be employed in this reaction.

F. M. G. M.

Saturated δ-Ketonic Esters and their Derivatives. DOROTHY A. HAHN AND ANGIE G. ALLBEE (*Amer. Chem. J.*, 1913, **49**, 171—179).—Kohler (A., 1911, i, 384) has described a general method for the preparation of unsaturated δ-ketonic esters; this method has now been applied to the production of the corresponding saturated compounds.

Ethyl β-anisoyl-α-phenylethylmalonate,

$$OMe\cdot C_6H_4\cdot CO\cdot CH_2\cdot CHPh\cdot CH(CO_2Et)_2,$$

m. p. 78°, obtained by the condensation of ethyl malonate with anisyl styryl ketone in presence of piperidine, crystallises in plates or stout needles. The corresponding *methyl* ester, m. p. 104°, forms plates or slender needles. When an alcoholic solution of the ethyl ester is treated with concentrated aqueous solution of potassium hydroxide, the *potassium* salt of β-anisoyl-α-phenylethylmalonic acid separates, which

is converted by acids into the *potassium hydrogen* salt and subsequently into the acid itself. *β-Anisoyl-α-phenylethylmalonic acid*, m. p. 165° (decomp.), crystallises from water in slender needles containing water of crystallisation, which is eliminated below 130°. By the action of bromine on a solution of ethyl β-anisoyl-α-phenylethylmalonate in chloroform, the *β-bromo*-derivative,

$$OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CHBr{\cdot}CHPh{\cdot}CH(CO_2Et)_2,$$

m. p. 97°, is obtained, which forms large, six-sided prisms.

When β-anisoyl-α-phenylethylmalonic acid is heated at 165—170° until the evolution of carbon dioxide ceases, *γ-anisoyl-β-phenylbutyric acid*, $OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}CHPh{\cdot}CH_2{\cdot}CO_2H$, m. p. 152°, is obtained, which crystallises in plates or prisms; its *methyl* ester, m. p. 86°, forms long plates or prisms, and is hydrolysed by potassium hydroxide with formation of the *potassium* salt, which crystallises with $1H_2O$. On the addition of bromine to a solution of γ-anisoyl-β-phenylbutyric acid in chloroform, two isomeric *γ-bromo*-derivatives,

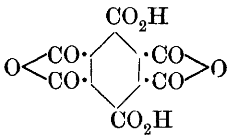
$$OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CHBr{\cdot}CHPh{\cdot}CH_2{\cdot}CO_2H,$$

are obtained with m. p. 144° (decomp.) and 119° respectively, which both behave in the same way when treated with sodium carbonate, yielding *γ-anisoyl-β-phenyl-γ-butyrolactone*,

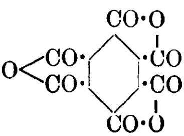
$$OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CH{<}\begin{matrix}CHPh\\O{-}CO\end{matrix}{>}CH_2,$$

m. p. 109°, which forms large, six-sided prisms. The methyl ester also yields two *γ-bromo*-derivatives, m. p. 84° and 122°. E. G.

A New Oxide of Carbon, $C_{12}O_9$. HANS MEYER and KARL STEINER (*Ber.*, 1913, **46**, 813—815).—When mellitic acid is subjected to the action of dehydrating agents, either it remains unchanged or, by more drastic treatment, it is converted into the anhydride of pyromellitic acid. As intermediate product, an anhydrocarboxylic *acid* (annexed formula) appears to be formed. This substance can be isolated in the pure state by prolonged boiling of mellitic acid with thionyl chloride or by heating these substances at 160° during several hours. It forms a white, crystalline powder, which unites with the calculated quantity of water to form mellitic acid, and which, when strongly heated, yields pyromellitic anhydride and carbonised products.



The *oxide* [*mellitic anhydride*] (annexed formula) is obtained when mellitic acid is boiled under reflux with much benzoyl chloride during six hours. It separates from boiling benzoyl chloride in colourless crystals, which are perfectly stable and non-hygroscopic. It is practically insoluble in cold water, but unites with warm water to form mellitic acid. It gives characteristic colorations with various solvents of high b. p.; thus with naphthalene, retene, phenanthrene, and fluorene it yields rose-red to bluish-red solutions, and with nitrobenzene a bluish green solution. It darkens when heated above 320°. H. W.



Constituents of Essential Oils. [Degradation of the Diketone, $C_{13}H_{20}O_2$, Obtained from Selinene.] FRIEDRICH W. SEMMLER and FELIX RISSE (*Ber.*, 1913, **46**, 599—603. Compare this vol., i, 66, 188).—The diketone, $C_{13}H_{20}O_2$, obtained by the oxidation of natural selinene and also the diketo-monocarboxylic acid, obtained by the action of ozone on ortho(α)selinene, have been further oxidised, whereby a tribasic acid, $\begin{array}{l}CH_2\text{—}CH_2\text{—}CH\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H \\ CHMe\cdot CH_2\cdot CH\cdot CO_2H\end{array}$, has been obtained.

The diketone was most advantageously oxidised by a cold solution of bromine in aqueous sodium hydroxide. The *acid*, $C_{12}H_{18}O_6$, so obtained was purified by solution in alcohol and addition of chloroform, when the precipitated product was found to contain chloroform (about one mol. of chloroform to two mols. of acid), which could only be completely removed by heating it in a vacuum at the temperature of boiling xylene. The pure acid had m. p. 188°. Its tribasic nature was shown by converting it into the methyl *ester*, $C_{15}H_{24}O_6$, b. p. 200—205°, D^{20} 1·140, n_D 1·47948, α_D −27°48′, by the action of methyl iodide on the *silver* salt. The acid could be recovered unchanged after saponification of the ester.

The same acid was obtained when the diketo-monocarboxylic acid, $C_{14}H_{22}O_4$, was oxidised by bromine in alkaline solution or by nitric acid. H. W.

Studies in the *cyclo*Pentadiene Series. III. Certain Derivatives of 5-Nitro-2 : 3-dibenzoyl-$\Delta^{1:3}$-*cyclo*pentadiene. WILLIAM J. HALE and LAMBERT THORP (*J. Amer. Chem. Soc.*, 1913, **35**, 262—272. Compare A., 1912, i, 566; this vol., i, 184).—In the earlier papers, it has been shown that the formation of a *cyclo*pentadiene ring by the condensation of a 1 : 3-dialdehyde with diphenacyl proceeds more slowly than with acetonylacetone. A study has now been made of the behaviour of *pp′*-dimethyl-, *pp′*-dibromo-, and *p*-bromo-diphenacyl. The results show that the effect of methyl groups in the phenyl rings of diphenacyl is to retard the activity of the methylene groups of this ketone, whilst the presence of bromine atoms increases their activity.

By the condensation of *pp′*-dimethyldiphenacyl (Limpricht, A., 1900, i, 600) with sodium nitromalonaldehyde, *5-nitro-2 : 3-di-*p*-toluoyl-$\Delta^{1:3}$-*cyclo*pentadiene*, $NO_2\cdot CH<\begin{array}{l}CH:C\cdot CO\cdot C_6H_4Me \\ CH:C\cdot CO\cdot C_6H_4Me\end{array}$, was obtained in a yield of about 75% of the theoretical; it crystallises in yellow prisms, and decomposes at 243—244°. The *silver* salt decomposes at about 200°, and the *monoxime* at 150—151°.

Ethyl p-*bromophenacylbenzoylacetate*,

$$C_6H_4Br\cdot CO\cdot CH_2\cdot CHBz\cdot CO_2Et,$$

m. p. 81°, obtained in 75% of the calculated yield by the condensation of *p*-bromophenacyl bromide with the sodium derivative of ethyl benzoylacetate, forms colourless needles, and when boiled with dilute potassium hydroxide, is converted into p-*bromodiphenacyl*,

$$CH_2Bz\cdot CH_2\cdot CO\cdot C_6H_4Br,$$

m. p. 116°, which crystallises in white plates with a pearly lustre. The yield of the latter compound amounted to 45% of the theoretical. 5-*Nitro*-3-*benzoyl*-2-p-*bromobenzoyl*-$\Delta^{1:3}$-cyclo*pentadiene*,

$$NO_2\cdot CH\left\langle\begin{matrix}CH:C\cdot CO\cdot C_6H_4Br\\ CH:C\cdot CO\cdot C_6H_5\end{matrix}\right. ,$$

was obtained in a yield of about 75% of the calculated by the condensation of *p*-bromodiphenacyl with nitromalonaldehyde; it forms small, yellow prisms and decomposes at 240—241°.

The *sodium* derivative of *ethyl* p-*bromobenzoylacetoacetate* was prepared by Claisen's method. When the ester itself is warmed with aqueous ammonia, *ethyl* p-*bromobenzoylacetate*,

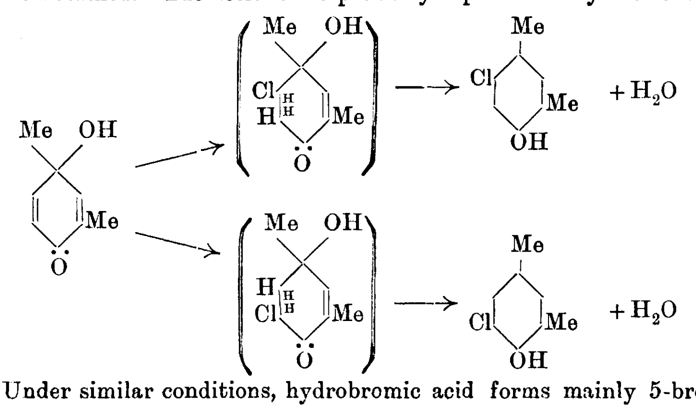
$$C_6H_4Br\cdot CO\cdot CH_2\cdot CO_2Et,$$

is obtained as a pale yellow, oily liquid which cannot be distilled without decomposition even under 5 mm. pressure. Its sodium derivative condenses with *p*-bromophenacyl bromide to form *ethyl* p-*bromobenzoyl*-p-*bromophenacylacetate*, $C_6H_4Br\cdot CO\cdot CH_2\cdot CH(CO\cdot C_6H_4Br)\cdot CO_2Et$, m. p. 75°, which crystallises in small, colourless prisms; a 60% yield of the theoretical was obtained. When this ester is boiled with dilute potassium hydroxide, it gives 30% of the calculated yield of *pp'*-dibromodiphenacyl, $C_6H_4Br\cdot CO\cdot CH_2\cdot CH_2\cdot CO\cdot C_6H_4Br$, m. p. 182°, which forms lustrous, colourless plates, and condenses with nitromalonaldehyde with production of 5-*nitro*-2 : 3-*di*-p-*bromobenzoyl*-$\Delta^{1:3}$-cyclo*pentadiene*,

$$NO_2\cdot CH\left\langle\begin{matrix}CH:C\cdot CO\cdot C_6H_4Br\\ CH:C\cdot CO\cdot C_6H_4Br\end{matrix}\right. ,$$

which forms yellow crystals and decomposes at 230—232°. E. G.

Action of Hydrochloric and Hydrobromic Acids on 2 : 4-Dimethylquinol [2 : 4-Dimethyl-$\Delta^{2:5}$-*cyclo*hexadiene-4-ol-1-one]. EUGEN BAMBERGER and EMIL REBER (*Ber.*, 1913, **46**, 787—813).—It has been previously shown (Bamberger and Brady, A., 1901, i, 142) that aqueous sulphuric acid converts 2 : 4-dimethyl-$\Delta^{2:5}$-*cyclo*hexadiene-4-ol-1-one into *p*-xyloquinol. Hydrochloric acid, in aqueous solution, transforms it mainly into 5-*chloro*-m-4-*xylenol* and 6-*chloro*-m-4-*xylenol*, whilst, in anhydrous glacial acetic acid solution, the latter isomeride is alone obtained. The actions are probably represented by the scheme:



Under similar conditions, hydrobromic acid forms mainly 5-bromo-

m-4-xylenol and 6-bromo-*m*-4-xylenol. The identity of the products was also synthetically established. In the light of the present work, a modified interpretation is given to the observation of Bamberger, Büsdorf, and Szolayski (A., 1899, i, 341) that *p*-nitrosotoluene is converted by hydrochloric and hydrobromic acids into 3-chloro-*p*-cresol, in that hemiquinols are now assumed to be formed as intermediate products.

An improved method for the preparation of 1 : 3-dimethylphenylhydroxylamine is described (compare Bamberger and Brady, *loc. cit.*).

2 : 4-Dimethyl-$\Delta^{2:5}$-*cyclo*hexadiene-4-ol-1-one was heated during one hour at 100° with fuming hydrochloric acid, the mixture diluted with water, and extracted with ether. After drying the ethereal extract, the ether was removed, the residue was allowed to solidify as completely as possible, the solid portions filtered off, and the liquid part submitted to fractional distillation with steam. The following substances were obtained: 5-chloro-*m*-4-xylenol, b. p. 86·5—87°/9 mm. (*phenylurethane*, m. p. 129—130°; p-*nitrobenzoate*, white needles, m. p. 94—95°); 6-chloro *m*-4-xylenol, white, silky needles, m. p. 90—91° (*benzoate*, glassy prisms, m. p. 84·5—85·5°); a *substance*, m. p. 169—170°, possibly chlorodixylenol; a *substance*, m. p. 190°, reddish-yellow needles, possibly chloro-*p*-xyloquinol; traces of *p*-xyloquinol and resin. In a second experiment, dixylenol was obtained in addition to *p*-xyloquinol and *p*-xyloquinone.

5-Chloro-*m*-4-xylenol was prepared by pouring a diazotised solution of 5-amino-*m*-4-xylenol into boiling cuprous chloride solution, and had b. p. 100—101°/17 mm. The phenylurethane and *p*-nitrobenzoate obtained from it were identical with those obtained above.

The synthesis of 6-chloro-*m*-4-xylenol was effected in the following manner: 6-nitro-*m*-4-xylidine was diazotised and treated with cuprous chloride solution, whereby 4-chloro-6-nitro-*m*-xylene, m. p. 42°, was obtained (compare Ahrens, *Annalen*, 1892, **271**, 17). The latter was reduced by tin and hydrochloric acid to 6-chloro-*m*-4-xylidine, leaflets, m. p. 98·5—99°, which, according to Bamberger and Cadgène (*Dissert.*, 1903), is also formed by the action of concentrated hydrochloric acid on *as*-*m*-xylylhydroxylamine. The *hydrochloride, sulphate,* and *oxalate* were also prepared. The *acetyl* derivative forms silky needles, m. p. 158·5°. *Phenyl-4-chloro-*m*-xylylcarbamide*, $C_6H_2Me_2Cl\cdot NH\cdot CO\cdot NHPh$, white, silky needles, has m. p. 217—218° after previous softening. It immediately re-solidifies, melting again at 255° (decomp.). The corresponding *thiocarbamide* has m. p. 140—140·5° when rapidly heated. When slowly heated it melts at a lower temperature. Diazotisation and subsequent boiling of the aqueous solution converts 6-chloro-*m*-4-xylidine into 6-chloro-*m*-4-xylenol, which is identical with the substance described above.

The action of hydrogen chloride dissolved in glacial acetic acid on 2 : 4-dimethyl*cyclo*hexadienolone gave 6-chloro-*m*-4-xylenol, chloro-*p*-xyloquinol, traces of an oily chloroxylenol, resin, and, possibly, *p*-xyloquinol.

2 : 4-Dimethyl*cyclo*hexadienolone, when heated on the water-bath with aqueous hydrobromic acid, b. p. 122—123°, yielded 5-bromo-*m*-4-xylenol (which possibly contained small quantities of 6-bromo-*m*-4-

xylenol, *as*-m-xylenol, and *p*-xyloquinone), dixylenol, *p*-xyloquinol (or *p*-xyloquinone), and an amorphous *acid.*

To determine the constitution of the above bromoxylenol, it was treated with bromine in glacial acetic acid solution. The *product* obtained, long, white needles, m. p. 179·5—180°, had the same m. p. as 2 : 3 : 6-tribromo-*p*-5-xylenol (obtained by bromination of *p*-xylenol) and 2 : 5 : 6-tribromo-*m* : 4-xylenol (obtained by brominating *m*-xylenol), whilst mixtures of any of the three compounds showed no noticeable depression of m. p. When acted on by benzoyl chloride, however, the *benzoates*, m. p. 151—152°, obtained from 2 : 5 : 6-tribromo-*m* : 4-xylenol, and from the product of the successive action of hydrobromic acid and bromine on 2 : 4-dimethyl*cyclo*hexadienolone, proved to be identical, whereas 2 : 3 : 6-*tribromo*-p-*xylenyl*-5-*benzoate* had m. p. 128—129° ; hence, the above monobromoxylenol is probably 5-bromo-*m*-4-xylenol. The *benzoate* and *phenylurethane* of the latter were prepared.

The direct synthesis of 5-bromo-*m*-4-xylenol (compare Stoermer and Göhl, A., 1903, i, 848 ; Orton, Coates, and Burdett, T., 1907, **91**, 53) was effected by the action of cuprous bromide solution on a diazotised solution of 5-amino-*m*-4-xylenol hydrobromide. It had b. p. 121·5—122·5°/37 mm., and yielded a benzoate, m. p. 49—50·5°, and a phenylurethane, m. p. 136·5—137°, after previous softening, which proved to be identical with the above-mentioned products.

2 : 4-Dimethyl*cyclo*hexadienolone, when treated with hydrogen bromide in anhydrous glacial acetic acid solution, gave 6-bromo-*m*-4-xylenol, m. p. 76—76·5°, 5-bromo-*m*-4-xylenol, probably *p*-xyloquinone, possibly crude monobromo-*p*-xyloquinol and resin. The constitution of the solid bromoxylenol follows from its identity with the product obtained from 6-nitro-*m*-4-xylidine by conversion of the latter into 4-bromo-6-nitro-*m*-xylene, reduction of this substance by iron filings and acetic acid to 6-bromo-*m*-4-xylidine and diazotisation of the latter substance (compare Noelting, Braun, and Thesmar, A., 1901, i, 589). H. W.

Preparation of Derivatives of *p*-Benzoquinone. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 253091).—When the dinaphthylamino-*p*-benzoquinones (and their derivatives), obtained by the action of *p*-benzoquinone on α- and β-naphthylamines, are heated with reagents having a high boiling point, they furnish highly coloured compounds, which after sulphonation are of technical importance.

Di-2-naphthylaminodichloro-*p*-benzoquinone, $C_6O_2Cl_2(NH\cdot C_{10}H_7)_2$ (obtained from tetrachloro-*p*-benzoquinone and β-naphthylamlne), when boiled during three hours with nitrobenzene furnishes the *compound*, $C_{26}H_{15}O_2NCl$, glistening, green crystals, m. p. above 300°, whilst the isomeric *compound* from α-naphthylamine has similar properties.

The *compound*, $C_{52}H_{29}O_4N_4Cl$, is obtained from di-2-naphthylaminochloro-*p*-benzoquinone, whilst that from di-2-naphthylamino-*p*-benzoquinone, $C_6H_2O_2(NH\cdot C_{10}H_7)_2$, forms a brownish-yellow powder.

F. M. G. M.

Preparation of Chloroanthraquinones. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 254450. Compare A., 1908, i, 994, and this vol., i, 49, 61).—The preparation of α-chloroanthraquinones by the replacement of a nitro-group by chlorine has been described (*loc. cit.*), and the reaction has now been extended to the β-nitroanthraquinones.

When a suspension of 2-nitro-3-methylanthraquinone in trichlorobenzene is treated with chlorine at 150—180°, it gives rise to a yellow precipitate consisting of a mixture of ω-2-tetrachloro- and ω-2-trichloro-3-methylanthraquinones, which by the action of hot concentrated sulphuric acid, followed by treatment with sodium carbonate, furnishes a readily separable mixture of 2-*chloroanthraquinone*-3-*carboxylic acid*, m. p. 280°, and of 2-*chloroanthraquinone*-3-*aldehyde*, m. p. 229°, whilst the technical mixture of 1 : 6- and 1 : 7-dinitroanthraquinones give rise on similar treatment to 1 : 6-*dichloroanthraquinone*, $C_{14}H_6O_2Cl_2$, m. p. 202—204°. F. M. G. M.

Preparation of 1-Halogen-2-aminoanthraquinones. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 253683. Compare A., 1904, i, 256).—When 2-aminoanthraquinone-3-sulphonic acid is treated with a halogen (1 mol.) it readily yields a 1-halogen-2-aminoanthraquinone-3-sulphonic acid, which by heating with 80% sulphuric acid is converted into the corresponding 1-halogen-2-aminoanthraquinone.

Sodium 1-*chloro*-2-*aminoanthraquinone*-3-*sulphonate* forms orange-red crystals; 1-*chloro*-2-*aminoanthraquinone*, yellow needles, m. p. 228—229°; *sodium* 1-*bromo*-2-*aminoanthraquinone*-3-*sulphonate*, orange-red leaflets, and 1-*bromo*-2-*aminoanthraquinone*, glistening, brownish-red leaflets, m. p. 305°, which on further bromination yields 1 : 3-dibromo-2-aminoanthraquinone. F. M. G. M.

Preparation of Nitro-*p*-acyldiaminoanthraquinone. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D. R.-P. 254185).—Nitro-*p*-acyldiaminoanthraquinones are readily obtained by the action of nitric acid (D 1·5) at temperatures not exceeding 25° on diacyl-1 : 4-diaminoanthraquinones, the nitro-group entering the ortho-position with respect to an amino-group.

2-*Nitro*-1 : 4-*diacetyldiaminoanthraquinone* forms yellowish-brown needles, m. p. 237° (decomp.), and on hydrolysis furnishes 2-*nitro*-1 : 4-*diaminoanthraquinone* as a blue, crystalline powder.

2-*Nitro*-1 : 4-*diaminoanthraquinoneurethane*, orange-red needles, m. p. 230—232°, is obtained in a similar manner from 1 : 4-diaminoanthraquinoneurethane. F. M. G. M.

Preparation of Dianthraquinonylthio-ethers. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 254561).—Dianthraquinonyl thio-ethers are readily prepared by heating anthraquinone mercaptans.

ββ-*Dianthraquinonyl thio-ether*, yellow needles, is thus obtained from anthraquinone β-mercaptan; the isomeric αα-*dianthraquinonyl thio-ether* is a reddish-brown, crystalline powder, whilst αβ-*dianthraquinonyl thio-ether* is prepared by heating together molecular proportions of α- and β-anthraquinone mercaptans.

6-Chloro-1-benzoylaminoanthraquinone when treated with sodium

sulphide furnishes 1-benzoylaminoanthraquinone 6-mercaptan; this, when heated, gives rise to 1 : 1′-*dibenzoyldiamino*-6 : 6′-*dianthraquinonyl thio-ether*, which crystallises from nitrobenzene in yellow needles.

F. M. G. M.

Anthraflavone-G. Eduard Hepp, Rudolf Uhlenhuth, and Fritz Römer (*Ber.*, 1913, **46**, 709—712).—To the above dye (D.R.-P. 199756) has been attributed the structure 1 : 2 : 5 : 6-diphthaloylanthracene (Bohn, A., 1910, i, 405). In its preparation by the action of calcium hydroxide on ω-dichloromethylanthraquinone, the occurrence of large quantities of anthraquinone-2-carboxylic acid as by-product suggests that the first product of the reaction is anthraquinone-2-aldehyde, which then undergoes change into the corresponding acid and alcohol, the latter of which then condenses to anthraflavone. According to this view the dye must be diphthaloylstilbene, and its formation by the action of lead oxide on 2-methylanthraquinone and its derivatives would be analogous to the well-known formation of stilbene from toluene. A convincing proof of the untenability of the older view with regard to the structure is given by the preparation of the dye in better yields than hitherto, from ω-dibromo-2-methylanthraquinone by the action of copper powder or sodium iodide on solutions in nitrobenzene and acetone respectively.

The last method of preparation can be extended to substituted anthraflavones. 1-*Chloro-2-methylanthraquinone*, yellow needles, m. p. 171°, obtained from 2-methylanthraquinone-1-sulphonic acid by heating with potassium chlorate and hydrochloric acid, when treated with bromine in nitrobenzene solution is converted into 1-*chloro-ω-dibromomethylanthraquinone*, yellow leaflets, m. p. 176°; the action of sodium iodide on the acetone solution of this substance produces 1 : 1′-*dichloroanthraflavone* (2 : 2′-dichloro-3 : 4 : 3′ : 4′-diphthaloylstilbene), a yellow, crystalline powder.

The new formula for this class of dye also gives a satisfactory explanation of other properties, such as the quantitative conversion into the corresponding anthraquinonecarboxylic acids.

D. F. T.

2-Methylanthraquinone. Fritz Ullmann and Karl Ludwig Klingenberg (*Ber.*, 1913, **46**, 712—725).—The authors have found that for the preparation of anthraquinone-2-aldehyde in larger quantities, the best method is by the intermediate formation of ω-dibromomethylanthraquinone. The stilbene structure for anthraflavone (see Hepp, Uhlenhuth, and Römer, preceding abstract) is confirmed.

Anthraquinone-2-aldehyde can be obtained by the gradual addition of a mixture of chromic acid and acetic acid to a suspension of 2-methylanthraquinone in acetic anhydride containing a little sulphuric acid, and also by heating ω-dibromomethylanthraquinone (prepared by the action of bromine on the methylanthraquinone in nitrobenzene solution at 150—160°) with concentrated sulphuric acid at 125—130°. The aldehyde forms pale yellow leaflets or needles, m. p. 188—189° (corr.); *phenylhydrazone*, reddish-violet needles, m. p. 242° (corr.); *oxime*, straw-yellow needles, m. p. 238—239°; *semicarbazone*, yellow needles, m. p.

397° (corr.); *azine*, yellow needles, m. p. 410°: *sodium disulphite* compound, colourless crystals.

When a suspension of anthraquinone-2-aldehyde in dimethylaniline with zinc chloride is heated on a water-bath, condensation occurs; the same substance, 2-*anthraquinonyltetramethyldiaminodiphenylmethane*, is obtained when ω-dibromomethylanthraquinone is warmed with dimethylaniline and zinc chloride; it crystallises in red needles, m. p. 240—241° (corr), and can be oxidised to a green colouring matter.

The reaction between ω-dibromomethylanthraquinone and dimethylamine or diethylamine follows a different course at the b. p. of the mixture, the product being the same as that from the action of copper powder on dibromomethylanthraquinone, namely, anthraflavone,

$$C_6H_4{<}{}^{CO}_{CO}{>}C_6H_4\cdot CH{:}CH\cdot C_6H_4{<}{}^{CO}_{CO}{>}C_6H_4$$

(diphthaloylstilbene, dianthraquinonylethylene), identical with the known dye; it is oxidised by sodium dichromate and nitric acid to anthraquinone-2-carboxylic acid, m. p. 285°, and when boiled with bromine in nitrobenzene solution yields the *dibromide*, m. p. above 400°; this on boiling with diethylaniline regenerates the anthraflavone.

If ω-dibromomethylanthraquinone is heated at 240—250°, hydrogen bromide is eliminated and 2 : 2′-*dianthraquinonylacetylene dibromide*, yellow needles, m. p. 360°, is obtained; when heated with diethylaniline or alkali phenoxide, the last substance is converted into 2 : 2′-*dianthraquinonylacetylene* (*diphthaloyltolane*), yellow leaflets, m. p. 350—353°, which unites with bromine to yield the dibromide, and is oxidised by chromic acid in the presence of nitric acid to anthraquinone-2-carboxylic acid; it can also be reduced by hyposulphite to a red vat, which dyes cotton yellow. D. F. T.

Action of Carbon Dioxide on the Magnesium Compound of Fenchyl Chloride. GUSTAV KOMPPA and S. V. HINTIKKA (*Ber.*, 1913, **46**, 645—648).—Fenchyl chloride reacts with magnesium in the course of a week, and when carbon dioxide is passed through the product, the reaction leads to as complicated a mixture as Houben experienced in the case of pinene hydrochloride (A., 1893, i, 42). When the ethereal extract is shaken with sodium carbonate it gives, starting from inactive fenchyl chloride, a clear aqueous solution containing hydrofenchenecarboxylic acid and an emulsion from which a small quantity of *hydrodifenchenecarboxylic acid*,

$$C_{10}H_{17}\cdot C_{10}H_{16}\cdot CO_2H,$$

may be isolated in the form of long, glistening needles, m. p. 106°, whilst the predominating, neutral portion, on fractionation, yields an almost inactive *hydrodifenchene*, $C_{20}H_{34}$, as a glycerol-like liquid, b. p. 155—157°/10 mm., D_4^{17} 0·9564, n_D 1·50928, and also inactive fenchene, and probably some fenchyl alcohol.

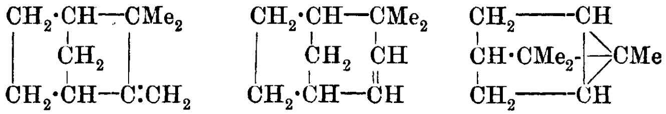
Active fenchyl chloride, α_D^{18} − 6°0′, however, gives a better yield of *hydrofenchenecarboxylic acid*, $C_{10}H_{17}\cdot CO_2H$, in the form of a white, very soluble, inactive mass, b. p. 140—142°/20 mm., m. p. 52—53°, which yields an *amide*, m. p. 107°, and an *anilide*, m. p. 105—106°. On the other hand, no hydrodifenchenecarboxylic acid is obtained, and less neutral substances are formed, from which active *hydrodifenchene*,

b. p. 155—156°/10 mm., D_4^{17} 0·9652, n_D 1·51299, a_D^{18} +5°30′, and an active fenchene, a_D^{20} +4°17′, have been isolated. J. C. W.

Preparation of Esters of Dibromo-β-phenylpropionic Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 254666. Compare this vol., i, 63).—*Fenchyl dibromo-β-phenylpropionate*, colourless, tasteless prisms, m. p. 105°, and of therapeutic value, is readily prepared by heating together fenchyl alcohol and dibromo-β-phenylpropionyl chloride in benzene solution. F. M. G. M.

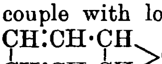
Preparation of a Fenchyl Ester. CHEMISCHE FABRIK VON KERESZTY, WOLF & CIE (D.R.-P. 253756).—*Fenchyl salicylate*, m. p. 51°, is of therapeutic value, and can be prepared by known methods from fenchyl alcohol and salicylic acid (or methyl salicylate). F. M. G. M.

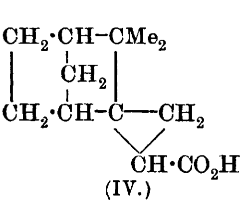
The Constitution of Camphene. EDUARD BUCHNER and WILHELM WEIGAND (*Ber.*, 1913, **46**, 759—768).—Of the three suggested formulæ for camphene:



(I.) (II.) (III).

the first (Wagner's formula) has been received with most favour (compare Semmler, A., 1909, i, 170; Harries and Palmén, A., 1910, i, 497; Komppa, A., 1911, i, 388), and has received additional support from molecular refractivity considerations (von Auwers, A., 1912, ii, 214). A final decision on purely chemical grounds appears to be possible by the application of ethyl diazoacetate.

It has already been shown that benzene and ethyl diazoacetate couple with loss of nitrogen to form ethyl norcaradienecarboxylate,  which after hydrolysis can be oxidised to *cyclo*propane-*trans*-1 : 2 : 3-tricarboxylic acid (Braren and Buchner, A., 1901, i, 385). If this reaction could be applied generally, a substance of formula I should yield 2 : 2-dimethylnorcamphane-3-*spirocyclo*propanecarboxylic acid (formula IV annexed), which might be oxidised to *cyclo*propane-1 : 1 : 2-tricarboxylic acid; a substance of formula II would give finally *cyclo*propane-1 : 2 : 3-tricarboxylic acid, whilst a substance of formula III would not react with ethyl diazoacetate. Experiment gives results in entire accord with the first of these possibilities, thus providing apparently final evidence in favour of formula I.



(IV.)

It is interesting to note that the condensation product of ethyl diazoacetate and camphene is a *spirane* molecule with three-ring systems, this view being supported by determinations of the molecular refraction and dispersion.

The camphene used was mainly prepared from bornyl chloride by the action of aniline (Ullmann and Schmid, A., 1911, i, 70); the same condensation product was always obtained. For the condensation, a mixture of 5 grams of camphene with 5 grams of methyl diazoacetate was gradually added to 30 grams of camphene (m. p. 44—45°; b. p. 156—157°/745 mm.; $[a]_D^{20} + 62·59°$) containing 1 gram of copper powder as catalyst, at 160—165°. A practically theoretical volume of nitrogen is liberated, and *methyl* 2 : 2-*dimethylnorcamphane*-3-spirocyclo*propanecarboxylate* is obtained as a colourless oil, b. p. 126°/14 mm., $[a]_D^{18·5}$ +6·79°, $D_4^{18·5}$ 1·0268, $n_D^{18·5}$ 1·48567, with an odour resembling camphene; in suspension in sodium carbonate solution it is stable towards potassium permanganate. The corresponding *ethyl* ester, obtained by the application of ethyl diazoacetate, has b. p. 128—136°/14 mm The esters can be hydrolysed to the corresponding acid (formula IV) by alcoholic potassium hydroxide, and the product was purified by conversion into the acid *chloride*, which is changed by concentrated aqueous ammonia into the *amide*, colourless leaflets, m. p. 124°; 2 : 2-*dimethylnorcamphane*-3-spirocyclo*propanecarboxylic acid*, obtained by hydrolysis of this, forms colourless needles, m. p. 108°; the *calcium*, *barium*, *lead*, and *silver* salts were obtained by precipitation from an aqueous solution of the *ammonium* salt. When an intimate mixture of the amide with sodium hypobromite solution is warmed on a water-bath, 2 : 2-*dimethylnorcamphane*-3-spiro*amino*cyclo*propane* is produced as an unpleasant smelling oil; *hydrochloride*, colourless leaflets, m. p. 253° (decomp.); yellow *aurichloride*, m. p. 160° (decomp.); *platinichloride*, golden prisms decomposing at 237°; yellow *picrate*, m. p. 201°.

If the methyl ester obtained by the condensation of camphene and methyl diazoacetate is treated in alcoholic solution with sodium, it becomes reduced to 2 : 2-*dimethylnorcamphane*-3-spirocyclo*propanemethylol*, $C_{11}H_{17}·CH_2·OH$, a colourless, viscous liquid, b. p. 129°/12 mm., a_D^{20} +26·79°, D_4^{19} 0·9972, n_D^{19} 1·50205, with an odour resembling that of camphene; *phenylurethane*, needles, m. p. 234°.

The oxidation of 2 : 2-dimethylnorcamphane-3-*spirocyclo*propanecarboxylic acid was effected in dilute sulphuric acid by potassium permanganate, the last substance is added as required, and the process occupies many hours; the oxidation tends to proceed too far, and only a relatively small quantity of *cyclo*propane-1 : 1 : 2-tricarboxylic acid was obtained, which on heating lost carbon dioxide with formation of a mixture of *cyclo*propane-1 : 2-*cis*dicarboxylic acid and the corresponding anhydride; acetyl chloride dehydrated this to the pure anhydride, which was definitely recognisable. D. F. T.

The Constituents of Ethereal Oils. High-boiling Camphor Oil. FRIEDRICH W. SEMMLER and IRENE ROSENBERG (*Ber.*, 1913, **46**, 768—774).—A more careful investigation of the constituents of the blue-coloured, high-boiling camphor oil (compare Schimmel & Co., A., 1909, i, 816).

The oil was separated by distillation into three fractions, b. p. 130—150°/10 mm., 150—170°/10 mm., and 170—190°/10 mm.

The first fraction contained limene and a little cadinene, which were

identified by their hydrogen chloride additive compounds; limene trihydrochloride, m. p. 79°, has before solidification the following properties, b. p. 177—189°/8 mm., D^{20} 1·0370, n_D 1·50152, $[\alpha]_D \pm 0°$. The presence of three ethylenic linkings in limene was proved by reduction in acetic acid with hydrogen and platinum black to *hexahydrolimene*, an optically inactive liquid, b. p. 123—125°, D^{20} 0·8244, n_D 1·45423. This fraction also contained a sesquiterpene, $C_{15}H_{24}$, b. p. 129—133°, D^{20} 0·9015, n_D 1·50058, $[\alpha]_D + 3°$, for which the name *sesquicamphene* is suggested; although the data suggest a bicyclic diolefinic substance, no solid hydrogen chloride additive compound was obtainable.

The second fraction had as almost sole constituent a sesquiterpene alcohol, $C_{15}H_{26}O$, b. p. 159—162°, D 0·95413, for which the name *sesquicamphenol* is suggested; it was purified by conversion into the sodium alcoholate and regeneration by treatment with water; by heating with potassium hydrogen sulphate at 180° for two hours a molecule of water is eliminated with formation of a *hydrocarbon*, b. p. 125—130°, D^{20} 0·9138, n_D 1·50895, $[\alpha]_D + 50°$, which is probably a reduced naphthalene derivative; no solid hydrochloride was obtainable.

The least volatile fraction consisted chiefly of hydrocarbons, from which small quantities of oxygen compounds were removed by heating with sodium; the purified product, b. p. 180—190°/11 mm., D^{20} 0·9276, n_D 1·51986, $[\alpha]_D + 1°$, is a diterpene, $C_{20}H_{32}$, a class of substance generally absent from ethereal oils. If this crude product is treated in ethereal solution with hydrogen chloride, a *tetrahydrochloride*, thin tablets, m. p. 129—131°, is obtained, from which the hydrocarbon can be regenerated in a purer condition by treating successively with a mixture of sodium acetate and acetic acid and then alcoholic potassium hydroxide; it then has b. p. 177—178°/6 mm., D^{20} 0·8870, n_D 1·50339, $[\alpha]_D \pm 0°$. This monocyclic hydrocarbon, for which the name *α-camphorene* is proposed, is reduced by hydrogen and platinum black to *octahydro-α-camphorene*, $C_{20}H_{40}$, b. p. 174—176°/9 mm., D^{20} 0·8526, n_D 1·46470, $[\alpha]_D \pm 0°$. From the oily residue obtained in the preparation of the tetrahydrochloride, could be regenerated by alcoholic potassium hydroxide a bicyclic isomeride, *β-camphorene*, $C_{20}H_{32}$, b. p. 170—180°/10 mm., D^{20} 0·930, n_D 1·518°, $[\alpha]_D \pm 0°$, which gives no solid additive compound with hydrogen chloride.

The blue colour of all high-boiling fractions of camphor oils is due to such small traces of a coloured substance that no particulars of its composition could be determined. D. F. T.

Caoutchouc and Guttapercha Resins. G. H. Hillen (*Arch. Pharm.*, 1913, **251**, 94—121).—Proximate analyses have been made of the resinous portions of various kinds of caoutchouc and allied products.

The resinous portion of "pontianac," "bresk" or "dead Borneo," an inferior "rubber" obtained from the latex of *Dyera costulata*, Hook, was found to contain lupeol acetate, α-amyrin acetate, β-amyrin acetate, and a resen (compare Sack and Tollens, A., 1904, i, 1011; Cohen, A., 1907, i, 211, 230). The formula $C_{26}H_{42}O$ is suggested for lupeol.

The caoutchouc (Ceara rubber) of *Manihot glaziovii*, prepared by the

Lewa process in German East Africa, contains 7% of resin, composed of *iso*cholesterol acetate, a soft resin, and a green, amorphous substance.

Guayule caoutchouc contains 16% of resin, composed of soft resinous material, probably formed by the oxidation of the essential oil contained in the plant, which contains no substances giving the phytosterol reactions (compare Alexander, A., 1911, i, 897).

"Malabuwai guttapercha" from *Alstonia grandifolia*, Miq., contains α-amyrin acetate, β-amyrin acetate, an oily substance, and traces of a yellow resen.

The resin of *Palaquium Gutta* from German New Guinea contains lupeol cinnamate, an oily substance, and a small quantity of a resen.

A table giving the percentages of resin, the appearance of the resins under the microscope, and their reactions with the usual phytosterol reagents for a number of commercial caoutchoucs is provided.

The colour reactions of most of the substances referred to in the paper with phytosterol reagents are tabulated. T. A. H.

The Viscous Transformation of Caoutchouc. A. VON ROSSEM (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 78—83).—According to Gorter (*Mededeelingen over Rubber*, 1911) the transformation of ordinary caoutchouc into the viscous, glue-like modification under the influence of heat, light, and certain chemical reagents is due to depolymerisation. It is suggested that normal polymerised caoutchouc is under ordinary conditions metastable, and that the formation of the viscous variety simply corresponds with the transition from the metastable to the stable form. In support of this view, Gorter describes experiments which show that if a benzene solution of caoutchouc, prepared and kept in the dark, is mixed with a caoutchouc solution which has been exposed to sunlight for some time, the viscosity of the mixed solution gradually diminishes when the solution is protected from the light by means of red glass. In exactly similar circumstances, the viscosity of the original solution was found to remain constant, and the difference in behaviour is supposed to be due to the "inoculation" of the original solution with the stable modification when this solution is mixed with the insolated solution.

To test this theory, measurements of the viscosity of 1% solutions of caoutchouc have been made, with special reference to the influence of light. After exposure to the light from an arc lamp for some hours, the viscosity is found to have diminished, but the subsequent fall is very slow if the solution is kept in the dark, and does not differ from that exhibited by a portion of the original solution which has not been exposed to the arc light. If diffused daylight is allowed access to the solution, the subsequent fall in the viscosity is very much more rapid.

Similar experiments were made with solutions exposed to the light from a Uviol lamp. The results obtained in both series show that there is no after-effect of the light in so far as the viscosity of the solutions is concerned. In some of these experiments the caoutchouc solutions were exposed to the Uviol lamp in glass vessels, whilst in others, quartz vessels were employed. After six and three-quarter

hours' exposure, the time of out-flow of a certain volume of solution was found in a particular case to have fallen from 560 to 412 seconds with the glass apparatus, whilst the time required by the solution after exposure in the quartz tube was only 56 seconds. These results indicate that the active rays are the short-waved rays which are absorbed by glass. H. M. D.

The Hydrohaloids of Artificial and Natural Caoutchoucs, and the Caoutchouc-like Substances Regenerated from Them. CARL D. HARRIES (*Ber.*, 1913, **46**, 733—743).—Contrary to the statement of Weber (A., 1900, i, 353), caoutchouc forms additive compounds with hydrogen bromide and hydrogen iodide, as well as with hydrogen chloride. The method followed was to saturate the chloroform solution of the caoutchouc with the gas, and then after several hours to precipitate by alcohol.

Natural caoutchouc unites with two molecules of each acid, forming substances: $C_{10}H_{18}Cl_2$, $C_{10}H_{18}Br_2$, $C_{10}H_{18}I_2$; guttapercha, caoutchouc obtained by the polymerisation of isoprene under the influence of heat and of sodium, and also caoutchouc obtained from dimethylbutadiene, behave in a similar manner, except that the additive compounds of the two former synthetic caoutchoucs with hydrogen iodide, after precipitation, contain only one molecule of hydrogen iodide.

The halogen hydride is only partly removed by treatment with organic bases, but pyridine and piperidine at 125—145° act on the compounds, if necessary in benzene solution, with elimination of the two molecules of hydracid. The products are not identical with natural caoutchouc, but resemble more the synthetic substance obtained by the action of sodium (Harries, A., 1911, i, 798). The elimination of halogen hydride by heating with sodium hydroxide or sodium amide gives a halogen-free caoutchouc, which, however, is apparently different from the natural product and from that obtained by polymerisation with sodium. The dihydrochloride of guttapercha, when treated for the elimination of two molecules of hydracid, yields a compound resembling caoutchouc, possibly indicating a conversion of guttapercha into caoutchouc.

From a consideration of the difficulty with which the above new forms of caoutchouc undergo ozonisation, it is tentatively suggested that their molecules include a conjugated pair of ethylenic linkings, for example, $CHMe{<}\begin{matrix}CH_2\cdot CH_2\cdot CH_2\\ CH{:}CH\text{—}CH\end{matrix}{>}CMe$ and

$$CHMe{<}\begin{matrix}CH_2\text{—}CH{:}CH\\ CH_2\cdot CH_2\cdot CH\end{matrix}{>}CMe,$$

whilst the arrangement in natural caoutchouc is

$$CMe{\lessdot}\begin{matrix}CH\cdot CH_2\text{—}CH\\ CH_2\cdot CH_2\cdot CH\end{matrix}{>}CMe.$$

[With EWALD FONROBERT.]—From natural caoutchouc were prepared the dihydrochloride, *dihydrobromide*, and *dihydriodide*; from caoutchouc, obtained by polymerisation on warming, were prepared a *dihydrochloride, dihydrobromide*, and a *hydriodide*; "sodium polymerised" caoutchouc yielded a *dihydrochloride*, a *hydrobromide*, and a *hydriodide*; "dimethylbutadiene" caoutchouc yielded a *dihydrochloride, dihydro-*

bromide, and a *dihydriodide*; guttapercha yielded a *dihydrochloride*, *dihydrobromide*, and a *dihydriodide*. Although affected by hydrofluoric acid no hydrofluoride was obtainable from any of the preceding hydrocarbon substances. The above hydrohaloids are amorphous, sometimes viscous, substances, which undergo decomposition at temperatures between 100° and 200°.

The caoutchouc regenerated from the dihydrochlorides by treatment with pyridine or piperidine at 125—135° resembles "sodium isoprene" caoutchouc in solubility and slow absorption of ozone to produce a diozonide, but yields a relatively stable *dihydrobromide* and *dihydriodide*.

D. F. T.

Theory of Vulcanisation. DAVID SPENCE (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 84—85).—Polemical against Kindscher and Hinrichsen (A., 1912, i, 1007) and Ostwald (A., 1912, i, 706).

H. M. D.

α- and β-Antiarin and on Crystallised Albumin from Antiaris Latex. HEINRICH KILIANI (*Ber.*, 1913, **46**, 667—680. Compare A., 1897, i, 91, and A., 1911, i, 138).—Crystallised rhamnose, m. p. 93—94°, and antiarigenin, m. p. 188°, have been obtained from β-antiarin by means of dilute hydrochloric acid. The α- and β-antiarins only differ in their sugars, and careful analyses lead to the formulæ $C_{27}H_{40}O_{10},4H_2O$ and $C_{27}H_{40}O_{10},3H_2O$ respectively, whilst antiarigenin receives the formula $C_{21}H_{28}O_5$. The hydrolysis of these glucosides by means of dilute acids is accompanied by the extensive formation of resinous matter, which seems to indicate the presence of a labile aldehyde or ketone group in antiarigenin. The action of the common moulds is quite unavailing, although the glucosides soon disappear from unpreserved antiaris latex, which may, therefore, contain a specific enzyme.

Antiarose could not be obtained crystalline, but the lactone of antiaronic acid, well-defined monoclinic crystals of the epidote type, has been converted into the following derivatives, which differ from those of the known metameric acids: *phenylhydrazone*, long needles, m. p. 143—145°; *quinine* salt, very slender needles, m. p. 180—181°, more soluble in cold water than the *quinine* salt of rhamnonic acid, which forms nodules of silky needles, m. p. 180—182°; *brucine* salt, small, pointed needles with $2H_2O$, m. p. 118—119°; brucine salt of rhamnonic acid, large crystals with $7H_2O$, m. p. 120—126°.

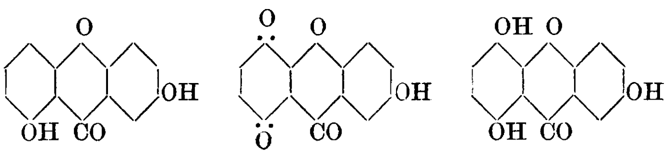
α-Antiarin is considerably attacked by sodium amalgam, and forms an *oxime*, $C_{27}H_{41}O_{10}N,2H_2O$, m. p. 239—240°, which, however, like the parent substance, is unaffected by aluminium amalgam in the cold. Antiarigenin yields a *semicarbazone*, $C_{22}H_{31}O_5N_3$, which begins to sinter at 225°.

Attempts to oxidise the glucosides with silver oxide or hydrogen peroxide were without result, but the action of chromic acid, nitric acid, or permanganate promises to throw light on their constitution.

"Antiaris residue," the portion of the latex which is insoluble in alcohol, contains a protein which may be extracted to the extent of 6·3% by means of 0·8% acetic acid (compare Kotake and Knoop,

A., 1912, ii, 81). It may be recrystallised from hot 10% acetic acid in the form of white, hygroscopic crystals, which darken at 250°, $[\alpha]_D$ −15·2°. The substance may be titrated, using phenolphthalein, but it could not be shown that the magnesium which accompanies the crude protein is combined as a salt. J. C. W.

Anthocyanin. III. An Anthocyanin-like Oxidation Product of Euxanthone. MAXIMILIAN NIERENSTEIN (*Ber.*, 1913, **46**, 649—650. Compare A., 1912, i, 42, 292).—When euxanthone (2:8-hydroxyxanthone) (I), which is obtained by treating Indian-yellow with hydrochloric acid and ammonia, is oxidised by chromic acid in glacial acetic acid, *2-hydroxy-5 : 8-quinoxanthone* (II) is formed in small, sparkling, deep red needles, which give a blue solution in alkalis and a red in concentrated sulphuric acid. On reduction with zinc dust in acetic anhydride suspension, an amorphous product is obtained, which, on hydrolysis, yields *2:5:8-trihydroxyxanthone* (III) in small, light yellow, silky needles with $2H_2O$, m. p. 328—330°. This compound, like its isomeride, gentisein, gives a blood-red colour with sodium amalgam, and its alcoholic solution dyes mordanted cotton. It forms a *triacetyl* derivative, $C_{19}H_{14}O_8$, in faintly yellow needles, m. p. 226—230°, and with diazomethane a *trimethoxyxanthone*, $C_{16}H_{14}O_5$, in pale yellow needles, m. p. 194—195°.



(I.) (II.) (III.)

J. C. W.

Action of Sodium Methoxide on Bilirubic Acid, Bilirubin, and Hemibilirubin. HANS FISCHER and HEINRICH RÖSE (*Ber.*, 1913, **46**, 439—442).—Bilirubin and hemibilirubin resemble the earlier examined pyrrole derivatives (this vol., i, 71, Fischer and Bartholomäus, this vol., i, 209) in their behaviour towards sodium methoxide at elevated temperatures. When heated with sodium methoxide in alcoholic solution at 220—230°, each gives rise to 2 : 4 : 5-trimethylpyrrole-3-propionic acid (identified by the picrate; compare Fischer and Bartholomäus, *loc. cit.*), together with a little xanthobilirubic acid (see below).

Bilirubic acid under similar treatment gives in good yield an acid *substance*, yellow prisms, m. p. 274°, for which the name *xanthobilirubic acid* (or *xanthopyrrolecarboxylic acid*) is proposed; *sodium* salt sparingly soluble. It is possible that the acid is the pure form of the dehydrobilic acid of Piloty and Thannhauser (A., 1912, i, 925). On reduction by a mixture of hydriodic and acetic acids it is reconverted into bilirubic acid.

The above results must be regarded as a proof of the presence of a third pyrrole ring in bilirubin and hemibilirubin. D. F. T.

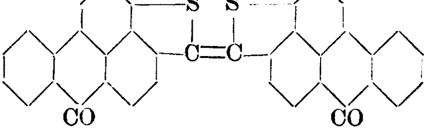
The Identity of Baphinitone with Homopterocarpin. HUGH RYAN and R. FITZGERALD (*Proc. Roy. Irish Acad.*, 1913, **30**, 106—108).—Baphinitone, $C_{17}H_{16}O_4$, obtained from barwood, forms colourless, acicular crystals, m. p. 84° (Anderson, T., 1876, ii, 582, gives m. p. about 88°, and formula $C_{26}H_{26}O_6$). In 4% solution in chloroform it has $[\alpha]_D^{20}$ $-211{\cdot}7°$. Similarly, homopterocarpin, obtained from santalin by the method of Cazeneuve and Hugounenq (A., 1887, 971; 1889, 160), was found to melt at 84° (Brooks, A., 1911, i, 154, gives 86°), and to have $[\alpha]_D^{20}$ $-211°$ in 4% solution in chloroform. In appearance, solubility and m. p., homopterocarpin is identical with baphinitone, and a mixture of the two substances melts at the same temperature as each of its constituents.

A solution of homopterocarpin in chloroform reacts readily with bromine in bright sunlight with the formation of a *substance*, $C_{17}H_{14}Br_2O_4$, colourless needles, m. p. 200°, and of a yellow, amorphous *solid*. Contrary to Cazeneuve's statement, homopterocarpin does not yield methyl iodide when treated with hydriodic acid, and thus contains no methoxy-group; nevertheless, a phenolic substance is obtained by the action of hydriodic acid on it. H. W.

Optical Activity of Tannin. EMANUEL NAVASSART (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 97—99).—The rotatory power of tannin solutions has been examined with reference to the influence of concentration. In the case of aqueous solutions, the rotatory power varies very considerably with the concentration, the value of $[\alpha]_D^{20}$ increasing from 49·8° to 89·7° when the concentration falls from 20% to 0·08%. When dissolved in ethyl alcohol, acetone, and acetic acid, the rotatory power of tannin is much smaller, and varies less with the concentration. For concentrations between 1% and 20%, the observed values of $[\alpha]_D^{20}$ vary from 12·7° to 16·9° in alcohol, from 12·9° to 15·1° in acetone, and from 9·4° to 14·5° in acetic acid. These results seem to show that the rotatory power of the tannin increases as the degree of dispersity of the substance in the various solvents diminishes.

H. M. D.

[Preparation of Derivatives of Benzanthrone Containing Sulphur.] GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE (D.R.-P. 254098).—The action of chlorine (or chlorinating reagents) on 2-methylbenzanthrone (m. p. 199°) gives rise to *chloromethylbenzanthrone*, m. p. 175°; this, when heated with sulphur or polysulphides during two hours at 200—240°, yields the *compound* (annexed formula), glistening, coppery needles.



The preparation of *bromomethylbenzanthrone*, *dichloro-2-methylbenzanthrone*, and of *nitro-* and *amino-benzanthrone* with their sulphur derivatives is also described. F. M. G. M.

Preparation of Homologues of Hydroquinine. Vereinigte Chininfabriken Zimmer & Co. (D.R.-P. 254712. Compare A., 1892, 1253).—The alkylation of hydrocupreine has furnished the following derivatives: *Ethylhydrocupreine*, $C_{21}H_{28}O_2N_2$, is amorphous, but its *sulphate* forms colourless needles, whilst *propylhydrocupreine*, $C_{22}H_{30}O_2N_2$, colourless crystals, has m. p. 142°. F. M. G. M.

Alkaloids of Javanese Coca [Erythroxylon novogranatense]. Anne W. K. de Jong (*Rec. trav. chim.*, 1911, **30**, 204—210; 1912, **31**, 249—259. Compare A., 1906, ii, 315).—The method of analysis previously described has been slightly modified, since it is found that the insoluble barium salts, obtained by heating the alkaloids with barium hydroxide, contain small quantities of barium cinnamate in addition to barium β-truxillate. The cinnamic acid is recovered by agitating the mixed acids with chloroform. The mixed acids obtained from the soluble barium salts are also treated with chloroform, when α-truxillic acid, possibly containing also the β-isomeride, remains. The acids obtained from the chloroform solution were found to contain about 50·3% cinnamic acid and 37·9% benzoic acid.

A second specimen of mixed acids was obtained by decomposing the alkaloids by means of hot hydrochloric acid and solution of the product in ether, which left a small residue of impurities. The ethereal solution was shaken with potassium hydroxide, the latter acidified with hydrochloric acid, and again treated with ether, whereby a small quantity of α-truxillic acid remained undissolved. The ethereal solution was evaporated to dryness, and the residue extracted with chloroform, which left a small residue consisting of a mixture of α- and β-truxillic acids. The acids obtained from the chloroform solution contained 52·1% cinnamic acid, and 34% benzoic acid mixed with acids of higher molecular weight or with neutral substances.

In the second paper the author has worked out a process for the separation of the acids obtained by the decomposition of the alkaloids of Javanese coca, and has ascertained the presence of the following substances in a specimen of these acids: cinnamic, benzoic, *allo*-cinnamic, α-truxillic, β-truxillic and δ-truxillic acids, resinous acids, and neutral substances, together with an acid, m. p. about 150° (probably identical with protococaic acid obtained by Hesse, A., 1903, i, 192), and an acid, m. p. about 190°, possibly identical with β-cocaic acid.

The properties of the truxillic acids and their salts have been investigated. The former are insoluble in light petroleum, but are dissolved in the presence of benzoic or cinnamic acids, the solubility of the α- and γ-acids being, however, only slightly affected. α-, β-, and γ-Truxillic acids are only sparingly soluble in chloroform at the ordinary temperature. Hot chloroform dissolves the β-acid, particularly in the presence of benzoic and cinnamic acids. The δ-acid is soluble in chloroform. The α- and γ-acids are insoluble in benzene, whereas the β- and δ-acids are more soluble in the hot than in the cold solvent. The latter acids may be crystallised from boiling water, in which the α- and γ-acids are but slightly soluble.

One hundred c.c. of an aqueous solution of barium β-truxillate, saturated at 26°, contain 0·028 gram of the salt.

The following salts are sparingly soluble in water: the zinc, cadmium, iron, lead, copper, mercury, and silver salts of the α-acid; the calcium, barium, strontium, zinc, cadmium, manganese, iron, cobalt, nickel, lead, copper, mercury, and silver salts of the β-acid; the lead, copper, mercury, and silver salts of the γ-acid; the same salts of the δ- as of the β-acid, and in addition the magnesium salt. The magnesium salt of the β-acid is soluble in water. H. W.

Preparation of Therapeutically Valuable Double Salts from Morphine and Narcotine. C. F. BOEHRINGER & SOEHNE (D.R.-P. 254502).—The following therapeutically valuable double salts are readily obtained by treating a hot alcoholic solution of the acid with the requisite amount of the other components. *Morphine narcotine meconate*, $C_7H_4O_7,C_{17}H_{19}O_3N,C_{22}H_{23}O_7N,4H_2O$. *Morphine dinarcotine benzenetrisulphonate*, $C_6H_3(SO_3H)_3,C_{17}H_{19}O_3N,(C_{22}H_{23}O_7N)_2,2H_2O$. *Morphine narcotine phenoldisulphonate*,

$$OH{\cdot}C_6H_3(SO_3H)_2,C_{17}H_{19}O_3N,C_{22}H_{23}O_7N,2H_2O.$$

Morphine dinarcotine disulphosalicylate,

$$OH{\cdot}C_6H_3(SO_3H)_2{\cdot}CO_2H,C_{17}H_{19}O_3N,(C_{22}H_{23}O_7N)_2,H_2O.$$

Dimorphine narcotine disulphosalicylate,

$$OH{\cdot}C_6H_3(SO_3H)_2{\cdot}CO_2H,(C_{17}H_{19}O_3N)_2,C_{22}H_{23}O_7N,2H_2O.$$

Morphine narcotine sulphate, $H_2SO_4,C_{17}H_{19}O_3N,C_{22}H_{23}O_7N,4\frac{1}{2}H_2O$. They form colourless crystals, sparingly soluble in cold, readily in hot water, and somewhat insoluble in the ordinary organic media.

F. M. G. M.

Preparation of Morphine Esters of Alkyl- and Aryloxy-fatty Acids. CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.-P. 254094).—*Diethoxyacetylmorphine*, an oil, is prepared by heating morphine (10 parts) with ethoxyacetic anhydride (37 parts) during several hours at 40—45°; the *hydrochloride*, glistening leaflets, decomposes at about 142°.

Ethoxyacetylmorphine, m. p. 155° (about), is obtained accompanied by the foregoing compound when the proportions of the reacting components are varied, and the mixture heated at 40—50°; the *hydrochloride*, needles, has m. p. 183—186°. *Diphenoxyacetylmorphine*, m. p. 125° (decomp.), faintly-coloured crystals, is prepared in an analogous manner. F. M. G. M.

Alkaloids of Pareira Root. MAX SCHOLTZ (*Arch. Pharm.*, 1913, **251**, 136—151. Compare A., 1913, i, 87, and Faltis, 1912, i, 796).—As the result of further analyses, the author now reverts to the formula $C_{18}H_{21}O_3N$, which he used originally for the bebeerines. Bebeerine, *iso*-bebeerine, and β-bebeerine can all be represented by the extended formula $OH{\cdot}C_{16}H_{14}O(OMe){\colon}NMe$. The first and third isomerides yield with acetic anhydride the same optically inactive hydroxytriacetylbebeerine. The latter appears to be formed by the opening of a ring containing nitrogen, the attachment of an acetyl group to the N-atom, and of the residue $CH_3{\cdot}CO{\cdot}O$ to the carbon atom formerly linked to the N-atom.

*iso*Bebeerine yields two hydroxytriacetyl*iso*bebeerines, one dextrorotatory and the other inactive.

*iso*Bebeerine, $C_{18}H_{21}O_3N$, m. p. 297° (decomp.), is the chief constituent of "crystallised bebeerine sulphate" (Merck); the *hydriodide*, m. p. 300° (approx. decomp.), forms prisms from water; the *hydrochloride* is precipitated as colourless needles on adding hydrochloric acid to a solution of the sulphate; the *methiodide*, B,MeI, m. p. 275° (decomp.), forms large, prismatic crystals containing water of crystallisation. On heating with acetic anhydride, *iso*bebeerine yields (1) *α-hydroxytriacetyl*iso*bebeerine*, m. p. 130—140°, $[\alpha]_D^{20}$ + 68·1° in pyridine, which is colourless and amorphous, and *β-hydroxytriacetyl*iso*bebeerine*, m. p. 291° (approx.), $[\alpha]_D = 0°$, which crystallises in colourless needles and is only soluble in pyridine. On hydrolysis by sodium hydroxide in alcohol, each triacetyl derivative yields a corresponding *hydroxymonoacetyl*iso*bebeerine*; the α-compound, m. p. 280° (approx.), crystallises in colourless, slender needles, and the β-isomeride, m. p. 332° (approx.), forms microscopic needles. Both are insoluble, except in solutions of the alkali hydroxides. *Benzoyl*iso*bebeerine*, m. p. 215° (approx.), obtained by the action of benzoic anhydride on *iso*bebeerine, crystallises from alcohol in glancing, yellow leaflets.

β-Bebeerine, $C_{18}H_{21}O_3N$, is amorphous, but yields a crystalline *methiodide*, B,MeI, m. p. 80° (hydrated) or 258—259° (dry, decomp.). Both bebeerine and β-bebeerine on heating with acetic anhydride yield the same *hydroxytriacetylbebeerine*, $C_{24}H_{29}O_7N$, m. p. 125—135°, which is amorphous, and loses two acetyl groups on treatment with potassium hydroxide in alcohol. T. A. H.

Zygadenine, the Crystalline Alkaloid of Zygadenus intermedius. Frederick W. Heyl, F. E. Hepner, and Sylvester K. Loy (*J. Amer. Chem. Soc.*, 1913, **35**, 258—262).—It has been shown already (A., 1911, ii, 325) that the leaves of *Zygadenus intermedius* yield 0·3—0·4% of a mixture of alkaloids. Further work on this subject has resulted in the isolation of a pure alkaloid, *zygadenine*, $C_{39}H_{63}O_{10}N$, m. p. 200—201°, $[\alpha]_D$ − 48·2°, which crystallises from benzene in clusters of lustrous needles, and from alcohol in orthorhombic prisms containing 2Et·OH; the *aurichloride* forms long, dense prisms. The alkaloid gives a yellowish-orange coloration with concentrated sulphuric acid, changing to a brilliant cherry-red. Its physiological action resembles that of veratrine. E. G.

Electrochemical Reductions. III. Reduction of Nitrosoamines. Hilmar Johannes Backer (*Rec. trav. chim.*, 1913, **32**, 39—47. Compare A., 1912, i, 339, 730).—Nitrosopiperidine suspended in sulphuric acid (10%) was electrolysed at a cathode of tinned copper when an 81% yield of the corresponding hydrazine (estimated by oxidation to the tetrazone) was obtained (compare Knorr, A., 1884, 467; Ahrens, A., 1897, i, 369). At a platinum electrode, the hydrogen was incompletely utilised, and the yield of hydrazine sank to 32%. An excess of hydrogen was found to be practically without effect on the hydrazine.

Diaminopiperazine was obtained in 55% yield by the action of zinc

dust and acetic acid on dinitrosopiperazine (compare Schmidt and Wichmann, A., 1892, 210). Electrolytic reduction at a tinned copper cathode of a suspension of the latter in a mixture of acetic and sulphuric acids gave a 38% yield of diaminopiperazine, which, however, increased to 72% when the mixture of acids was replaced by an aqueous solution of sodium sulphate to which a few drops of sulphuric acid had been added. An attempt to convert dinitrosopiperazine into dinitropiperazine by the action of nitric acid was unsuccessful.

Phenylmethylhydrazine (compare Fischer, A., 1878, 312; 1887, 138) was formed by electrolytic reduction of phenylmethylnitrosoamine suspended in dilute acetic acid at a tinned copper cathode. The yield was 79% of the theoretical.

α-Nitroso-α-methylcarbamide, $NH_2\cdot CO\cdot NMe\cdot NO$, was readily reduced in sulphuric acid suspension at a tin cathode with the formation of methylsemicarbazide (compare Brüning, A., 1890, 23; Young and Oates, T., 1901, **79**, 662), which was identified by conversion into benzylidenemethylsemicarbazone, white needles, m. p. 163°. Young and Oates (*loc. cit.*) give 159—160° as m. p. of this substance, whilst Michaelis and Hadanck (A., 1908, i, 1020) found 162°. H. W.

Indole. RUDOLF WEISSGERBER (*Ber.*, 1913, **46**, 651—659).—The difficulty experienced in preparing derivatives of indole is chiefly due to the lability of the imino-hydrogen atom. If this atom is replaced by a group which can be subsequently removed, it is found possible to obtain halogen derivatives by direct substitution and to disrupt the indole ring so that anthranilic acid results.

[With ARNO KLEMM.]—Halogens react violently with indole, and only by working in very dilute solutions could Pauly and Gundermann obtain iodoindole (A., 1909, i, 71). When 1-benzoylindole (A., 1911, i, 155), however, is treated in the cold with bromine in carbon disulphide, *bromo*-1-*benzoylindole*, $C_{15}H_{10}ONBr$, is obtained in thick plates, m. p. 97—98°, which may be hydrolysed by dilute ammonia or, more conveniently, by means of sodium ethoxide in alcoholic solution, when water precipitates *bromoindole*, C_8H_6NBr, in silvery leaflets which have a strong fœcal odour and undergo vigorous decomposition at 67°. The compound is not very stable, but the bromine atom resists the action of alkalis.

1-Benzoylindole also combines with chlorine, and the *chloro*-1-*benzoylindole*, colourless prisms, m.p. 97—99°, may be hydrolysed to the chloroindole which Mazzara and Borgo obtained by the action of sulphuryl chloride on indole (A., 1906, i, 304). Since the benzoyl derivatives may be oxidised to benzoylanthranilic acid, the halogen is present in the pyrrole ring, and, from their similarity to Pauly's 3-iodoindole, the constitution of which was satisfactorily determined, the conclusion is drawn that the bromo- and chloro-derivatives are also substituted in position 3, although all three compounds give 2-oxindole when treated with dilute acids.

[With O. HERZ.]—The oxidation of indole itself results in the formation of amorphous masses, but the benzoyl compound is readily converted by permanganate in acetone solution into benzoylanthranilic acid, and this, by hydrolysis, into anthranilic acid itself.

[With F. Kraft.]—The conversion of an indole derivative into indigotin has been accomplished by passing ozone through a strongly alkaline solution of 3-indolecarboxylic acid (A., 1911, i, 155). The reaction commences quickly, but the yield is only about 38%, anthranilic acid being isolated from the by-products. Other oxidising agents do not yield indigotin, neither does 2-indolecarboxylic acid give rise to that dye. J. C. W.

Preparation of Substituted Indoles by the Catalytic Decomposition of Hydrazones. Alexander E. Arbuzov and V. M. Tichvinski (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 70—74).—When heated with cuprous chloride or bromide, or platinous or zinc chloride, hydrazones of aldehydes and ketones undergo catalytic decompositions in directions depending on their structures and on the magnitudes of the radicles present. In the cases already investigated, the principal products are substituted indole derivatives.

Methyl-ethyl-ketone-phenylhydrazone (50 grams), when heated at 180—230° in presence of cuprous chloride (0·1 gram), yields 2 : 3-dimethylindole, the yield being about 60%.

Similarly, propaldehydephenylhydrazone gives skatole in 73—74% yield, whilst propaldehydetolylhydrazone gives 3 : 5-dimethylindole, $C_{10}H_{11}N$, which crystallises in feathery masses of colourless, silky needles, m. p. 74—74·5°. T. H. P.

5-, 6-, and 8-Iodoquinolines and Their Derivatives. Johann Howitz, Hedwig Fraenkel, and Else Schroeder (*Annalen*, 1913, **396**, 53—75).—8-Aminoquinoline is obtained by the reduction of 8-nitroquinoline best by iron and acetic acid. When tin or stannous chloride and hydrochloric acid are used, the resulting 8-aminoquinoline is contaminated with 5-chloro-8-aminoquinoline. 8-*Iodoquinoline*, C_9NH_6I, m. p. 36°, colourless needles, prepared from diazotised 8-aminoquinoline in the usual manner, forms a *platinichloride*,

$$2C_9NH_6I,H_2PtCl_6,2H_2O,$$

m. p. 251°, orange needles, and *methiodide*, m. p. 200°, yellow needles. By oxidation with alkaline potassium ferricyanide, the latter yields 8-*iodo*-1-*methyl*-2-*quinolone*, $C_6H_3I{<}\begin{matrix}NMe\cdot CO\\ CH{=}CH\end{matrix}$, m. p. 168°.

The 8-iodoquinoline, m. p. 136°, described by Claus and Grau in 1893, is 5-chloro-8-iodoquinoline, produced from the impure 8-aminoquinoline mentioned above.

8-Iodoquinoline is readily nitrated by concentrated sulphuric acid and nitric acid (D 1·5) in the cold, yielding 8-*iodo*-5-*nitroquinoline*, m. p. 192°, pale yellow needles. 8-*Iodo*-5-*aminoquinoline*,

$$C_9NH_5I\cdot NH_2,H_2O,$$

m. p. 148° (anhydrous, 155°), brown prisms (*benzoyl* derivative,

$$C_{16}H_{11}ON_2I,H_2O,$$

m. p. 218°, leaflets), yields 5 : 8-*di-iodoquinoline*, m. p. 162°, and 5-*chloro*-8-*iodoquinoline*, m. p. 138°, by the usual methods.

By the Sandmeyer process, 5-aminoquinoline yields 5-chloroquinoline, m. p. 44—45° (Claus and Junghanns give 31°), the nitration of which

produces 5-chloro-8-nitroquinoline, m. p. 136° (184°, Claus and Junghanns). 5-Chloro-8-aminoquinoline, m. p. 75° (69°, Claus and Junghanns), forms an *acetyl* derivative, m. p. 140°, and is converted into 5-chloro-8-iodoquinoline by the usual method.

8-Iodoquinoline is readily attacked by 40% fuming sulphuric acid in the cold, yielding 8-*iodoquinoline-5-sulphonic acid*, $C_9NH_5I{\cdot}SO_3H$, silver-grey leaflets, of which the *sodium* and *barium* salts are described. The *silver* salt, $C_9NH_5I{\cdot}SO_3Ag,\frac{1}{2}H_2O$, when dehydrated, reacts with methyl iodide at 120—130° to form chiefly the *betaine*, m. p. 292° (decomp.), of 8-iodo-1-methylquinoline-5-sulphonic acid, and with ethyl iodide at 130—140° to form *ethyl* 8-*iodoquinoline-5-sulphonate*,

$$C_9NH_5I{\cdot}SO_3Et,$$

m. p. 156°, colourless leaflets, and the *betaine*, m. p. about 340° (decomp.), of 8-iodo-1-ethylquinoline-5-sulphonic acid. Sodium 8-iodoquinoline-5-sulphonate and phosphorus pentachloride at 125—130° yield 8-*iodoquinoline-5-sulphonyl chloride*, m. p. 116°, yellow needles or prisms, from an ethereal solution of which and dry ammonia the *sulphonamide*, $C_9NH_5I{\cdot}SO_2{\cdot}NH_2$, m. p. 212°, is obtained. The position of the sulpho-group in 8-iodoquinoline-5-sulphonic acid is proved by nitration, whereby the sulpho- is replaced by the nitro-group, and 8-iodo-5-nitroquinoline, m. p. 192°, is obtained.

5-Iodoquinoline methiodide is oxidised to 5-*iodo*-1-*methyl*-2-*quinolone*, m. p. 172°, yellow leaflets, by alkaline potassium ferricyanide. 5-*Iodo* 8-*nitroquinoline*, m. p. 160°, yellow needles, obtained by the nitration of 5-iodoquinoline on the water-bath, yields by reduction 5-*iodo*-8-*aminoquinoline*, m. p. 122°, brown needles (*benzoyl* derivative, m. p. 161°), from which 5:8-di-iodoquinoline, m. p. 161°, and 8-*chloro*-5-*iodoquinoline*, m. p. 118°, are prepared by the usual methods; the formation of the di-iodo-compound determines the orientation of the nitro-group in nitrated 5-iodoquinoline.

The following derivatives of 6-iodoquinoline have been prepared: 6-*Iodo*-1-*methyl*-2-*quinolone*, $C_{10}H_8ONI$, m. p. 129°, yellow needles or leaflets; 6-*iodo*-5-*aminoquinoline*, m. p. 176° (*acetyl* derivative,

$$C_{11}H_9ON_2I,H_2O,$$

m. p. 197°); 5:6-*di-iodoquinoline*, m. p. 125°, and 5-*chloro*-6-*iodoquinoline*, m. p. 141°. C. S.

2-*op*-Dinitrophenyl*iso*quinolinium Chloride and its Products of Transformation. THEODOR ZINCKE and G. WEISSPFENNING (*Annalen*, 1913, **396**, 103—131).—The authors' experiments have not realised their expectations that the action of arylamines or of cyanogen bromide on 2-*op*-dinitrophenyl*iso*quinolinium chloride would yield the glutacondialdehyde derivative, $CHO{\cdot}C_6H_4{\cdot}CH_2{\cdot}CHO$, or colour bases, $NAr{:}CH{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}NHAr$, analogous to those obtained in the pyridine series (A., 1904, i, 448, 921; 1905, i, 467, 923; 1907, i, 625).

2-op-*Dinitrophenyl*iso*quinolinium chloride*,

$$C_6H_3(NO_2)_2{\cdot}NCl{<}\begin{matrix}CH{\cdot}C_6H_4\\ |\\ CH{:}CH\end{matrix},$$

decomp. 130°, stout, rhombic crystals, is obtained by keeping an ethereal solution of *iso*quinoline and 1-chloro-2:4-dinitrobenzene for

several weeks or months at the ordinary temperature. It forms a *platinichloride*, m. p. 222°, and *periodide*, $C_{15}H_{10}O_4N_3I_3$, dark brown needles, and is readily hydrolysed by hot aqueous sodium nitrite, yielding *iso*quinoline, hydrogen chloride, and 2:4-dinitrophenol (in the form of the dinitrophenyl*iso*quinolinium and *iso*quinoline salts; the latter has m. p. 127°). Hydrogen sulphide decomposes the chloride, 2:4-dinitrophenyl mercaptan being produced in the aqueous solution and 2:4-dinitrophenyl sulphide in alcoholic solution.

Dinitrophenyl*iso*quinolinium chloride is converted by aqueous ammonia or sodium carbonate or by an aqueous solution of methylamine or aniline, less satisfactorily by aqueous sodium hydroxide, into the *ψ base*, $C_6H_3(NO_2)_2\cdot N<\begin{matrix}CH(OH)\cdot C_6H_4\\ CH{=\!=\!=}CH\end{matrix}$, orange-red needles, m. p. 141—142°, darkening at about 90°, which is reconverted into dinitrophenyl*iso*quinolinium chloride by dilute hydrochloric acid, and yields ethers, $C_6H_3(NO_2)_2\cdot N<\begin{matrix}CH(OR)\cdot C_6H_4\\ CH{=\!=\!=}CH\end{matrix}$, by warming with alcohols; the *methyl ether*, m. p. 149°, dark red crystals, *ethyl ether*, m. p. 135°, pale red prisms, and iso*butyl ether*, m. p. 122°, orange-red crystals, have been prepared. These ethers, which are also produced directly from dinitrophenyl*iso*quinolinium chloride and ammonia dissolved in the alcohol, are converted one into another by warming with the necessary alcohol.

By heating with water at 90—95° for some hours, or with acetone at 100°, or with boiling acetic anhydride, the freshly precipitated ψ-base is converted into an *isomeride*, m. p. 151°, dark red crystals with a violet shimmer. The isomeride is only slowly attacked by warm dilute hydrochloric acid, does not form ethers by boiling with alcohols, and is slowly converted into dinitrophenyl*iso*quinolinium chloride by hot concentrated hydrochloric acid. It does not react with phenylhydrazine, and is, therefore, not the aldehydo-base, $CHO\cdot C_6H_4\cdot CH{:}CH\cdot NH\cdot C_6H_3(NO_2)_2$; probably it has the constitution $NHR\cdot CH{:}CH\cdot C_6H_4\cdot CH(OH)\cdot O\cdot CH<\begin{matrix}NR{-}CH\\ C_6H_4\cdot CH\end{matrix}$ [where R is $C_6H_3(NO_2)_2$], and is formed by the union of the ψ-base and the aldehydo-base.

When boiled in alcoholic solution with aniline or *p*-toluidine, dinitrophenyl*iso*quinolinium chloride or, better, the ψ-base or the violet isomeride is decomposed into 2:4-dinitroaniline and the 2-aryl*iso*quinolinium chloride. 2-*Phenyl*iso*quinolinium chloride*, $C_{15}H_{12}NCl,2H_2O$, long needles, forms a *platinichloride*, m. p. 228—229°, orange needles, and *mercurichloride*, m. p. 183—184°; the *dichromate*, decomp. about 195°, and *picrate*, m. p. 136—137°, yellow needles, are described. 2-p-*Tolyl*iso*quinolinium chloride*, $C_{16}H_{14}NCl,2H_2O$, colourless needles, forms a *platinichloride*, m. p. 216—217°, orange-yellow needles.

Dinitrophenyl*iso*quinolinium chloride is converted into the ψ-base by hydrazine hydrate, but reacts with phenylhydrazine in boiling alcohol just as does dinitrophenylpyridinium chloride (A., 1904, i, 448), yielding the *dinitroanilinophenylhydrazone*,

$$C_6H_3(NO_2)_2\cdot NH\cdot CH{:}CH\cdot C_6H_4\cdot CH{:}N\cdot NHPh,$$

m. p. 183—184°, black needles. In a similar manner the *dinitroanilino*-p-*tolylhydrazone*, $C_{22}H_{19}O_4N_5$, m. p. 185—186°, black leaflets with a red shimmer, and the *dinitroanilino-phenylmethylhydrazone*, $C_{22}H_{19}O_4N_5$, m. p. 181—182°, reddish-brown leaflets, have been obtained. These three substances are decomposed by boiling alcohol and hydrochloric acid, D 1·19, into 2:4-dinitroaniline and 2-*anilino*iso*quinolinium chloride*, $C_9H_7N(NHPh)Cl$, m. p. 198—200°, faintly yellow, monoclinic prisms (*platinichloride*, m. p. 190° [decomp.]), 2-p-*toluidino*iso*quinolinium chloride*, rhombic plates, and 2-*methylanilino*iso*quinolinium chloride*, faintly yellow needles (*picrate*, m. p. 170°; *platinichloride*, m. p. 185°; *mercurichloride*, m. p. 174°), respectively. 2-Anilino*iso*quinolinium chloride yields *iso*quinoline (aniline could not be detected) by reduction with zinc dust and dilute hydrochloric acid, and by treatment with aqueous sodium hydroxide, sodium carbonate, or ammonia yields a red precipitate which is apparently a mixture of the ψ-base, $C_6H_4<\begin{matrix}CH(OH)\cdot N\cdot NHPh \\ CH{=\!=\!=}CH\end{matrix}$, and the azo-compound,

$$C_6H_4<\begin{matrix}CH{:}N{:}NPh \\ CH{:}CH\end{matrix}.$$

C. S.

Bromination of 6-Methylquinoline and 6-Quinolinealdehyde. JOHANN HOWITZ and J. PHILIPP (*Annalen*, 1913, **396**, 23—37).—The dibromide of 6-methylquinoline hydrobromide is obtained as a brick-red, crystalline powder by saturating a cold chloroform solution of 6-methylquinoline with hydrogen bromide and subsequently adding bromine (1 mol.). By carefully heating it at 170—180° for two hours, cooling to 140°, and adding more bromine (1 mol.), and heating again at 170—180° for two hours, the substance is converted into 6-*dibromomethylquinoline*, $C_9NH_6\cdot CHBr_2$, m. p. 159—160°, white needles (*platinichloride*, $2C_{10}H_7NBr_2,H_2PtCl_6$, m. p. 235°, orange crystals), and 3-*bromo*-6-*dibromomethylquinoline*, $C_{10}H_6NBr_3$, m. p. 141°, yellowish-white needles, each of which loses two atoms of bromine by hydrolysis with alcoholic potassium hydroxide.

By boiling with water for ten to fifteen minutes and basifying, 6-dibromomethylquinoline is converted into 6-*quinolinealdehyde*, $C_{10}H_7ON$, glistening needles containing H_2O, m. p. 55° (anhydrous, 75—76°), which exhibits the usual reducing and additive properties of an aldehyde. It yields quinoline-6-carboxylic acid by oxidation, forms a *platinichloride*, $2C_{10}H_7ON,H_2PtCl_6$, m. p. 244°, reddish-yellow needles, *aldazine*, $N_2({:}CH\cdot C_9NH_6)_2$, m. p. 261°, yellow needles, *semicarbazone*, m. p. 239°, *oxime*, m. p. 191°, *phenylhydrazone*, m. p. 185°, yellow crystals containing H_2O, *anil*, $NPh{:}CH\cdot C_9NH_6$, m. p. 99°, and o-*tolil*, m. p. 97°, and condenses with dimethylaniline in the presence of zinc chloride to form *tetramethyldiaminodiphenyl*-6-*quinolylmethane*,

$$C_9NH_6\cdot CH(C_6H_4\cdot NMe_2)_2,$$

m. p. 160°, almost colourless needles, which yields a green *dye* by oxidation with lead peroxide. When heated with methyl iodide at 100°, 8-quinolinealdehyde yields a *methiodide*, $CHO\cdot C_9H_6NMeI$, m. p. 218°; the latter is oxidised by cold alkaline potassium ferricyanide to 1-*methyl*-2-*quinolone*-6-*aldehyde*, $CHO\cdot C_6H_3<\begin{matrix}NMe\cdot CO \\ CH{=}CH\end{matrix}$, m. p. 164°,

colourless needles, or the corresponding *acid*, $C_{11}H_9O_3N$, m. p. above 300°, according to the duration of the reaction.

3-Bromo-6-dibromomethylquinoline is hydrolysed by an excess of potassium carbonate and a little water at 115—120°, yielding 3-*bromo-quinoline*-6-*aldehyde*, m. p. 139°, white needles (*aldazine*, m. p. 194°, pale yellow needles; *oxime*, m. p. 217°; *phenylhydrazone*, m. p. 195°; *anil*, m. p. 124°), in which the position of the halogen is determined by its oxidation to 3-bromopyridine-5 : 6-dicarboxylic acid by hot alkaline potassium permanganate. By oxidation with chromic and sulphuric acids, the aldehyde yields 3-*bromoquinoline*-6-*carboxylic acid*, m. p. 245°, long white needles. C. S.

8-Quinolyl Ketones and their Derivatives. JOHANN HOWITZ and O. KÖPKE (*Annalen*, 1913, **396**, 38—52).—Hitherto, only quinolyl ketones have been known containing the carbonyl group attached to the pyridine nucleus. Bromoquinolines and 8-bromomethylquinoline do not react with magnesium in ether. The interaction of 8-quinolinealdehyde (Howitz and Schwenk, A., 1905, i, 471) and magnesium phenyl bromide in ether at 0°, leads to the formation of *phenyl*-8-*quinolylcarbinol*, $OH\cdot CHPh\cdot C_9NH_6$, m. p. 104°, large colourless plates, in about 60% yield. The carbinol forms a *platinichloride*, m. p. 198° (decomp.), and a *benzoate*, m. p. 146°, and is oxidised by chromic and acetic acids on the water-bath to *phenyl* 8-*quinolyl ketone*,

$$COPh\cdot C_9NH_6,$$

m. p. 94°, colourless plates (*platinichloride*, m. p. 213° [decomp.]). By treatment with hydroxylamine hydrochloride and potassium hydroxide in boiling alcohol, the ketone yields an *oxime*, $C_{16}H_{12}ON_2,H_2O$, m. p. 121°, which is converted into an *isomeride*, $C_{16}H_{12}ON_2,H_2O$, m. p. 165°, by heating at 120°, and then crystallising from alcohol. By treating a cold ethereal solution of the oxime, m. p. 121°, with phosphorus pentachloride, and decomposing the precipitated imino-chloride with water at 0°, 8-*benzoylaminoquinoline*, $C_9NH_6\cdot NHBz$, m. p. 93°, is obtained, the identity of which is established by its formation by the benzoylation of 8-aminoquinoline and by its decomposition into 8-aminoquinoline and benzoic acid by concentrated hydrochloric acid at 160°. The oxime, m. p. 121°, is therefore anti-*phenyl* 8-*quinolyl ketoxime*, $\begin{matrix} C_9NH_6\cdot CPh \\ HO\cdot N \end{matrix}$. In a similar manner, the oxime, m. p. 165°, is proved to be syn-*phenyl* 8-*quinolyl ketoxime*, $\begin{matrix} C_9NH_6\cdot CPh \\ N\cdot OH \end{matrix}$, by its conversion by the Beckmann transformation into the anilide of quinoline-8-carboxylic acid; unfortunately, neither the anilide nor the quinolinecarboxylic acid produced by its hydrolysis has been isolated, but only the aniline resulting in the latter operation.

Phenyl 8-quinolyl ketone forms a *phenylhydrazone*, m. p. 190°, *semicarbazone*, m. p. 188°, and *azine*, $C_{32}H_{22}N_4$, m. p. 287°.

8-*Quinolylmethylcarbinol*, $OH\cdot CHMe\cdot C_9NH_6$, m. p. 65° (*platinichloride*, m. p. 197° [decomp.], orange-yellow crystals; *benzoate*, m. p. 100°), obtained ultimately from magnesium methyl iodide and 8-quinolinealdehyde in ether, is oxidised to 8-*quinolyl methyl ketone*, $C_9NH_6\cdot COMe$, m. p. 45°, b. p. about 295°, by potassium dichromate

and very dilute sulphuric acid on the water-bath. The ketone forms a *semicarbazone*, m. p. 223°, and an *oxime*, m. p. 137°; the latter has only been obtained in one modification, which is *syn*-8-quinolyl methyl ketoxime, since it yields 8-acetylaminoquinoline by the Beckmann transformation.

8-*Quinolylethylcarbinol* (*platinichloride*, m. p. 210° [decomp.]; *benzoate*, m. p. 82°) and 8-*quinolyl ethyl ketone*, b. p. about 290° (*semicarbazone*, m. p. 203°), have been prepared by methods similar to the preceding.

C. S.

Preparation of 9-Methylcarbazole. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 255304).—The technically valuable 9-methylcarbazole can be prepared in about 70% yield by the following method.

Dry potassium carbazole is heated with freshly distilled ethyl chloroacetate during about three hours, yielding *ethyl carbazole*-9-*acetate*, m. p. 97°; this when hydrolysed with an alkaline hydroxide gives rise to *carbazole*-9-*acetic acid*, glistening, colourless leaflets, m. p. 215°, which, when carefully heated at 250—270°, evolves carbon dioxide and furnishes pure 9-methylcarbazole, m. p. 87°. F. M. G. M.

Kehrmann's Interpretation of Chromo-Isomeric Acridonium Salts as "Quinhydrone Salts" which Contain Hydroacridine. ARTHUR HANTZSCH (*Ber.*, 1913, **46**, 682—684. Compare this vol., i, 298).—Kehrmann's view that the dark green iodide obtained from methylphenazonium salts is a quinhydrone salt composed of one molecule of azonium tri-iodide and two molecules of methyldihydrophenazine, is combated.

According to Kehrmann, the salt should be decomposed by water into phenylmethylacridonium iodide, phenylmethylhydroacridine, and hydrogen iodide, but in reality it gives a clear, neutral solution, and behaves as a normal binary electrolyte. J. C. W.

"Halochromism" of the Derivatives of Phenyl*iso*oxazolone and of the Indogenides. ANDRÉ MEYER (*Compt. rend.*, 1913, **156**, 714—717. Compare Baeyer and Villiger, A., 1901, i, 658; 1902, i, 380, 769; Meyer, A., 1912, i, 1019).—The indogenides and in particular the *iso*oxazole-indogenides give coloured compounds with acids and metallic salts, comparable to the oxonium salts, and the author has prepared a number of such compounds.

On passing dry hydrogen chloride into a suspension of piperonylidene-*iso*oxazolone in benzene at − 10°, a deep red additive *compound* is formed and crystallises out.

Condensation products are also formed from the *iso*oxazolones and stannic chloride, ferric chloride, or aluminium chloride, and a number of such stannichlorides, prepared by the addition of anhydrous stannic chloride to benzene solutions of the *iso*oxazolones, are described.

*Phenylbenzylidene*iso*oxazolone stannichloride*, $C_{16}H_{11}O_2N,SnCl_4$, a yellow, microcrystalline powder, decomposes at 200°.

*Phenylpiperonylidene*iso*oxazolone stannichloride*, $C_{17}H_{11}O_4N,SnCl_4$, deep red leaflets, decomposes at 160°.

*Phenylanisylidene*iso*oxazolone stannichloride*, $C_{17}H_{13}O_3N,SnCl_4$, a deep yellow powder, decomposes at 155°.

Phenyl-o-*methoxybenzylidene*iso*oxazolone stannichloride*,

$$2C_{17}H_{13}O_3N,SnCl_4,$$

an orange powder, decomposes at 130°.

*Phenylvanillylidene*iso*oxazolone stannichloride*, $C_{17}H_{13}O_4N,SnCl_4$, a brownish-red, microcrystalline powder, decomposes at 150°.

*Phenyldimethylaminobenzylidene*iso*oxazolone stannichloride*,

$$C_{18}H_{16}O_2N_2,2SnCl_4,$$

a bright red powder, decomposes above 250°.

The indogenides furnish similar compounds, such as *piperonylidenehydroxythionaphthen stannichloride*, $C_{15}H_{10}O_3S,SnCl_4$, a violet-black, microcrystalline powder, decomposing at 230°.

All these substances are hydrolysed by water and are practically insoluble in organic solvents, their colours being deeper than those of the parent substances.

The mixed azo-derivatives of phenyl*iso*oxazolone are also "halochromes" and give coloured stannichlorides, the one described being *benzeneazophenyl*iso*oxazolone stannichloride*, $C_{15}H_{11}O_2N_3,SnCl_4$, an orange-yellow powder, decomposing at 130°. W. G.

Some Derivatives of the Methoxyphenyl*iso*oxazolones. ANDRÉ WAHL and C. SILBERZWEIG (*Bull. Soc. chim.*, 1913, [iv], **13**, 236—240. Compare Wahl and Meyer, A., 1908, i, 368; Wahl, *ibid.*, 1909, i, 260).—The authors have condensed *o*-, *m*-, and *p*-methoxyphenyl*iso*oxazolone with a number of aldehydes, and have thus prepared the following substances: 3-o-*methoxyphenyl*-4-*benzylidene*iso*oxazolone*, yellow leaflets, m. p. 150°; 3-m-*methoxyphenyl*-4-*benzylidene*iso*oxazolone*, yellow needles, m. p. 110°; 3-p-*methoxyphenyl*-4-*benzylidene*iso*oxazolone*, yellow leaflets, m. p. 170°; 3-o-*methoxyphenyl*-4-*anisylidene*iso*oxazolone*, pale yellow, m. p. 154°; 3-m-*methoxyphenyl*-4-*anisylidene*iso*oxazolone*, yellow crystals, m. p. 164°; 3-p-*methoxyphenyl*-4-*anisylidene*iso*oxazolone*, pale yellow leaflets, m. p. 165°; 3-o-*methoxyphenyl*-4-*cinnamylidene*iso*oxazolone*, orange-yellow, m. p. 163°; 3-m-*methoxyphenyl*-4-*cinnamylidene*iso*oxazolone*, orange-yellow, m. p. 146—147°; 3-p-*methoxyphenyl*-4-*cinnamylidene*iso*oxazolone*, orange needles, m. p. 163°; 3-o-*methoxyphenyl*-4-*furfurylidene*iso*oxazolone*, yellow crystals, m. p. 171—172°; 3-p-*methoxyphenyl*-4-*furfurylidene*iso*oxazolone*, yellow needles, m. p. 141—142°; 3-o-*methoxyphenyl*-4-p-*dimethylaminobenzylidene*iso*oxazolone*, red needles, m. p. 190°; 3-m-*methoxyphenyl*-4-p-*dimethylaminobenzylidene*iso*oxazolene*, red needles, m. p. 140°; 3-p-*methoxyphenyl*-4-p-*dimethylaminobenzylidene*iso*oxazolone*, red leaflets, m. p. 192°; 3-p-*methoxyphenyl*-4-o-*hydroxybenzylidene*iso*oxazolone*, yellow leaflets, m. p. 195°; 3-o-*methoxyphenyl*-4-p-*hydroxybenzylidene*iso*oxazolone*, orange-yellow, m. p. 218°; 3-m-*methoxyphenyl*-4-p-*hydroxybenzylidene*iso*oxazolone*, yellow leaflets, m. p. 215°; 3-p-*methoxyphenyl*-4-p-*hydroxybenzylidene*iso*oxazolone*, golden-yellow needles, m. p. 204—205°; 3-o-*methoxyphenyl*-4-p-*hydroxy*-m-*methoxybenzylidene*iso*oxazolone*, yellow crystals, m. p. 168°; 3-m-*methoxyphenyl*-4-p-*hydroxy*-m-*methoxybenzylidene*iso*oxazolone*, orange-yellow crystals, m. p. 203°; 3-p-*methoxyphenyl*-4-p-*hydroxy*-m-*methoxybenzylidene*iso*oxazolone*, yellow crystals, m. p. 199°; 3-o-*methoxyphenyl*-

4-mp-*dihydroxybenzylidene*iso*oxazolone*, orange crystals, m. p. 209°; 3-m-*methoxyphenyl*-4-mp-*dihydroxybenzylidene*iso*oxazolone*, orange-red needles, m. p. 184°; 3-p-*methoxyphenyl*-4-mp-*dihydroxybenzylidene*iso*oxazolone*, orange crystals, m. p. 193°; with *o*-vanillin, the 3-*o*- and *p*-methoxyphenyl*iso*oxazolones form yellow *leaflets*, m. p. 195°, and orange-yellow *leaflets*, m. p. 208°, respectively, whilst with resorcylaldehyde, 3-*o*-, *m*- and *p*-methoxyphenyl*iso*oxazolones yield orange-yellow *crystals*, m. p. 235°, orange-yellow *crystals*, m. p. 240°, and yellow *crystals*, m. p. 209°, respectively. The phenolic derivatives dissolve in alkali, forming solutions in which the colour varies from yellow to reddish-violet. Presence of excess of alkali rapidly discharges these colorations, yielding colourless solutions from which acids re-precipitate the original substance. The action of excess of alkali probably causes a rupture of the lactonic grouping according to the scheme:

$$O{<}\begin{matrix}CO\cdot C{:}CH\cdot R\\ N{=}C\cdot C_6H_4\cdot OCH_3\end{matrix} \quad \underset{\overleftarrow{\text{HCl}}}{\overset{\text{NaOH}}{\longrightarrow}} \quad \begin{matrix}CO_2Na\cdot C{:}CH\cdot R\\ HO\cdot N{=}C\cdot C_6H_4\cdot OCH_3\end{matrix}.$$

The three methoxyphenyl*iso*oxazolones have been condensed with 5-bromoisatin chloride, yielding the three 3-*methoxyphenyl*iso*oxazolone-5-bromo-2-indoles*, $\begin{matrix}N{:}C\cdot C_6H_4\cdot OCH_3\\ O\text{———————}CO\end{matrix}{>}C{:}C{<}\begin{matrix}NH\\ CO\end{matrix}{>}C_6H_3Br$, the properties of which are similar to those of the previously described indigoid dyes derived from the three methoxyphenyl*iso*oxazolones and isatin chloride. If, however, sodium hyposulphite is added to their solution in alkali, the yellow colour of the latter persists. Addition of acid causes the formation of a flocculent, yellow *precipitate*. The latter dissolves in alcohol, forming a red solution, the colour of which deepens on addition of an oxidising agent, the initial dye being ultimately formed. The yellow precipitate appears to be the leuco-derivative of the dye. It presents no marked affinity for the textile fibres.

H. W.

Action of Acetic Anhydride on some Benzylideneanthranilic Acids. II. JOHN B. EKELEY AND STILES CLINTON (*J. Amer. Chem. Soc.*, 1913, **35**, 282—284).—Ekeley and Dean (A., 1912, i, 211) have shown that a series of oxazines can be obtained by the action of acetic anhydride on benzylideneanthranilic acids. The reaction seems to be of general application, and further compounds are now described.

Protocatechuylideneanthranilic acid, m. p. 204°, obtained by the condensation of protocatechualdehyde with anthranilic acid, forms orange-red crystals, and is converted by acetic anhydride into 4-*acetyl*-3-(3′ : 4′)*dihydroxyphenyldihydro*-2 : 4-*benzoxazine*-1-*one*,

$$C_6H_4{<}\begin{matrix}CO\text{—}O\\ NAc\cdot CH\cdot C_6H_3(OH)_2\end{matrix},$$

m. p. 121°. *Bromosalicylideneanthranilic acid*, m. p. 198°, crystallises in yellow needles, and furnishes 4-*acetyl*-3-(4′ : 2′-)*bromohydroxyphenyldihydro*-2:4-*benzoxazine*-1-*one*, m. p. 170°. o-*Nitrobenzylideneanthranilic acid*, m. p. 67°, forms straw-coloured needles, and yields 4-*acetyl*-3-o-*nitrophenyldihydro*-2:4-*benzoxazine*-1-*one*, m. p. 167·5°. o-*Methoxybenzylideneanthranilic acid*, m. p. 122°, gives 4-*acetyl*-3-o-*methoxyphenyldihydro*-2:4-*benzoxazine*-1-*one*, m. p. 165°. *Resorcylideneanthranilic acid* begins to

decompose at about 150°; *4-acetyl-3-(1:3)-dihydroxyphenyldihydro-2:4-benzoxazine-1-one* has m. p. 192°. *p-Dimethylaminobenzylidene-anthranilic acid*, m. p. 176°, yields *4-acetyl-3-p-dimethylaminophenyl-dihydro-2:4-benzoxazine-1-one*, m. p. 162°. E. G

A Gelatinous Mercury Salt of an Organic Sulphonic Acid. W. DÖHLE and BERTHOLD RASSOW (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 71—74).—By the action of fuming sulphuric acid on benzothiazole-methenesulphide, a monosulphonic acid of the composition:

$$C_8H_6NS_2\cdot SO_3H$$

is obtained. When aqueous solutions of the potassium salt and of mercuric chloride are mixed together, a yellow solution is obtained, which, sooner or later, depending on the concentration, solidifies to a jelly. The jelly-forming substance is the normal mercuric salt, and its activity is such, that even in $N/100$-solution it is capable of producing a jelly at the ordinary temperature. The mercury salt is unstable, and the jellies sooner or later become cloudy in consequence of the formation of the basic salt, $Hg(C_8H_6NS_2\cdot SO_3)_2,HgO$, which separates out in the form of very small crystals. The stability of the jellies increases with the concentration of the mercury salt and those prepared from $N/5$-solutions of the potassium salt and mercuric chloride can be kept for some time before they begin to exhibit opalescence as a result of the initial precipitation of the basic salt.

The colloidal mercury salt is coagulated by electrolytes and alcohol, the coagulum being converted into the crystalline basic salt on contact with water.

From the examination of freshly prepared solutions of the mercury salt, it has been found that the viscosity increases with time, the rate of increase varying very considerably from one solution to another even when the conditions under which the solutions were prepared, were exactly the same. Most electrolytes increase the viscosity, but potassium iodide increases it to a remarkable extent. H. M. D.

Aromatic ψ-Thiocarbamides and Orthothiocarbonic Esters. FRITZ ARNDT (*Annalen*, 1913, **396**, 1—22. Compare A., 1911, i, 918).—*Phenyl-ψ-thiocarbamide*, $NH:C(NH_2)\cdot SPh$, m. p. 96—97° (decomp.), glistening needles, prepared from phenyl mercaptan and cyanamide, forms a sparingly soluble *nitrate-sulphate*,

$$3C_7H_8N_2S,H_2SO_4,HNO_3,$$

m. p. 206° (decomp.), which, however, is distinctly more soluble than the nitrate-sulphate of *p*-tolyl-ψ-thiocarbamide (*loc. cit.*); in fact, the salts of phenyl-ψ-thiocarbamide are much more soluble than those of the *p*-tolyl homologue. *p-Chlorophenyl-ψ-thiocarbamide*,

$$NH:C(NH_2)\cdot S\cdot C_6H_4Cl,$$

forms a *nitrate-sulphate*, $3C_7H_7N_2SCl,H_2SO_4,HNO_3$, m. p. 222° (decomp.).

The substance previously described as nitroso-*p*-tolyl-ψ-thiocarbamide (*loc. cit.*) is now shown to be the *p*-tolyl-ψ-carbamide salt of *dinitroso-p-tolyl-ψ-thiocarbamide*, $OH\cdot N:N\cdot C(SC_7H_7):N\cdot NO$. The salt is decomposed by cold glacial acetic acid into nitrogen and *p*-tolyl thiocyanate, and by cold concentrated hydrochloric acid into nitrous acid and *p*-tolyl-ψ-thiocarbamide. The yellow substance obtained by

its decomposition by boiling methyl alcohol receives the constitution $C_7H_7S\cdot CO\cdot N\colon NOH$, since it yields *p*-tolylthiocyanate and mercaptan by treatment with concentrated hydrochloric acid. By gradually adding the *p*-tolyl-ψ-thiocarbamide salt of dinitroso-*p*-tolyl-ψ-thiocarbamide to a gently boiling methyl-alcoholic solution of potassium acetate (saturated in the cold), the *potassium* salt,

$$C_8H_7O_2N_4SK,H_2O,$$

of the dinitroso-derivative is obtained. It crystallises in glistening needles, yields the *calcium, barium,* and *ferric* salts by double decomposition, and the *benzamidine* salt, white leaflets, by treatment with aqueous benzamidine hydrochloride, and by the action of dilute acetic acid yields the free dinitroso-compound, which, however, instantly decomposes into nitrous acid and *nitroso*-p-*tolyl*-ψ-*thiocarbamide*,

$$C_7H_7S\cdot C(\colon NH)\cdot N\colon N\cdot OH,$$

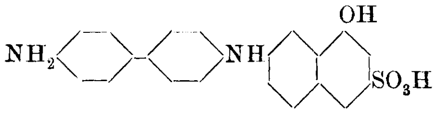
decomp. 115—120°, golden-yellow leaflets. The latter yields nitrous acid and *p*-tolyl-ψ-thiocarbamide by treatment with concentrated hydrochloric acid, and nitrogen and *p*-tolyl thiocyanate with warm glacial acetic acid. By treatment with sodium nitrite and hydrochloric acid, phenyl-ψ-thiocarbamide and *p*-chlorophenyl-ψ-thiocarbamide each yield ψ-thiocarbamide salts of the dinitroso-ψ-thiocarbamide.

As mentioned previously (*loc. cit.*), *p*-tolyl *ortho*-thiocarbonate is obtained by treating a methyl-alcoholic solution of the *p*-tolyl-ψ-thiocarbamide salt of dinitroso-*p*-tolyl-ψ-thiocarbamide with aqueous ammonia. This reaction could not be explained when the *p*-tolyl-ψ-thiocarbamide salt was considered to be a nitroso-compound. Its course is now clear. The ammonia liberates *p*-tolyl-ψ-thiocarbamide and converts it into *p*-tolyl mercaptan, which then reacts with the dinitroso-compound (or its ammonium salt) in accordance with the equation: $C_7H_7S\cdot C(\colon N\cdot NO)\cdot N\colon N\cdot OH + 3C_7H_7\cdot SH = C(SC_7H_7)_4 + 2N_2 + 2H_2O$. The orthothiocarbonate is also obtained by treating a methyl-alcoholic solution of the *p*-tolyl-ψ-thiocarbamide salt or the potassium salt of dinitroso-*p*-tolyl-ψ-thiocarbamide directly with *p*-tolyl mercaptan.

Phenyl orthothiocarbonate, $C(SPh)_4$, m. p. 159°, small leaflets, and p-*chlorophenyl orthothiocarbonate*, $C(S\cdot C_6H_4Cl)_4$, m. p. 212—213°, are prepared by methods similar to the preceding. p-*Chlorophenyl orthothioformate*, $CH(S\cdot C_6H_4Cl)_3$, m. p. 111—112°, almost colourless leaflets, is obtained by boiling *p*-chlorophenyl mercaptan in aqueous sodium hydroxide with an excess of chloroform. *Phenyl tri*-p-*chlorophenyl orthothiocarbonate*, $SPh\cdot C(S\cdot C_6H_4Cl)_3$, small, white leaflets, m. p. about 191°, obtained by warming potassium dinitrosophenyl-ψ-thiocarbamide and the calculated amount of *p*-chlorophenyl mercaptan in methyl alcohol, is converted by crystallisation from acetic acid into a mixture of the tetraphenyl and the tetra-*p*-chlorophenyl esters of orthothiocarbonic acid; the latter has been isolated. *Tri*-p-*chlorophenyl*-p-*tolyl orthothiocarbonate*, m. p. about 193°, is prepared in a similar manner, and also tends to change to the unmixed esters. By reduction with boiling glacial acetic acid and zinc dust, it is converted into *di*-p-*chlorophenyl*-p-*tolyl orthothioformate*, $C_7H_7S\cdot CH(S\cdot C_6H_4Cl)_2$, m. p. 96—97°, white leaflets, which is not changed by crystallisation from glacial acetic acid. C. S.

Preparation of 6-Aminodiarylamino- and 7-Aminodiarylamino-1-naphthol-3-sulphonic Acids with their Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 254510).—Numerous compounds obtained by the condensation of aromatic benzenoid amines with aminonaphthols in the presence of sodium hydrogen sulphite have been previously described (A., 1905, i, 585), and the reaction has now been extended to the diphenyl series.

4′-*Amino*-7-*diphenylamino*-1-*naphthol*-3-*sulphonic acid* (annexed formula) is obtained when 1 : 7-dihydroxynaphthalene-3-sulphonic acid (240 parts) is boiled during forty-eight hours with benzidine (184 parts) and an aqueous solution of sodium hydrogen sulphite (2400 parts); the *sodium* salt forms grey leaflets.



The following compounds are also described: 3′-*sulpho*-4′-*amino*-6-*diphenylamino*-1-*naphthol*-3-*sulphonic acid*; 3′-*sulpho*-4′-*amino*-7-*diphenylamino*-1-*naphthol*-3-*sulphonic acid*, from 7-amino-1-naphthol-3-sulphonic acid with benzidinesulphonic acid; 4′-*amino*-6-*diphenylamino*-1-*naphthol*-3-*sulphonic acid*, from benzidine with 1 : 7-dihydroxynaphthalene-3-sulphonic acid; and the *compound*, from 7-amino-1-naphthol-3-sulphonic acid with benzidinesulphonic acid and a mixture of ammonium and sodium hydrogen sulphites; the *sodium* salt forms glistening, grey leaflets. F. M. G. M.

Catalytic Decomposition of Phenylhydrazine by Cuprous Salts. ALEXANDER E. ARBUZOV and V. M. TICHVINSKI (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 69—70).—When heated with cuprous chloride, bromide or iodide, phenylhydrazine undergoes catalytic decomposition according to the equation:

$$3NHPh{\cdot}NH_2 + CuX = 3NH_2Ph + N_2 + NH_3 + CuX$$

(compare Struthers, P., 1905, 95). In all cases, an unstable intermediate compound is formed, that given by the iodide having the composition $CuI,2NHPh{\cdot}NH_2$. Cuprous chloride is the most effective and the iodide the least so. T. H. P.

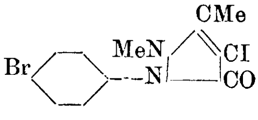
A Process for the Preparation of New Colouring Matters and its Application. BRONISLAW PAWLEWSKI (*Bull. Soc. ind. Mulhouse*, 1912, **82**, 682—683).—When aniline in acid or alcoholic solution is oxidised at 50—60° with ammonium persulphate, a black *dye* is obtained, which is considered to be bisimino-*p*-benzoquinone,

$$O:C_6H_4:N{\cdot}N:C_6H_4:O.$$

By changing the conditions, other brown or black anilinoquinones are formed. Similar colouring matters containing oxygen have been prepared from *m*-phenylenediamine, *o*-dianisidine, and benzylaniline. They are easily fixed by cotton, linen or silk, with or without the aid of mordants. J. C. W.

Preparation of 1-*p*-Bromo-4-iodophenyl- and of 4-Bromo-1-*p*-iodophenyl-2 : 3-dimethyl-5-pyrazolone. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 254487).—The introduction of bromine and iodine into the molecule of 1-phenyl-2 : 3-dimethyl-5-pyrazolone confers on it a markedly increased therapeutic activity.

1-p-*Bromo*-4-*iodophenyl*-2 : 3-*dimethyl*-5-*pyrazolone* (annexed formula),



colourless crystals, m. p. 163°, is obtained when a benzene solution of *p*-bromophenyl-2 : 3-dimethyl-5-pyrazolone (A., 1900, i, 695) is treated with finely powdered iodine and heated at 50—60° during two hours, whilst 4-*bromo*-1-p-*iodophenyl* 2 : 3-*dimethyl*-5-*pyrazolone*, pale yellow leaflets, m. p. 170°, is prepared by the bromination of 1-*p*-iodophenyl-2 : 3-dimethyl-5-pyrazolone (A., 1907, i, 84). F. M. G. M.

Hydantoins. XXI. Action of Ammonium and Potassium Thiocyanates on α-Amino-acids. TREAT B. JOHNSON and BEN H. NICOLET (*Amer. Chem. J.*, 1913, **49**, 197—204).—In an earlier paper (this vol., i, 203), it has been pointed out that ammonium and potassium thiocyanates behave somewhat differently towards α-amino-acids. It has now been found that both salts combine with the acids to form the same thiohydantoins, but that the best yields are obtained by means of the ammonium salt.

When asparagine is treated with ammonium thiocyanate, 2-thio-3-acetylhydantoin-4-acetamide (Johnson and Guest, A., 1912, i, 807) is obtained in a yield amounting to 50% of the theoretical, whilst with the potassium salt a yield of only 6% is obtained.

Phenylalanine gives with ammonium thiocyanate a 94% yield of 2-thio-3-acetyl-4-benzylhydantoin, m. p. 170° (not 257° as stated by Johnson and O'Brien, A., 1912, i, 806); a somewhat smaller yield is obtained by the use of the potassium salt.

By the action of ammonium thiocyanate on tyrosine, a 94% yield is obtained of 2-*thio*-4-p-*hydroxybenzylhydantoin*,

$$\begin{matrix} NH\cdot CO \\ | \\ CS\cdot NH \end{matrix}\!\!>\!CH\cdot CH_2\cdot C_6H_4\cdot OH,$$

m. p. 211°, which forms pale yellow needles; if potassium thiocyanate is employed, only a very small yield is obtained.

2-Thio-3-benzoylhydantoin (Johnson and Nicolet, A., 1912, i, 53) is obtained in 85—88% yield by the action of ammonium thiocyanate on hippuric acid, but in not more than 50% yield by the action of the potassium salt.

In the case of alanine, an excellent yield of 2-thiol-3-acetyl-4-methylhydantoin (Johnson, A., 1912, i, 390) is obtained with ammonium thiocyanate, but only about 34% with the potassium salt.

The thiohydantoin of pyrrolidonecarboxylic acid (Johnson and Guest, A., 1912, i, 317) is readily obtained in good yield by means of ammonium thiocyanate, but only in small amount by the action of the potassium salt. E. G.

The Reactivity of the β-Unsubstituted Pyrrole Ring. III. Action of Cyanogen Bromide and Pyridine on Indoles. WALTER KÖNIG and R. SCHRECKENBACH (*J. pr. Chem.*, 1913, [ii], **87**, 241—257). —In view of the parallelism, previously shown to exist (A., 1911, i, 808), in the reactivity of primary aromatic amines and phenols on the one hand, and of 3-unsubstituted indole derivatives on the other, the author has examined the behaviour of the latter compounds toward pyridine and cyanogen bromide, and finds that they yield dyes which have the general formula :

$$NH<\overset{C_6H_4}{\underset{CR}{}}>C\cdot CH:CH\cdot CH:CH\cdot CH:C<\overset{C_6H_4}{\underset{CR}{}}>NHX,$$

and are, therefore, closely related to the pyridine dyes derived from aromatic amines.

α-2-Methylindyl-ε-2-methylindolidene-Δ^{αγ}-pentadiene hydrobromide, $NH<\overset{C_6H_4}{\underset{CMe}{}}>C\cdot CH:CH\cdot CH:CH\cdot CH:C<\overset{C_6H_4}{\underset{CMe}{}}>NHBr$, is obtained in lustrous, golden leaflets by the action of hot acetone on its additive *compound*, $C_{23}H_{21}N_2Br,C_5H_5N,HBr$, with pyridine hydrobromide. The latter compound separates in green needles by the successive addition of pyridine and cyanogen bromide in ethereal solution to 2-methylindole, dissolved in methyl alcohol. The *dihydrobromide*, prepared by warming the monohydrobromide with acetone and hydrobromic acid, crystallises in lustrous, silky, bluish-green needles.

On treatment with aqueous sodium hydroxide and methyl alcohol, the hydrobromide yields the *dye-base*, $C_{23}H_{20}N_2$. This forms bluish-black needles, and is converted at 220° into a yellow *substance*, m. p. 265°, which probably has the same composition as the original dye-base, yields a *phenylhydrazone* (decomp. 160—170°), and when heated at 160° under diminished pressure decomposes, yielding 2-methylindole. The dye-base reacts with phenylhydrazine in alcoholic solution, yielding 2-methylindole and the *phenylhydrazone*,

$$NH<\overset{C_6H_4}{\underset{CMe}{}}>C\cdot CH:CH\cdot CH:CH\cdot CH:N\cdot NHPh,$$

which forms an amorphous, light yellow powder (decomp. 170—180°) containing alcohol (1 mol.).

On treatment with dry hydrogen chloride, the dye-base yields a *hydrochloride*, $C_{23}H_{21}N_2Cl$; the *perchlorate*, $C_{23}H_{21}O_4N_2Cl$, forms small, compact, green crystals having a golden lustre, and crystallises with methyl alcohol in long, slender, bluish-green needles.

α-Indyl-ε-indolidene-Δ^{αγ}-pentadiene hydrobromide, $C_{21}H_{17}N_2Br$, prepared from indole, cyanogen bromide, and pyridine in methyl alcoholic solution, forms a microcrystalline, dark blue powder, containing pyridine (1 mol.).

α-2 : 4-Dimethylindyl-ε-2 : 4-dimethylindolidene-Δ^{αγ}-pentadiene hydrobromide, prepared from 2 : 4-dimethylindole, yields on treatment with aqueous sodium hydroxide and methyl alcohol the *dye-base*, $C_{25}H_{24}N_2$, which forms microcrystalline, bluish-black needles ; a *dihydrobromide* and a *perchlorate*, crystallising in green leaflets of a golden lustre, are also described.

The action of cyanogen bromide and pyridine on phloroglucinol and

resorcinol gives rise to blue pyridine dyes, which, however, are too unstable to be isolated. F. B.

[Preparation of 4-Chloro-5-bromoisatin.] KALLE & Co. (D.R.-P. 254468).—4-*Chloroisatin*, a yellow, crystalline powder, m. p. 254°, is prepared by treating a cooled acetic-chromic acid solution of 4 : 4′-dichloroindigotin with concentrated nitric acid; when warmed with bromine (in acetic acid solution) it gives rise to 4-*chloro-5-bromoisatin*, red needles, m. p. 255°, which on treatment with phosphorus pentachloride furnishes 4-*chloro-5-bromoisatin chloride*, brown needles, m. p. 278°; the corresponding anilide was also prepared. F. M. G. M.

Preparation of 5 : 6 : 5′ : 6′-Tetrachloroindigotin. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 254467).—4 :5-*Dichloro-2-nitrobenzaldehyde*, yellow prisms, m. p. 73°, is prepared by the nitration of 4 : 5-dichlorobenzaldehyde; this when condensed with acetone in the presence of sodium hydrogen sulphite furnishes *dichloronitrophenyl-lactyl ketone*, m. p. 116°, which is readily converted by known methods into 5 : 6 : 5′ : 6′-*tetrachloroindigotin*, a substance possessing valuable tinctorial properties. F. M. G. M.

Preparation of Dinitro-1 : 1′-dianthrimide. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 254186).—The nitration of dianthrimide (which has previously been described) takes place more smoothly and yields a definite characteristic product when carried out in the presence of boric acid.

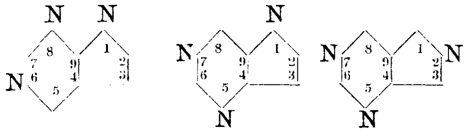
1 : 1′-Dianthrimide (100 parts) and boric acid (65 parts) are dissolved in 1000 parts of concentrated sulphuric acid, treated at 5—10° with 27% nitric acid (122 parts), and left during two to three days at the ordinary temperature, when about 87% of the 4 : 4′-dinitro-1 : 1′-dianthrimide separates in glistening, coppery crystals. The m. p. is above 300°, and it is identical with the compound previously obtained by condensing 4-nitro-1-amino- with 4-chloro-1-amino-anthraquinone; on reduction it furnishes 4 : 4′-diamino-1 : 1′-dianthrimide. F. M. G. M.

Preparation of ω-Methylsulphites of Substituted Aminoarylpyrazolones. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 254711).—Compounds having valuable therapeutic properties are obtained when the substituted 4-amino-1-phenyl-2 : 3-dimethyl-5-pyrazolones are heated with formaldehyde and sodium hydrogen sulphite; *compounds* obtained in this manner from the following pyrazolones have now been prepared. From 4-amino-1-phenyl-2 : 3-dimethyl-5-pyrazolone, sintering and decomposing at 231—233°; from 4-amino-1-*p*-tolyl-2 : 3-dimethyl-5-pyrazolone, sintering at 120°, decomposing at 125°; from 1-*p*-aminophenyl-2 : 3-dimethyl-5-pyrazolone, isolated as its hygroscopic, crystalline *sodium* salt; from 1-*p*-aminophenyl-2 : 3 : 4-trimethyl-5-pyrazolone, also isolated as a crystalline

sodium salt; from 4-amino-1-*p*-ethoxyphenyl-2:3-dimethyl-5-pyrazolone, m. p. 113—115°, decomp. at 133—135°. The foregoing 4-*amino*-p-*ethoxyphenyl*-2:3-*dimethyl*-5-*pyrazolone*, m. p. 132—133°, is obtained by the reduction of 4-nitroso-*p*-ethoxy-2 : 3-dimethyl-5-pyrazolone.

F. M. G. M.

Pyrimidines. LIX. Barbituryl- and 2-Thiobarbituryl-5-acetic Acids. TREAT B. JOHNSON and EDWARD F. KOHMANN (*Amer. Chem. J.*, 1913, **49**, 184—197).—An account is given of experiments undertaken with a view to the preparation of compounds containing condensed pyrimidine and pyrrole nuclei, and corresponding with the indoles and pyrindoles (Perkin and Robinson, T., 1912, **101**, 1787). Compounds of this new class are termed 1 : 6 : 8-, 1 : 5 : 7-, and 2 : 5 : 7-pyrimazoles (annexed formulæ).



A 1 : 6 : 8-pyrimazole has already been obtained by heating ethyl 6-chloro-2-ethylthiolpyrimidine-5-acetate with alcoholic ammonia (A., 1911, i, 575); this compound, previously termed 2-ethylthiol-5 : 6-α-pyrrolidone-pyrimidine, is now designated 2-keto-7-ethylthiol-1 : 6 : 8-pyrimazole.

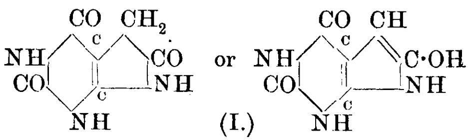
When ethyl ethane-ααβ-tricarboxylate is treated with carbamide in the presence of sodium ethoxide, the *sodium* salt of barbituryl-5-acetamide is obtained, which crystallises with $4H_2O$. *Barbituryl*-5-*acetamide*,

$$CO<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>CH\cdot CH_2\cdot CO\cdot NH_2,$$

m. p. 258—261° (decomp.), crystallises in needles. *Barbituryl*-5-*acetic acid*, $CO<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>CH\cdot CH_2\cdot CO_2H$, obtained by the action of 20% hydrochloric acid on the sodium salt of the amide, separates in plates, becomes charred at 230°, and decomposes at 250°. An attempt to condense the amide to a 1 : 6 : 8-pyrimazole by the action of phosphoryl chloride on its sodium salt was not successful.

Thiobarbituryl-5-*acetamide*, $CS<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>CH\cdot CH_2\cdot CO\cdot NH_2,H_2O$, prepared by the condensation of thiocarbamide with ethyl ethane-ααβ-tricarboxylate, crystallises in needles and decomposes at 272°; the *sodium* salt forms long, colourless prisms. *Thiobarbituryl*-5-*acetic acid*, $CS<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>CH\cdot CH_2\cdot CO_2H,2H_2O$, crystallises in needles and decomposes above 230°.

Ethyl cyanosuccinate condenses with carbamide with formation of a pyrimidine. The reaction does not take place smoothly, and only small yields of condensation products are obtained. In one experiment, barbituryl-5-acetic acid was pro-



(I.)

produced, together with 2 : 5 : 7-*triketo*-1 : 6 : 8-*pyrimazole* (formula I), which forms a brown powder and does not melt below 320°. In another experiment, barbituryl-5-acetic acid and 4-*iminobarbituryl*-5-*acetic acid*,

$$CO<\begin{matrix}NH\text{———}CO\\NH\cdot C(:NH)\end{matrix}>CH\cdot CH_2\cdot CO_2H,$$

were isolated; the latter substance is a brown powder, and does not melt below 338°. E. G.

Preparation of Azimino-[Triazole]-compounds in the Anthraquinone Series. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 254745).—The azimino-compounds having the general formula $A<\begin{matrix}NR\\N\end{matrix}>N$, where A is anthraquinone and R hydrogen, alkyl or aryl groups, and prepared by the action of nitrous acid on *o*-diaminoanthraquinones, are of technical value for the preparation of dyes. The preparation of the following *compounds* is described: From 1 : 2-diaminoanthraquinone, needles; from 2 : 3-diaminoanthraquinone, and from 1-*p*-tolylamino-2-amino-3-bromoanthraquinone, citron-yellow needles. The tinctorial properties of these compounds are enhanced by the introduction of halogens into the molecule.

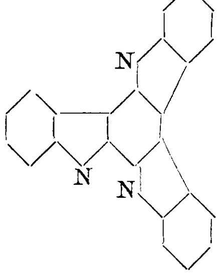
F. M. G. M.

Polymeric Indoles. K. KELLER (*Ber.*, 1913, **46**, 726—733).—The high-boiling residue obtained in the distillation of practically pure indole consists of a trimeride, *tri-indole*, which after recrystallisation from benzene can be obtained in colourless crystals, m. p. 167°. The polymerisation can be better effected by heating indole with an aqueous solution of metaphosphoric acid. When distilled in a vacuum, tri-indole decomposes completely into indole; it gives a *monoacetyl* derivative, colourless crystals, m. p. 202°, and a *monobenzoyl* derivative, colourless, crystalline powder, m. p. 207°. These acyl compounds are remarkably resistant to alkalis. When benzoyltri-indole is heated in a vacuum, indole distils away, leaving a residue of *benzoyldi-indole*, colourless needles, m. p. 198°; this resisted all attempts at acetylation and hydrolysis. The easiest method for the preparation of benzoyltri-indole is by boiling together a benzene solution of indole with anhydrous sodium carbonate and benzoyl chloride, whilst a slow current of hydrogen chloride is passed through the mixture; the yield is then 90% of the indole taken.

The action of hydrogen chloride on a solution of indole in benzene yields a colourless salt of composition

$$(C_8H_7N)_2,HCl,$$

presumably *di-indole hydrochloride*, but it was not found possible to isolate the corresponding base in a pure state.



From a consideration of the behaviour of the above tri-indole derivatives, the annexed structure is suggested for the base, the reactive indole nucleus being that on the left; this differs from the remaining two by being attached to the rest of the molecule at carbon atoms which are each adjacent to nitrogen atoms. D. F. T.

Preparation of Formaldehyde Derivatives of Xanthine and its Substitution Products. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 254488).—When xanthine, its derivatives, or the purine bases are gently heated in aqueous or hydrochloric acid solution with formaldehyde (or its generators), they furnish *compounds* of marked therapeutic value. The following are described: (1) From 1 : 3-dimethylxanthine and formaldehyde in aqueous solution, contains 14% formaldehyde, m. p. 265° when slowly heated, but if suddenly subjected to a temperature of 165—170°, violent decomposition occurs with regeneration of 1 : 3-dimethylxanthine.

(2) From 3 : 7-dimethylxanthine with paraformaldehyde in fuming hydrochloric acid solution, it forms characteristic needles, contains 14% formaldehyde, and does not melt below 300°.

(3) From xanthine and formaldehyde, contains 32% formaldehyde; and (4) from 3-methylxanthine contains 16% of formaldehyde. These compounds readily decompose in the organism with elimination of formaldehyde. F. M. G. M.

The Anomalies in the Solubility of Uric Acid (Colloidal Uric Acid). HEINRICH SCHADE and E. BODEN (*Zeitsch. physiol. Chem.*, 1913, **83**, 347—380).—If uric acid is suspended in boiling water, and alkali is then added very slowly until the mixture is just alkaline to phenolphthalein, the acid appears to pass into solution. This solution can be made by one of the following methods to set to a solid gel: (*a*) by the addition of concentrated sodium chloride solution; (*b*) by addition of other salt solutions, such as ammonium sulphate, which are ordinarily employed for the precipitation of colloids; (*c*) by addition of alcohol, and (*d*) by rapid cooling. The same phenomenon can be produced when the acid is neutralised by ammonia, lithium, sodium and potassium hydroxides, by the alkaline earths, and even ferric hydroxide. The appearance of the gel thus produced is described in great detail, and also the phenomena of its gradual transformation into the ordinary crystalline form. The colloid appears to be a supersaturated uric acid solution, in which the uric acid forms an adsorption compound with the alkali, which causes it to retain the colloidal form, and this adsorption compound appears to be a preliminary stage in the formation of the true chemical crystalline compound. The view here advanced can explain certain anomalies, to which Bechhold and Ziegler have called attention as regards the solubility of uric acid in serum. S. B. S.

Purines. VIII. 2 : 8-Dihydroxy-1 : 9-dimethylpurine and 2-Hydroxy-6 : 9-dimethylpurine. CARL O. JOHNS (*J. Biol. Chem.*, 1913, **14**, 1—7).—2 : 8-Dihydroxy-1 : 9-dimethylpurine is synthesised as follows: the potassium salt of 5-nitro-6-methylamino-2-hydroxypyrimidine (Johns, A., 1911, i, 506) when heated with methyliodide gives 5-*nitro*-6-*methylamino*-2-*hydroxy*-3-*methylpyrimidine*, the constitution of which is established by heating the methylated product with sulphuric acid, when 5-nitro-2 : 6-dihydroxy-3-methylpyrimidine (Behrend and Thurm, A., 1902, i, 833) is obtained.

On reducing the methylated product with freshly precipitated

ferrous hydroxide, it is converted into 5-*amino*-6-*methylamino*-2-*oxy*-3-*methylpyrimidine*, $N{<}\begin{array}{l} C(NHMe){\cdot}C{\cdot}NH_2 \\ CO{\cdot}NMe{-}CH \end{array}$ This is very soluble and purified only with difficulty. The crude base was accordingly heated with carbamide and converted into 2 : 8-*dioxy*-1 : 9-*dimethylpurine*, $\begin{array}{l} NMe{\cdot}CH{:}C{\cdot}NH{-} \\ CO{-\!-}N{:}C{\cdot}NMe \end{array}{>}CO.$

By heating the potassium salt of acetyl-5 : 6-diamino-2-oxy-4-methylpyrimidine, 2-*oxy*-6 : 9-*dimethylpurine*,

$$\begin{array}{l} N{:}CMe{-}C{\cdot}NH \\ CO{\cdot}NH{\cdot}C{-\!-}N \end{array}{>}CMe,$$

is obtained.

5-*Nitro*-6-*methylamino*-2-*oxy*-3-*methylpyrimidine* forms a bulky mass of hair-like crystals, m. p. 203°, to a colourless oil.

The *picrate* of 5-*amino*-6-*methylamino*-2-*oxy*-3-*methylpyrimidine* crystallises in long prisms, m. p. 200° (decomp.).

2 : 8-*Dioxy*-1 : 9-*dimethylpurine* crystallises in small, irregular plates, which do not melt or char at 320°.

2-*Oxy*-6 : 8-*dimethylpurine* separates in small prisms with square ends, which slowly turn brown at 315°; they give a murexide reaction. E. F. A.

Azomethines and Azo-dyes. CAMILLE G. VERNET (*Arch. Sci. phys. nat.*, 1913, [iv], **35**, 148—172).—The azomethines derived from a number of diamines and benzaldehyde or its derivatives are described. In general they are formed quantitatively, the amount isolated depending on the manner in which the condensation is effected and the dilution of the solvents employed.

2-Mononitrobenzidine forms with benzaldehyde a yellowish-brown *compound*, m. p. 157°; with one molecule of *p*-nitrobenzaldehyde the product is red, m. p. 200—201°, with two molecules it is yellow, m. p. 205—206°; with dimethyl-*p*-aminobenzaldehyde it is yellow with an ill-defined melting point; with *o*-vanillin it is red, m. p. 200°.

m-Dinitrobenzidine and *o*-vanillin yield a reddish-brown product.

Benzidinesulphone combines with one molecule of benzaldehyde to a yellow compound, m. p. 259—260°; with *p*-nitrobenzaldehyde to a brown compound, m. p. 302—304°; with dimethyl-*p*-aminobenzaldehyde the compound is yellow, m. p. 318°; with *o*-vanillin it is yellowish-red.

Diaminodiphenylamine and benzaldehyde form a yellow compound, m. p. 184—185°; with *p*-nitrobenzaldehyde the compound is black with a metallic lustre, m. p. 219°; with dimethyl-*p*-aminobenzaldehyde it is very similar, m. p. 222°; with *o*-vanillin it is brick-red, m. p. 207—208°.

3 : 3′-Diaminocarbazole and benzaldehyde yield a yellow substance, m. p. 186°; the product with *p*-nitrobenzaldehyde is red, m. p. 306—307°; with dimethyl-*p*-aminobenzaldehyde it is yellowish-brown, m. p. 266—268°; with *o*-vanillin it is brick-red, m. p. 254—255°.

trans-*o*-Diaminostilbene and benzaldehyde form a yellow product, m. p. 188°; with *p*-nitrobenzaldehyde it is orange-red, m. p. 228°; with

dimethyl-*p*-aminobenzaldehyde it is yellow, m. p. 227°, and with *o*-vanillin it is red, m. p. 228°.

p-Diaminostilbene yields a yellow compound with benzaldehyde, m. p. 254°; an orange-red compound with *p*-nitrobenzaldehyde, m. p. 242°; a reddish-yellow product with dimethyl-*p*-aminobenzaldehyde, m. p. 233°, and a red product with *o*-vanillin.

These azomethines are all very similar; the nitro-group has a greater effect in intensifying the colour than the substituted amino-group.

Most of the compounds have a normal composition with both amino-groups condensed, but traces of the condensation products with a single molecule of aldehyde are formed at the same time.

A comparison is made of the colours obtained by soaking the material impregnated with sodium-β-naphthoxide in the diazotised solutions of a number of diamines. Whereas benzidine gives a brown, thiobenzidine and benzidinesulphone give reddish-brown shades, mononitrobenzidine gives a red, *m*-dinitrobenzidine an orange, and the *o*-dinitro-derivative a garnet-red. With 2 : 2′- or 3 : 3′-diaminocarbazole the colour is almost black, and *p*-diaminostilbene gives a similar colour. The replacement of an atom of hydrogen by a univalent grouping has more influence on the colour than when two atoms of hydrogen are replaced by a bivalent substituent.

Each of the diamino-bases studied has been coupled with five acid compounds, namely, H-acid, chromotropic acid, Nevile and Winther's acid, resorcinol, and naphthoic acid. The resulting compounds have not been analysed, but were directly utilised for dyeing tests. The colours obtained are detailed in tabular form; they act as substantive colours for cotton, and dye wool from acid solutions. E. F. A.

Thiophenols. III. *pp*′-Azophenyl Methyl- and *pp*′-Azophenyl Ethyl-sulphide. Kurt Brand and Adolf Wirsing (*Ber.*, 1913, **46**, 820—829).—The authors have extended their previous work on *pp*′-azophenyl methyl sulphide (A., 1912, i, 666), and have investigated the corresponding ethyl derivative.

A concentrated aqueous solution of sodium hydroxide and sodium sulphide is gradually added to a boiling alcoholic solution of di-*p*-nitrodiphenyl disulphide. From the cooled reaction mixture, the *sodium* derivative of *p*-nitrophenyl mercaptan, $C_6H_4O_2NSNa,2H_2O$, separates in golden leaflets, which decompose when heated slightly above 100°. The salt dissolves in water, forming a yellow solution, which, on addition of acid, becomes colourless and deposits *p*-nitrophenyl mercaptan. The solution absorbs oxygen with the formation of the disulphide. When warmed with an excess of ethyl bromide, the above sodium salt is transformed into *p*-nitrophenyl ethyl sulphide, m. p. 48° (Blanksma, A., 1902, i, 282, gives 40°; L. Gattermann, 44°). pp′-*Azoxyphenyl ethyl sulphide*, $ON_2(C_6H_4{\cdot}SEt)_2$, is obtained when a methyl-alcoholic solution of p-nitrophenyl ethyl sulphide is added to a boiling solution of sodium methoxide in methyl alcohol. It forms pale yellow needles, m. p. 97—98°. A sulphinium compound could not be obtained from it by the action of methyl sulphate.

pp′-*Hydrazophenyl ethyl sulphide*, m. p. 76°, is obtained in the same manner as the corresponding methyl compound (*loc. cit.*). In alkaline alcoholic solution it is more readily oxidised by air than the

latter compound, and forms pp'-*azophenyl ethyl sulphide*, m. p. 132°. Treatment with concentrated hydrochloric acid transforms *pp'*-hydrazophenyl ethyl sulphide into p-*aminophenyl ethyl sulphide hydrochloride*, which readily gives up a portion of the hydrogen chloride. The free base, obtained from the hydrochloride by means of ammonia, has b. p. 165°/12 mm. (compare Auwers and Beger, A., 1894, i, 466; Monier-Williams, T., 1906, **89**, 278; Gattermann, A., 1912, i, 986). *p*-Acetylaminophenyl ethyl sulphide, m. p. 116°, is obtained by shaking an aqueous solution of *p*-aminophenyl ethyl sulphide hydrochloride with sodium acetate and acetic anhydride, or by boiling the free base with the same reagents.

pp'-Azophenyl ethyl sulphide, $N_2(C_6H_4 \cdot SEt)_2$, orange leaflets, m. p. 132°, is obtained by reduction of *p*-nitrophenyl ethyl sulphide by means of zinc and sodium hydroxide and oxidation of the hot, filtered solution by passing air through it. With mineral acids and strong organic acids it yields intensely blue solutions. The crystalline *hydrochloride* and *trichloroacetate* could not be obtained in the pure state, as they decompose during filtration. The *sulphate*,

$$C_{16}H_{18}N_2S_2,2H_2SO_4,$$

green metallic needles, is obtained by the addition of sulphuric acid to a solution of *pp'*-azophenyl ethyl sulphide in glacial acetic acid. The following double salts have been obtained: $C_{16}H_{18}N_2S_2,HCl,HgCl_2$, dark violet needles; $C_{16}H_{18}N_2S_2,HCl,FeCl_3$, green leaflets;

$$[C_{16}H_{18}N_2S_2,HCl]_2,FeCl_3,$$

dark green needles; $C_{16}H_{18}N_2S_2,HCl,SnCl_4$, green leaflets;

$$[C_{16}H_{18}N_2S_2,HCl]_2SnCl_4,$$

dark green needles. They were prepared by mixing *pp'*-azophenyl ethyl sulphide with the metallic chloride in hot glacial acetic acid solution, addition of hydrochloric acid being necessary in the first, third, and fifth cases. They are immediately decomposed by water.

When *pp'*-azophenyl ethyl sulphide is heated with methyl sulphate and the reaction mixture treated with alcohol, light red crystals, m. p. 158°, are obtained. The aqueous solution yields, on addition of potassium iodide, a sulphinium iodide, m. p. 158—160°, analyses of which gives results from which the authors conclude that the substance is *pp'*-azophenyldimethylsulphinium iodide. The discrepancy between the m. p. now found and that previously given (174—175°, *loc. cit.*) is attributed to impurity of the specimen.

In extension of their previous work, the authors have prepared the double *salt*, $(C_{14}H_{14}N_2S_2,HCl)_2SnCl_4$, green needles by the action of stannic chloride and hydrochloric acid on a solution of *pp'*-azophenyl methyl sulphide in glacial acetic acid. They also find that *pp'*-azophenyldimethylsulphinium methyl sulphate is more conveniently prepared by heating *p'*-azophenyl methyl sulphide and methyl sulphate for an instant at the boiling point and treatment of the resulting product with alcohol. When this salt is treated with sodium hydroxide, it forms a new *compound*, $C_{18}H_{26}O_8N_2S_4$, investigation of which is not yet completed. H. W.

The Lakes of Hydroxylic Dyes. RICHARD MÖHLAU (*Ber.*, 1913, **46**, 443—456).—[With JOHANNES MAETZEL]—A brief account is first

given of previous investigations of the compounds of dyes with mordants.

A number of compounds were prepared from various metallic mordants and hydroxylic dyes by precipitation. For the production of simple lakes derived from tervalent metals, solutions of a salt of the metal and of the potassium derivative of the dye were mixed. In order to obtain more complex lakes containing both tervalent and bivalent metals, the tervalent metal derivative was first prepared, and its solution in ammonium hydroxide was then treated with a solution of an equivalent amount of the salt of the bivalent metal (compare Liechti and Suida, A., 1884, 794; 1885, 315; Liebermann and Michaelis, A., 1895, i, 108, 671; Biltz, A., 1906, ii, 78).

The fact that the lakes with the tervalent metals will dissolve readily in ammonium hydroxide indicates that the metallic atom is attached to hydroxylic oxygen, producing phenolic salts; the further introduction of the bivalent metallic atoms is then due to replacement of the hydrogen of the carboxyl or remaining hydroxyl group.

The following lakes of alizarin with tervalent metals were prepared, of the type $Me'''(C_{14}H_7O_4)_3$: *aluminium*, dark brown powder; *chromium*, yellow powder; *iron*, bluish-black powder. These could give calcium derivatives of the general formula $Me_2'''Ca_3(C_{14}H_6O_4)_6$; *aluminium calcium*, violet-brown; *chromium calcium*, deep violet; *iron calcium*, bluish-violet.

Of *p*-nitrobenzeneazosalicylic acid (the acid of alizarin-yellow-R), the following lakes were obtained with tervalent metals of the general formula

$$[NO_2\cdot C_6H_4\cdot N_2\cdot C_6H_3(CO_2H)\cdot O\cdot]_3M''':$$

aluminium, red; *chromium*, brown; *iron*, chocolate. These gave calcium derivatives of the general formula

$$\left(NO_2\cdot C_6H_4\cdot N_2\cdot C_6H_3{<}_{O}^{CO_2}{>}\right)_6Ca_3Al_2:$$

aluminium calcium, brownish-red; *chromium calcium*, brown; *iron calcium*, brownish-black.

The simple tervalent metallic lakes are more stable towards dilute acid and alkali than the more complex lakes containing two metals; of the latter, the aluminium calcium lakes are most stable and the iron calcium least, and those of alizarin are more stable than the corresponding derivatives of *p*-nitrobenzeneazosalicylic acid.

Benzeneazonaphtholsulphonic acid, $N_2Ph\cdot C_{10}H_5(OH)\cdot SO_3H$, and azo-*o*-toluene-azonaphtholsulphonic acid,

$$C_6H_4Me\cdot N_2\cdot C_6H_3Me\cdot N_2\cdot C_{10}H_5(OH)\cdot SO_3H,$$

give unstable *chromium* lakes, brownish-red and claret-red respectively, which are decomposed by dilute alkali or mineral acid; they are consequently regarded as being normal chromium salts and not phenolic derivatives. Complex lakes containing two metals could not be prepared from them. D. F. T.

Preparation of Acetyl Derivatives of Aminoazobenzene, its Homologues and Analogues. KALLE & Co. (D.R.-P. 253884).— Acetyl derivatives of aminoazobenzene and of the aminoazo compound prepared from *o*-toluidine have been described previously; it is now

found that by prolonged heating with excess of the reagent, diacetyl derivatives are formed.

Diacetylaminoazotoluene exists in two modifications, long, reddish-yellow needles, m. p. 65°, and in crystals, resembling potassium dichromate with m. p. 75°; *diacetylaminoazobenzene* forms long, thin plates, m. p. 103—104°. F. M. G. M.

Density and Solution Volume of Certain Proteins. (Miss) HARRIETTE CHICK and CHARLES J. MARTIN (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 69—71).—From measurements of the density of casein, crystallised egg-albumin, crystallised serum-albumin and serum-globulin, and of the corresponding solution volumes in aqueous solution, it has been found that the density of the dissolved substance is in all cases greater than that of the free protein, the increase in density varying from 5 to 8%. In the case of serum-albumin and serum-globulin, the solution volume of the protein is independent of the concentration, whereas the contraction, which attends the dissolution of casein, diminishes as the concentration increases. H. M. D.

The Amount of *l*-Tyrosine in Proteins and the Accuracy of its Estimation. EMIL ABDERHALDEN and DIONYS FUCHS (*Zeitsch. physiol. Chem.*, 1913, **83**, 468—473).—The colorimetric method proposed for the estimation of *l*-tyrosine by Folin and Denis (A., 1912, ii, 1012) is shown to include other amino-acids, and to be untrustworthy. It is possible by crystallisation to separate completely the tyrosine from the products of protein hydrolysis, particularly when the necessary concentration of the liquids is effected under reduced pressure. Most of the published determinations of tyrosine in proteins have been made with insufficient care. E. F. A.

Colloidal Solutions. I. Certain Metallic Peptonates. EMANUELE PATERNÒ and FLORENTIN MEDIGRECEANU (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 65—68).—Solutions of iron, copper, zinc, and barium peptonate were subjected to prolonged dialysis, and after making up the volumes of the dialysed and residual solutions to the volume of the original solutions, measurements were made of the freezing point, total solids, ash, total nitrogen, and metal for each portion, the data being compared with the corresponding numbers for the original solutions. The observations seem to show that the substances formed by combination of peptone with the metal are, at any rate in the case of iron and copper, of colloidal nature.
H. M. D.

Porphyrinogen. HANS FISCHER and ERICH BARTHOLOMÄUS (*Ber.*, 1913, **46**, 511—514).—By the action of a mixture of glacial acetic acid and hydrogen iodide in presence of phosphonium iodide on hæmin in the cold, a colourless, crystalline reduction product, $C_{33}H_{42}O_4N_4$, of high molecular weight is obtained. This is termed porphyrinogen in view of its ready conversion into a red product having the spectroscopic properties of porphyrin.

Sodium methoxide acts on porphyrinogen forming phyllopyrrole;

also a porphyrin, of which the hydrochloride crystallises in centrically grouped needles—probably mesoporphyrin.

On oxidation, porphyrinogen yields methyl ethylmaleinimide and hæmatic acid.

The colourless porphyrinogen behaves as a sensibilising agent when injected into mice exposed to light rays. E. F. A.

Pepsin. II. SERAFINO DEZANI (*Atti R. Accad. Sci. Torino*, 1913, **48**, 194—200. Compare A., 1910, i, 449).—The pepsin prepared according to the method previously described contains very little chlorine, and the author now finds that by suitable purification this element can be removed almost completely without diminishing the activity of the product. It appears, therefore, that the statements of previous authors that chlorine is a constituent of the substance are incorrect. R. V. S.

Some Properties of Koji-diastase. G. KITA (*J. Ind. Eng. Chem.*, 1913, **5**, 220—222).—It has been generally assumed that koji (a culture of *Aspergillus oryzae* on steamed rice) contains two different saccharifying enzymes only, namely, amylase and glucase, and that the dextrose present in a liquid saccharified by means of koji is produced by these two enzymes. Comparative experiments on starch and maltose showed, however, that more dextrose was produced from the starch than from maltose, and the author concludes that koji contains a third enzyme which produces dextrose directly from starch without the aid of glucase.

Sodium chloride has a protecting action on koji-diastase when heated, but not on malt-diastase, whilst sodium phosphate, asparagine, and sulphuric acid impair its activity more quickly. The inhibitory action of the sodium chloride depends on the concentration of the diastase; in a dilute solution of the enzyme it is very marked, but not in a concentrated solution. The activity of koji-diastase may be conserved in brine solution for a long period. T. S. P.

The Reversibility of the Ferment Action of Emulsin. ÉMILE BOURQUELOT and J. COIRRE (*Compt. rend.*, 1913, **156**, 643—646; *J. Pharm. Chim.*, 1913, [vii], **7**, 236—240. Compare A., 1912, i, 928; this vol., i, 212).—The state of equilibrium attained during the synthesis or hydrolysis of a glucoside in alcoholic solution under the influence of emulsin is independent of the amount of emulsin used and depends solely on the proportions of the components of the glucoside in the solution. The action is thus a true reversible reaction, the only effect of varying the concentration of the emulsin being to vary the rate at which equilibrium is reached. W. G.

Hydrolysis of Amygdalin Under the Influence of Emulsin. LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1913, **251**, 85—89).—Krieble's observation (A., 1912, i, 482) that certain kinds of emulsin react with amygdalin to give *l*-benzaldehydecyanohydrin is confirmed, and a series of experiments has been made to determine the mode of formation of the latter. It is shown that a portion of the benzaldehyde and

hydrogen cyanide which result from the gradual breaking down of amygdalin through mandelonitrile-glucoside and *d*-benzaldehydecyanohydrin re-combine to form *i*-benzaldehydecyanohydrin, and if an emulsin such as that from cherry kernels, which is very rich in *d*-oxynitrilase, is used, hydrolysis of the *d*-component of the inactive cyanohydrin ensues, *l*-benzaldehydecyanohydrin being left unaltered.

T. A. H.

Distribution of Emulsin-like Enzymes. LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1913, **251**, 56—84).—The work done in recent years on "emulsin" shows that the latter may include different enzymes depending on its origin (A., 1910, i, 800; Armstrong and others, A., 1912, i, 816). The author has, therefore, investigated a large number of plants, particularly those which are known to be cyanogenetic, with a view to ascertaining which of the ordinary components of "almond emulsin" they contain. For this purpose the mixture of enzymes prepared from the plant was mixed with (1) a solution of amygdalin, (2) a mixture of benzaldehyde and hydrocyanic acid (A., 1909, i, 74, 622), and (3) *dl*-benzaldehydecyanohydrin (Feist, A., 1909, i, 589), and the products of the reaction, if any, investigated. The results are described in detail in the original, and are also tabulated for convenience of reference. The following points of special interest are recorded. Enzymes capable of producing asymmetric synthesis or decomposition (reactions 2 and 3 above) are widespread in plants, although less so that those capable of decomposing amygdalin; this apparent difference may, however, be due to the fact that enzymes of the last-mentioned type are easier to detect by means of their product of reaction. Enzymes of these types may occur in plants which do not yield hydrogen cyanide, but in such cases they are not found in the leaves. These enzymes are not identical with those which decompose amygdalin, since in certain cases, such as *Hydnocarpus Wightiana* seeds, *Pangium edule* seeds, and *Prunus laurocerasus* leaves, negative results were obtained in reaction (1) and positive results with (2) and (3). Similarly, in other cases positive results were obtained for reaction (2) and negative results for reaction (3). An enzyme preparation from the seeds of *Taraktogenos Blumei* furnished in reaction (2) *l*-benzaldehydecyanohydrin instead of the *d*-isomeride furnished by enzymes derived from plants of the order Prunaceæ; these seeds therefore appear to contain a *l*-oxynitrilese, which may also be present in the flowers of *Achillea millefolium*. No enzyme capable of producing optically active nitriles from ketones and hydrocyanic acid was observed. The enzyme of *Taraktogenos Blumei* is soluble in brine, but not in water.

T. A. H.

Oxydases. VI. Tyrosinase is also a Deamidising Enzyme. ROBERT CHODAT and K. SCHWEIZER (*Arch. Sci. phys. nat.*, 1913, **35**, 140—147. Compare A., 1912, ii, 399, 611).—It has been shown previously that for the completion of the colour reaction between tyrosinase and *p*-cresol, the presence of an amino-acid is necessary. It is now proved that tyrosinase has a deamidising action on glycine, which it converts into carbon dioxide, ammonia, and formaldehyde.

The change is greatly facilitated by the addition of lime water. The formation of formaldehyde is identified by means of Rimini's reagent (phenylhydrazine hydrochloride and potassium ferrocyanide), that of ammonia by means of Nessler's and Trilliat's reagents. The interaction of *p*-cresol, glycine, and tyrosinase is prevented by the addition of calcium hydroxide; in its absence the blue coloration is obtained, and formaldehyde and ammonia are detected amongst the products of reaction.

With alanine and tyrosinase, acetaldehyde is formed in place of formaldehyde. Benzaldehyde is obtained from phenylglycine and tyrosinase.

The presence of formaldehyde in plant tissues does not necessarily indicate photo-synthesis. Attention is drawn to the parallelism between the action of tyrosinase and of hydrogen peroxide on glycine (compare Dakin, A., 1906–1911). E. F. A.

Preparation of Derivatives of Nitrohydroxy- and Amino-hydroxy-arylarsinic Acids Containing Sulphur. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 253757).—When an alkaline solution of 3-nitro-4-hydroxyphenylarsinic acid is saturated with hydrogen sulphide at the ordinary temperature, it gives rise to *nitrohydroxyphenylarsenosesquisulphide*, $[NO_2 \cdot C_6H_3(OH) \cdot As]_2S_3$, which crystallises from xylene in hard, yellow, nodular crystals, m. p. 160° (about).

Compounds obtained by the action of sodium sulphide on 3-nitro-4-hydroxyphenylarsinic acid (a pale brown powder), of hydrogen sulphide on 3-amino-4-hydroxyphenylarsinic acid, and on its hydrochloride are also described. F. M. G. M.

Aromatic Arsenic Compounds. IV. Preparation of 3-Nitro-4-dimethylaminophenylarsinic Acid and of 3-Nitro-4-hydroxyphenylarsinic Acid. P. KARRER (*Ber.*, 1913, **46**, 515—517).—*p*-Dimethylaminophenylarsinic acid is readily nitrated on solution in a mixture of acetic and nitric acids. When the mononitrodimethylaminophenylarsinic acid, $NO_2 \cdot C_6H_3(NMe_2) \cdot AsO_3H_2$, is warmed with sodium hydroxide, it is converted into 3-nitro-4-hydroxyphenylarsinic acid (Benda and Bertheim, A., 1911, i, 63), which in turn, when reduced, gives rise to the base,

$$NH_2 \cdot C_6H_3(OH) \cdot As\colon As \cdot C_6H_3(OH) \cdot NH_2,$$

corresponding with salvarsan.

When 3-nitro-4-dimethylaminophenylarsinic acid is similarly reduced, tetramethyltetra-aminoarsenobenzene,

$$NMe_2 \cdot C_6H_3(NH_2) \cdot As\colon As \cdot C_6H_3(NH_2) \cdot NMe_2,$$

is obtained. This compound has no curative action towards mice infected with trypanosomes.

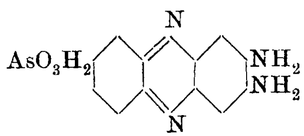
3-*Nitro*-4-*dimethylaminophenylarsinic acid* crystallises in lustrous, yellow needles.

The *hydrochloride* of *tetramethyltetra-aminoarsenobenzene* is a yellowish-white powder. E. F. A.

Aromatic Arsenic Compounds. III. Triazoarylarsinic Acids and Some of their Derivatives. P. KARRER (*Ber.*, 1913, **46**, 249—255).—Some triazophenylarsinic acids have been prepared

by the addition of sodium azoimide to the corresponding diazotised amines. They are very stable towards dilute sulphuric acid, and cannot be hydrolysed to aminophenols, but the *o*-nitrated azoimides give up nitrogen when heated and undergo rearrangement to *o*-dinitroso-compounds (compare Zincke and Schwarz, A., 1899, i, 751), which can be readily condensed with dimethylaniline to phenazine derivatives.

p-*Triazophenylarsinic acid*, $N_3 \cdot C_6H_4 \cdot AsO_3H_2$, from *p*-aminophenylarsinic acid, crystallises in stout, white crystals, and gives a *monosodium* salt. 3-*Iodo*-4-*triazophenylarsinic acid* forms white crystals, and 3-*nitro*-4-*triazophenylarsenic oxide*, $N_3 \cdot C_6H_3(NO_2) \cdot AsO$, prepared from 3-nitro-4-aminophenylarsenic dichloride, which, in turn, is obtained from the arsinic acid, is a yellow, crystalline powder. 3-*Nitro*-4-*triazophenylarsinic acid*, a yellow, crystalline powder, loses nitrogen at 75°, and changes into 3 : 4-*dinitrosophenylarsinic acid*, $C_6H_3(NO)_2 \cdot AsO_3H_2$; this condenses with dimethylaniline to form 2- (or 3-)-*dimethylaminophenazine*-7-*arsinic acid*, $C_{14}H_{12}O_3N_3As$, as a blue dye which is very soluble in acetic acid and in sodium hydroxide. 2-*Nitro*-3-*triazophenylarsinic acid* also condenses with dimethylaniline, but 2-(or 3-)-*dimethylaminophenazine*-8-*arsinic acid* is insoluble in sodium hydroxide and has a reddish tinge. 3-Nitro-4-triazophenylarsinic acid can also be condensed with *o*-phenylenediamine in glacial acetic acid, when the *acetate* of 2 : 3 - *diaminophenazine* - 7 - *arsinic acid* separates as a brick-red powder. The free base (annexed formula) is yellow, gives a *diacetyl* derivative as a yellowish-brown powder, and when treated with sodium nitrite and acetic acid deposits the *compound*,



$$AsO_3H_2 \cdot C_6H_3 \lessdot \substack{N \\ N} \gtrdot C_6H_2 \lessdot \substack{NH \\ N} \gtrdot N,$$

in the form of a brown powder. J. C. W.

Iso- and Hetero-poly-salts. VIII. Alkylarsinomolybdates.

ARTHUR ROSENHEIM and ROBERT BILECKI (*Ber.*, 1913, **46**, 539—557. Compare A., 1911, i, 109, 265; ii, 116, 612; this vol., ii, 59).—In order to examine further the extension of Werner's co-ordination theory to poly-acids by Miolati and Pizzighelli (A., 1908, ii, 595), the authors have prepared a series of alkylarsinomolybdates. They find that the number of MoO_4 or Mo_2O_7 radicles which unite with the alkylarsenates to form complex compounds is intimately connected with the number of oxygen atoms in the arsinate anion, and diminishes as the number of alkyl radicles present increases. The basicity of the hetero-poly-acids so formed is either equal to, or, generally, higher than, that of the corresponding alkylarsinates. Normal hetero-poly-salts could not in all cases be obtained. This is attributed to the fact that the acids contain weakly electro-negative complex ions which are hydrolysed on neutralisation of the solutions. The composition of the hetero-poly-salts is found to depend on the electro-affinity of the central atom; more powerfully electronegative anions, such as the phenylarsinate- and *p*-hydroxyphenylarsinate-anions unite with MoO_4

radicles, whilst the weaker electronegative anions, such as the dialkylarsinate-anion, unite with Mo_2O_7 radicles.

The authors' experiments on solutions of cacodylic and molybdic acids agree with those of Miolati (*loc. cit.*). The latter, however, found breaks in the graph for the electrical conductivity of solutions of molybdic and methylarsinic acids at the proportions

$$AsMeO_3H : MoO_3 = 2 : 5 \text{ and } 1 : 10.$$

Since these figures did not agree with those obtained by the authors, the latter have plotted Miolati's graph on a larger scale, and find that it is not exact, somewhat weak breaks actually occurring at the proportions $AsMeO_3H : MoO_3 = 1 : 6$ and $1 : 9$. The corrected result agrees with the authors' determinations.

A boiling aqueous solution of sodium methylarsinate was saturated with molybdic acid, and, after concentration, an excess of guanidinium chloride was added. Two *guanidinium* salts were thereby obtained, the less soluble of which was composed of rectangular plates having the formula $(CN_3H_6)_2[AsMe(Mo_2O_7)_3],11H_2O$, whilst the more soluble salt consisted of white needles having the composition

$$(CN_3H_6)_8H_2\left[\begin{array}{cc}\overset{\text{Me}}{As}(Mo_2O_7)_4 & (Mo_2O_7)_4\overset{\text{Me}}{As} \\ \multicolumn{2}{c}{—Mo_2O_7—}\end{array}\right],8H_2O.$$

In alkaline solution only the latter salt was obtained.

Sodium phenylarsinate, when similarly treated, also yielded two *guanidinium* salts. The less readily soluble salt, white leaflets,

$$(CN_3H_6)H[AsPh(MoO_4)_3],H_2O,$$

did not yield a neutral salt when boiled with excess of guanidinium carbonate. The more soluble salt, long, white needles,

$$(CN_3H_6)_5H_5\left[\begin{array}{ccc}AsPh(MoO_4)_4 & & (MoO_4)_4AsPh \\ | & MoO_4 & |\end{array}\right],6H_2O,$$

behaved according to conductivity measurements as the salt of a normal pentabasic substance. The hydrogen atoms could not be replaced by base in aqueous solution. In faintly alkaline solution, the more soluble salt was exclusively formed. When the latter salt was suspended in water and gently heated with guanidinium carbonate, the *salt*, $(CN_3H_6)_6H_2\left[\begin{array}{ccc}AsPh(MoO_4)_3 & & (MoO_4)_3AsPh \\ | & & | \\ OH & MoO_4 & OH\end{array}\right],4H_2O$, was obtained. Precisely similar salts were obtained from those derivatives of phenylarsinic acid which did not form too powerfully electronegative anions; thus, from sodium *p*-aminophenylarsinate, the *guanidinium* salt, $(CN_3H_6)_2\left[As\begin{array}{l}C_6H_4\cdot NH_2 \\ (MoO_4)_3\end{array}\right],5H_2O$, pale yellow leaflets, was prepared, whilst sodium *p*-hydroxyphenylarsinate yielded a *guanidinium* salt, $(CN_3H_6)_2\left[As\begin{array}{l}C_6H_4\cdot OH \\ (MoO_4)_3\end{array}\right],2H_2O$, white needles, and also a more soluble *salt*, crystallising in small plates. A complex salt derived from *p*-carboxyphenylarsinic acid could not be isolated.

Sodium cacodylate, when treated with molybdic acid and subsequently with guanidinum chloride, gave the *guanidinium* salt, $N_3H_6)_2\left[\begin{array}{c}AsMe_2(Mo_2O_7)_2 \\ (OH)_2\end{array}\right]$, colourless, anhydrous plates. The micro-

crystalline *lead*, *copper*, and *silver* salts were also prepared. The *potassium* salt, prepared from potassium cacodylate in the usual manner, formed microscopic needles of the formula $K_2H\left[\begin{matrix}AsMe_2(Mo_2O_7)_2\\ (OH)_2\end{matrix}\right]$. The correponding *barium* salt was obtained by the action of barium chloride on the sodium salt.

In a similar manner, the *guanidinium* salt,

$$(CN_3H_6)_2H\left[\begin{matrix}AsPh_2(Mo_2O_7)_2\\ (OH)_2\end{matrix}\right],H_2O,$$

white, hexagonal plates, was obtained from sodium diphenylarsinate.

An aqueous solution of trimethylarsonium hydroxide was saturated with molybdic acid at its boiling point. The solution, when concentrated, deposited a yellow, microcrystalline substance,

$$AsMe_3(OH)_3H_3\left[\begin{matrix}AsMe_3(Mo_2O_7)_2\quad(Mo_2O_7)_2AsMe_3\\ \text{—O—}\end{matrix}\right],3H_2O.$$

When, however, guanidinium chloride was added to the above solution before the latter compound had separated, the *guanidinium* salt,

$$(CN_3H_6)_3H_3\left[\begin{matrix}AsMe_3(Mo_2O_7)_2\quad(Mo_2O_7)_2AsMe_3\\ \text{—O—}\end{matrix}\right],$$

was obtained as microscopic, white plates.

When triphenylarsine oxide was dissolved in boiling aqueous sodium molybdate solution and the latter acidified by gradual addition of hydrochloric acid, a yellow, amorphous *substance*, $\left[As\begin{matrix}Ph_3\\ Mo_2O_7\end{matrix}\right]$, was obtained.

H. W

Preparation of Organic Arsenic Compounds. HEINRICH BART (D.R.-P. 254345. Compare this vol., i, 115).—When solutions of *iso*-diazo-compounds react with diarylarsenious oxides (or acids) they give rise to triarylarsine hydroxides or oxides :

$$RN:NOH + R_2As{\cdot}OH = N_2 + R_3AsO + H_2O.$$

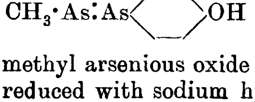
A 10% solution of sodium *p*-nitro*iso*diazobenzene is slowly treated with dinitrodiphenylarsenious acid and sodium hydroxide (1 mol.); on slowly heating to 75—80°, nitrogen is evolved, and on the addition of acid the trinitrotriphenylarsine oxide separates as a brown precipitate.

The required *dinitrodiphenylarsenious acid* is obtained by the careful reduction of dinitrodiphenylarsinic acid with hydrogen iodide in acetic acid solution; when heated it decomposes energetically without fusion.

F. M. G. M.

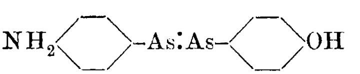
Preparation of Unsymmetrical Arseno-compounds. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 253226).—Unsymmetrical aromatic arseno-compounds have previously been prepared (this vol., i, 116), and this reaction has now been extended to the case of compounds containing both aliphatic and aromatic residues.

3-*Amino*-4-*hydroxybenzenearsenomethane* (annexed formula), a yellow powder soluble in dilute acids and alkaline hydroxides, is obtained when a methyl-alcoholic solution of 3-amino-4-hydroxyphenylarsenious oxide is treated with a similar solution of methyl arsenious oxide (A., 1906, i, 488), water added, and the mixture reduced with sodium hyposulphite.

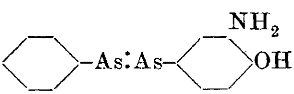


One or both of the arsenious oxides in the foregoing reaction can be replaced by the corresponding acids, in which case the reduction is carried out with stannous chloride and hydrogen iodide at $-10°$ to $-20°$. F. M. G. M.

Preparation of Aromatic Arseno-compounds. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 254187. Compare A., 1909, i, 347; 1910, i, 148).—When aromatic arsinic acids are reduced in strongly acid solution they give rise to primary arsines of general formula $R\cdot AsH_2$ ($R=$aryl), which can be condensed with aryl-arsenious oxides or haloids to yield aromatic arseno-derivatives (this vol., i, 117): $R\cdot AsH_2+R\cdot AsO=R\cdot As{:}As\cdot R+H_2O$; $R\cdot AsH_2+R\cdot AsCl_2=R\cdot As{:}As\cdot R+2HCl$.



4-*Amino*-4′-*hydroxyarsenobenzene* (annexed formula), a yellow powder, decomposes at about 200°; 3-amino-4-hydroxy-4′-glycylarsenobenzene (this vol., i, 116) darkens at 120° and decomposes violently at 150°, and 3-*amino*-4-*hydroxyarsenobenzene* (annexed formula) forms a yellow powder.



Other compounds mentioned as being prepared by this method are 4 : 4′-diaminoarsenobenzene and 3 : 3′-diamino-4 : 4′-dihydroxyarsenobenzene. F. M. G. M.

Preparation of Aromatic Stibinic Acids. CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.-P. 254421. Compare Trans., 1911, **99**, 2286).—Phenylstibinic acid has previously been prepared (Hasenbäumer and others) by a somewhat complicated series of reactions; the following simple method is now described.

Antimony trioxide (140 parts) is dissolved at the ordinary temperature in 764 parts of hydrochloric acid (D 1·123), treated with sodium hydroxide (600 parts) in water (3000 parts), and rapidly cooled to 0°, when part of the sodium antimonite separates. A solution of aniline-diazonium sulphate (prepared from 93 parts of aniline and 147 parts of sulphuric acid) is then rapidly stirred in, either with or without the addition of copper paste; after some hours the mixture is carefully neutralised with sulphuric acid, filtered, and the phenylstibinic acid precipitated by the addition of hydrochloric acid. To purify the product from antimony trioxide it is dissolved in hot hydrochloric acid (D 1·123), and the solution saturated with solid ammonium chloride, when on cooling *phenylstibinic oxychloride* separates in glistening leaflets; this is isolated, decomposed with sodium carbonate, and the pure phenylstibinic acid precipitated with hydrochloric acid. As thus prepared, phenylstibinic acid is stable at 250° (Hasenbaümer gives decomp. point 200°).

p-*Hydroxyphenylstibinic acid* and p-*acetylaminophenylstibinic acid* are similarly prepared from *p*-aminophenol and monoacetyl-*p*-phenylene diamine respectively; the *sodium* salt of the latter dissolves in water with a neutral reaction. p-*Aminophenylstibinic acid*, obtained by the hydrolysis of the foregoing acid, combines readily with aldehydes

(salicylaldehyde) to furnish hydroxybenzylidene derivatives or on diazotisation gives rise to a red azo-derivative with alkaline β-naphthol.

F. M. G. M.

Preparation of Nuclear Substituted Mercury Derivatives of Aromatic Hydroxy-acids. CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.-P. 255030).—The following therapeutically active organic derivatives of mercury have now been prepared.

Mercurydisalicylic acid, $Hg[C_6H_3(OH)\cdot CO_2H]_2$, a colourless powder, insoluble in water, is obtained by the reduction of *o*-hydroxymercurisalicylic anhydride with sodium formaldehydesulphenate, and is employed in the form of its neutral *alkali* salts.

Mercury-bis-sulphosalicylic acid, also employed in the form of its *sodium* salt, is similarly prepared from sodium mercurisulphosalicylate.

Mercury-bis-arsenosalicylic acid, a colourless powder, is obtained from mercury arsenosalicylic acid.

Sodium mercuri-bis-2-naphthol-3 : 6-disulphonic acid and *mercury-bis-4-hydroxy-*m*-tolyl-1-arsinic acid* are also employed in the form of their crystalline *sodium* salts.

F. M. G. M.

Physiological Chemistry.

The Influence of Phosphorus on Respiratory Metabolism. OTTO HIRZ (*Zeitsch. Biol.*, 1913, **60**, 187—310).—The respiratory exchange in rabbits sinks regularly during inanition. On the second day the nitrogenous output and the urea rise and remain at a constant level as the organ protein is utilised. In fat animals the consumption of the organ protein is delayed. In phosphorus poisoning the decrease in respiratory metabolism is not a specific effect of the poison on metabolism, but is secondary to pain and other symptoms produced. With small doses there is a slight increase in respiratory activity. The nephritis produced lessens the output of nitrogen, but in fat animals this is preceded by an increase. Carbohydrate metabolism is unaffected. The combustion of fat increases. No support is found for the hypothesis that the fat which appears in the organs ("fatty degeneration") is of protein origin. The permeability of the blood vessels is greatly increased.

W. D. H.

The Coagulation of Blood. WILHELM CRAMER and HAROLD PRINGLE (*Quart. J. expt. Physiol.*, 1913, **6**, 1—12).—If oxalate plasma is filtered through a Berkfeld filter, it does not clot when calcium chloride is added to it. This is due to removal of the platelets, which are still present in oxalate plasma prepared in other ways. The addition of calcium chloride to ordinary oxalate plasma liberates thrombokinase (Howell's thromboplastin) from the

platelets. Soluble calcium salts, in addition to this primary effect on the platelets, contribute also to the formation of fibrin under the influence of the substance liberated from the platelets. In paraffined tubes blood remains fluid because the platelets are intact; when transferred to glass tubes the platelets in contact with the glass disintegrate, and clotting ensues. The phenomena described by Nolf as "thromboplastic agencies" and "centres of coagulation" are due to the presence of platelets. Plasma free from platelets are not susceptible to the action of "thromboplastic agencies."

W. D. H.

The Plasma of Propeptone. HENRI STASSANO (*Compt. rend.*, 1913, **156**, 735—738).—The plasma obtained after the intravenous injection of propeptone differs in several respects from plasma, to which salts have been added. The first is coagulated when diluted either with distilled water or even with a solution of an anticoagulating salt, whilst the latter is only coagulated on dilution with water. The plasma of propeptone behaves thus as a mixture of serum and fibrinogen in decalcified solution. The coagulation of propeptone plasma on dilution is unaffected by change in temperature, whilst that of the saline plasma is checked by cooling. In tubes coated with paraffin wax, the former plasma coagulates on dilution with only a slight retardation, whilst the latter remains indefinitely liquid. The coagulating power of propeptone plasma towards the peritoneal serum from a horse is greater at the moment of dilution than two hours afterwards, whilst that of saline plasma steadily increases after dilution. These differences point to the fact that, whilst in the saline plasma the fibrin-ferment is in an inactive state, in the plasma of propeptone it is in the active state. W. G.

The Transference of the Digestion Products of Proteins from the Mother to the Fœtus. GIUSEPPE BUGLIA (*Biochem. Zeitsch.*, 1913, **48**, 362—372).—The distribution of nitrogen in the blood of the fœtus and mother in the case of dogs was determined both when digestion products had been injected into the jugular or femoral vein, and when either no injection had been made, or only saline had been administered. From the comparison of the various results obtained, the conclusion is drawn that protein digestion products can pass directly from the mother to the fœtus.

S. B. S.

The Influence of Nutrition on the Amylase Content of Human Saliva. C. LOVATT EVANS (*Biochem. Zeitsch.*, 1913, **48**, 432—447).—The amylase content (estimated by determining the amount of maltose produced from a given starch solution in a given time by Bertrand's method) increases after a meal. The increase commences twenty to thirty minutes after a meal, and lasts for two to three hours, when it reaches a maximum and then wanes. The activity remains then small until the next meal is taken. The content is not affected after mock feeding (mastication of food without swallowing). A meal of purely protein content does not

increase the amylase. The mechanism of the secretion can be explained by assuming that carbohydrates act on the mucous membrane of the stomach and produce a hormone. The increase in amylase content is to be ascribed principally to the saliva produced by the parotid gland, which has about four times the enzymatic activity of that of the remainder of the glands. The parotid, furthermore, produces about half the total volume of the saliva.

S. B. S.

The Behaviour of Plasteins in the Animal Body. I. The Relationships of Plasteins to Peptone Poisoning. ERICH VON KNAFFL-LENZ and ERNST P. PICK (*Arch. expt. Path. Pharm.*, 1913, **71**, 296).—If pepsin hydrochloric acid acts on a poisonous peptic digest, substances of higher molecular weight (plasteins) are formed which are not poisonous. The formation of plasteins in the body is regarded as protective. If the plasteins are again subjected to gastric action, poisonous products again arise; tryptic digestion is ineffective in this direction. The phenomenon is thus a reversible one. The final cleavage products of protein digestion are not poisonous. W. D. H.

Pancreatic Digestion. FRIEDRICH AUERBACH and HANS PICK (*Biochem. Zeitsch.*, 1913, **48**, 425—426).—Attention is called to the fact that, whereas natural pancreatic juice possesses the optimal hydroxyl ion concentration for lipoclastic or peptoclastic function, the digestion of proteins proceeds best in a medium more distinctly alkaline. This indicates that the preliminary digestion of proteins takes place for the most part in the stomach rather than in the intestine, the function of which is to digest the peptones. S. B. S.

Comparative Physiology of Digestion. VI. Cellulose and Cellulose-dissolving Enzymes in the Hepatopancreas of the Snail (Helix pomatia). JERZY STANISŁAW ALEXANDROWICZ (*Pflüger's Archiv*, 1913, **150**, 57—86).—Attention is directed to the two forms of crystalline cellulose, namely, those in plant sections, and the sphæro-crystals prepared *in vitro* by Gilson and Bütschli. The former have strong, doubly refracting properties; the sphærocrystals are only feebly anisotropic. In plant membranes hemicelluloses are present, which increase their anisotropy. Crystallised cellulose is dissolved by the snail's hepatopancreas. Hence celluloses of different origin differ a good deal in solubility in the juice. It is suggested that the enzymes which dissolve cellulose and hemicellulose may be investigated microscopically in the study of the chemical composition of vegetable membranes. W. D. H.

The Synthetic Powers of the Organism of the Dog. EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1913, **83**, 444—457).—The dog under observation was kept for three months on carbohydrate, fat, and the completely cleaved products of meat hydrolysis. It gained 10 kilograms in weight, and renewed its fur. Tryptophan and tyrosine are essential, and their absence is followed by untoward symptoms. Hopkins' view that tryptophan is essential for the formation of certain internal secretions is regarded as probable but unproven. W. D. H.

Action of Ammonium Salts, Glucosamine and Gelatin on the Nitrogen Balance. EMIL ABDERHALDEN and ARNO ED. LAMPÉ (*Zeitsch. physiol. Chem.*, 1913, **83**, 409—424).—Experiments similar to those previously carried out on dogs are now recorded on two pigs. On most days there was a loss of nitrogen; in this and some other details the results differ from those of Grafe on pigs. A further series of experiments on a dog yielded much the same results. This dog died of tetanus, which is attributed to tetanus spores in the gelatin given. This is the first recorded instance of tetanus infection through the alimentary tract.

W. D. H.

Utilisation of Calcium and Phosphoric Acid Compounds by the Animal Organism. GUSTAV FINGERLING (*Landw. Versuchs-stat.*, 1913, **79—80**, 847—870. Compare *ibid.*, **75**, 1).—Feeding experiments in which goats received, in addition to straw, blood nuclein, starch, and oil, the following substances as sources of phosphorus: phytin, lecithin, casein, nuclein, nucleic acid, and disodium phosphate. The food was mixed with molasses to make it palatable.

The results showed that there is no essential difference in the utilisation of the different forms of phosphorus. The imperfect assimilation of the phosphoric acid of crude foods must, therefore, be due to other causes.

N. H. J. M.

Comparative Investigations on the Content of Amino-acids in the Different Constituent Parts of the Nervous System. II. The Amino-acids of the Grey and White Substance of the Brain. EMIL ABDERHALDEN and ARTHUR WEIL (*Zeitsch. physiol. Chem.*, 1913, **83**, 425—440).—The results of the analyses of grey and white brain matter are given in tables, together with the methods used. The details relate to water, total nitrogen, ash, and various amino-acids.

W. D. H.

The Action of the Diastatic Enzyme on the Glycogen within the Cells. JULIUS GRODE and ERNST J. LESSER (*Zeitsch. Biol.*, 1913, **60**, 371—387).—The surviving liver and muscles of winter (glycogen-rich) frogs in oxygenated Ringer's solution lose little or none of their glycogen. The same was stated by Schiff in 1859. If the cells are destroyed mechanically, the glycogen disappears rapidly. The enzyme responsible for the change is considered to exist in the cells as a zymogen, which is converted into the active enzyme as the cells are killed.

W. D. H.

The Behaviour of the Glycogen of the Frog in Anoxybiosis and Restitution. III. ERNST J. LESSER (*Zeitsch. Biol.*, 1913, **60**, 388—398).—In the living summer frog (poor in glycogen) the anoxybiotic glycogen disappearance is about 50% in two hours at 20°. In restitution in the summer, contrary to what is seen in winter frogs, there is a well-marked new formation of glycogen. Under anoxybiotic conditions lasting two or three days, the

glycogen also is lowered by about 50%. Normal frog's blood contains no sugar when tested for by the method of Michaelis and Rona. In anoxybiosis the blood contains 0·07% sugar, and minute amounts may pass into the urine. W. D. H.

Comparative Anatomy and Physiology of the Pituitary Body. PERCY T. HERRING (*Quart. J. expt. Physiol.*, 1913, **6**, 73—108).—The pituitary bodies of the classes of vertebrates resemble one another in essential features. In elasmobranch fishes, however, the nervous lobe is absent.

No portion of the epithelial lobe in any case contained the active principles associated with the posterior lobe in mammalia. The *pars intermedia* by itself or the colloid matter separated from it have no specific effect on blood-pressure or kidney. The hormone which affects the mammary gland is obtainable from the skate's pituitary (which has no nervous lobe), and therefore appears to be a separate substance. It is still more abundant in the posterior (nervous) lobe in other animals; it is probable that it is a product of the epithelial lobe, and is stored in the *pars nervosa*. The latter is composed of modified ependyma and neuroglia cells permeated by a gelatinous substance containing fine granules and hyaline bodies. The granules are considered to be the representatives of the active principles of the nervous lobe; they are the products of the cells of the *pars intermedia* (in origin, a portion of the epithelial lobe); these are carried to, elaborated in, and stored by the *pars nervosa.* W. D. H.

The Effects of the Administration of Extracts of the Pituitary Body and Corpus Luteum to Milch Cows. W. GAVIN (*Quart J. expt. Physiol.*, 1913, **6**, 13—16).—Under conditions of farm practice, no commercial benefit arises from the administration to dairy cows of these glandular extracts, whether given by the mouth, under the skin, or intravenously. Intravenous injection of pituitary extract causes more milk to collect in the lower parts of the udder, but no alteration in the total quantity per diem, or in the quality of the milk, occurs. W. D. H.

The Effect of Pituitary and Corpus Luteum Extracts on the Human Mammary Glands. EDWARD A. SCHÄFER (*Quart. J. expt. Physiol.*, 1913, **6**, 17—20).—Observations on a woman of twenty-eight nursing her second child show that injection of pituitary extract intramuscularly, produced a tingling sensation in the breasts, and an increased flow of milk. The effect was not lasting, and a long time elapsed before there was again enough milk to feed the child. The effect of similar injections of extract of the corpus luteum was doubtful. W. D. H.

The Liberation of Ions and the Oxygen Tension of Tissues during Activity. HERBERT E. ROAF (*Proc. Roy. Soc.*, 1913, *B*, **86**, 215—218).—A preliminary account of an investigation of muscle by various kinds of electrodes, and the results give evidence that

hydrogen and probably chlorine ions are liberated during the act of contraction. There is also a fall in oxygen tension. W. D. H.

The Summation of Muscular Contractions. GEORGE R. MINES (*J. Physiol.*, 1913, **46**, 1—27).—Reasons are given for thinking that the liberation of acid in muscle as the result of excitation precedes the act of shortening and possibly causes it. When a second excitation can be produced before the first localised concentration of acid has had time to diffuse away, the result may be a summation of these localised concentrations, and so a greater effect on the contractile mechanism. Such an effect may, however, occur at a time when the general hydrogen ion concentration of the muscle is such that further increase tends only to diminish the power of the response of the muscle. W. D. H.

The Energy Degraded in the Recovery Processes of Stimulated Muscles. ARCHIBALD V. HILL (*J. Physiol.*, 1913, **46**, 28—80).—A thermoelectric apparatus is described by which it is possible to estimate and record rapidly the rise of temperature of a muscle to within a millionth of a degree. The production of heat in a muscle excited in oxygen either by a single shock or a short tetanus continues for long periods after the mechanical response is over; but after the muscle has been kept in nitrogen for an hour there is no trace of heat production following the contraction; on being restored to oxygen this returns. Previous excitations or a prolonged tetanus, which diminish the oxygen tension in the muscle, lessen the heat production after the contraction. The "delayed heat" is due to usage of oxygen in the process of recovery; and recovery does not occur in the absence of oxygen. It is suggested that the contraction is due to liberation of lactic acid from some precursor; the acid increases the tension in some colloidal structure of the tissue; this precursor is rebuilt after contraction, oxygen is used, and heat is produced; when oxygen is absent, the heat produced is due to the breakdown of the lactic acid precursor. The oxygen appears to be used largely in oxidations whereby the molecular machine (like a steam engine charging an accumulator) builds up substances containing considerable amounts of free energy, which, as in the accumulator, can be discharged on subjecting the muscle to stimuli. W. D. H.

The Extractives of Muscle. III. TEMISTOCLE JONA (*Zeitsch. physiol. Chem.*, 1913, **83**, 458—467).—Muscle extracts contain a fairly large percentage of gelatin, or rather of substances which behave like gelatin towards Schmidt's reagent. A dipeptide was also separated which, on analysis and determination of its constants, appears to be identical with the anhydride of *d*-alanyl-*d*-alanine, which E. Fischer prepared by treating the ethyl ester of this dipeptide with ammoniacal alcohol. W. D. H.

Products of Protein Cleavage which Produce Fatigue, and their Influence. WOLFGANG WEICHARDT and ERWIN SCHWENK (*Zeitsch. physiol. Chem.*, 1913, **83**, 381—402).—From the muscle-

proteins, by means of electrolysis, certain high molecular products were obtained which cause, when injected into animals (mice), certain toxic symptoms, such as the signs of fatigue, slowing of the respiration, and depression of the body temperature. The effect of these *keno-toxins*, as they are termed, can be counteracted by a number of substances of which the chemical composition is known, for instance, succinimide, glutarimide, phthalimide, piperidine, creatine, guanidine hydrochloride, and others. The same effect is produced by a group of substances of unknown composition which are spoken of as *retardins*; these can be extracted by acetone from digested protein. Further work on the relationships between activity and chemical composition is promised. W. D. H.

Physiological Permeability of Cells. V. Narcosis of Lipoid-rich and Lipoid-poor Tissues of the Same Kind. LOUIS CHOQUARD (*Zeitsch. Biol.*, 1913, **60**, 101—162).—Heart muscle is richer in lipoids than skeletal muscle; the effect of narcotics on each was tried in order to determine the influence of lipoids. According to the Meyer-Overton doctrine, narcotics of the aliphatic series should produce narcosis in less concentration when applied to cardiac muscle as compared to skeletal muscle. But to this a number of noteworthy exceptions were found; ether, acetone, and acetylacetone produce narcosis in smaller concentrations in the lipoid-poor skeletal than in the lipoid-rich heart muscle. Acetal narcotises heart muscle, however, in much smaller concentrations than are necessary for skeletal muscle (which is in consonance with the lipoid hypothesis), but acetal narcotises skeletal muscle in higher concentrations than ether. The introduction of a halogen atom into the molecule leads to the result that the heart muscle is narcotised by a smaller concentration than skeletal muscle. The partition coefficient, solubility in fat/solubility in water, does not account for this, for chloral hydrate, with the low coefficient of 0·22, narcotises heart muscle in the same concentration as ethyl bromide, which has a very high coefficient; probably the chemical influence of the halogenised material on the somewhat different biochemical structure of the two kinds of muscle is here being dealt with.

In the group of the univalent alcohols, the molecular weight increases as the lipoid solubility and the narcotic power in both tissues, but this relationship is not strictly parallel. For instance, the elevation of the partition coefficient of ethyl alcohol, as compared with propyl alcohol, is much greater than the rise in narcotic effect; the difference found was greater than stated by Overton.

Similar exceptional instances are found among the aldehydes. These experiments lead to the conclusion that the Meyer-Overton hypothesis is untenable. W. D. H.

The Presence of Boron in the Animal Series. GABRIEL BERTRAND and HENRI AGULHON (*Compt. rend.*, 1913, **156**, 732—735). —The authors have extended their work (compare A., 1912, ii, 854) on the presence of boron in animals, and have examined twenty-

seven other species from the different classes, finding boron in practically every case. They therefore consider that boron exists normally in very small proportions in the organism of all animals, being most abundant in the species of marine origin, whilst in others it is present only to the extent of 1 part in 100,000,000 of the living matter. W. G.

The Composition of the Tissues with Respect to Non-volatile Fatty Acids and Cholesterol, and the Possible Existence of a "Lipocytic Constant." André Mayer and Georges Schaeffer (*Compt. rend.*, 1913, **156**, 487—491).—The authors have determined the amount of non-volatile fatty acids and cholesterol in the various organs of a number of normal animals, and find that, whilst the variation in content of the same organ for different animals of the same species is moderately wide, more particularly in the case of the fatty acids, yet certain points stand out clearly, namely, whilst these variations occur for a given organ of animals of the same species, the values group themselves in moderate limits round a mean value, but from one species to another very different values are obtained for the content with respect to these substances for the same organ, the values being greater for birds than mammals, and still greater for eels. The so-called "lipocytic constant," $\frac{\text{cholesterol}}{\text{fatty acids}}$, is characteristic for each organ, and independent of the species. W. G.

The Action of Ultra-violet Rays on the Ear of the Rabbit. Venceslas Moycho (*Compt. rend.*, 1913, **156**, 577—579).—Exposure of the external surface of the ear to short irradiation (thirty seconds) produces no visible effect. If this is prolonged for one to twelve minutes, however, a series of phenomena appears. After two to five hours, local vaso-dilatation is noticeable, the portion which was exposed to the rays becoming red, this being accompanied by rise in temperature and tumefaction. The maximum effect is reached in twenty-four hours, then diminishes, and finally at the end of seven to twelve days the redness and high temperature completely disappear, and a persistent brown pigment appears. The irradiation appears to have a stimulating effect on the hair growth. The most active rays are those having $\lambda = 3100$—2900, and the cells acted on are situated at a depth of 1/10th to 1/6th mm. below the surface. W. G.

The Influence of Heat on the Physico-chemical Behaviour of Human Milk, Cow's Milk, and Butter-Milk. Paul Grosser (*Biochem. Zeitsch.*, 1913, **48**, 427—432).—The milk was submitted to ultra-filtration in Bechhold's apparatus before and after boiling, and the amounts of calcium, nitrogen, and phosphorus in the filtrates were compared. It was found that after heating, the phosphorus and nitrogen in the filtrate of cow's milk was scarcely affected, whereas that of human milk was appreciably diminished.

In both kinds of milk the calcium in the filtrate diminished after heating. S. B. S.

The Therapeutic Action of Yeast on the Alimentary Multiple Polyneuritis of Guinea-pigs and Pigeons. MAX BARSICKOW (*Biochem. Zeitsch.*, 1913, **48**, 418—424).—The addition of various yeast preparations to the insufficient diet which produces the beri-beri-like symptoms in animals was investigated. In the case of guinea-pigs fed on oats and water, or on this diet with rice alone, the addition of yeast preparations exerted no beneficial effect. In the case of pigeons, however, fed on a similar diet, the beneficial effect of certain yeast preparations was marked. This effect was produced both by yeast of which the enzymes were destroyed by heat, by living yeast, and by permanent yeast preparations, but not by "cerolin," a preparation containing only the constituents of yeast soluble in organic solvents. It is suggested that the therapeutic action is due to nucleins or salts. S. B. S.

The Behaviour of Blood Sugar in Normal and Pathological Cases. VI. Blood-sugar Content in Cases of Anæmia, Liver, Intestinal and Other Diseases. FR. ROLLY and FR. OPPERMANN (*Biochem. Zeitsch.*, 1913, **48**, 471—479. Compare this vol., i, 307).—Severe anæmia, with its accompanying diseases, causes generally an increase in blood sugar, which is more or less normal in quantity in mild cases. In Greves's disease there is an increase only in severe cases. In Addison's disease the amount is either normal or subnormal; in the latter case only when the disease is severe, and unaccompanied by infectious or toxic factors (tuberculosis, etc.). In scorbutic and eclamptic cases high values are generally found, which are due partly to the toxins. An increase was also found in cases of myasthenia and gangrene. In diseases of the liver and the alimentary tract there is an increase only when toxic factors are present (carcinoma, dyspnœa, abscesses, fever, etc.). S. B. S.

The Manganese Content of Transplanted Tumours. FLORENTIN MEDIGRECEANU (*Proc. Roy. Soc.*, 1913, *B*, **86**, 174—179).—The amount of manganese in transplanted mouse and rat tumours is small (0·004 to 0·012 mg. per 100 grams of fresh material), which is about the same as in the normal mammary gland of the mouse. No differences in the manganese of sarcoma and carcinoma were discoverable. W. D. H.

The Influence of Vapours of Technical Importance on the Organism. XXXII and XXXIII. Amyl Acetate and *cyclo*-Hexanyl Acetate. KARL B. LEHMANN (*Arch. Hygiene*, 1913, **78**, 260—273).—Both the substances investigated have a relatively small toxicity, the *cyclo*hexanyl acetate being about three times as toxic as amyl acetate, as measured by the amount necessary to produce narcosis. This greater toxic effect is, however, counterbalanced by the fact that it is considerably less volatile. Both substances can be safely employed in technical operations when the necessary precautions for ventilation, etc., are taken. S. B. S.

The Influence of Certain Cardiac Medicaments on the Electrocardiam Curve. ADOLF BICKEL and MICHAEL PAVLOV (*Biochem. Zeitsch.*, 1913, **48**, 459—470).—Certain digitalis and strophanthus preparations, and especially digistrophan, have the tendency to heighten certain points in the curve, whereas, in larger doses, the height of these points is diminished. In all cases there is a lengthening both of the heart phase and pause. Cardiotonin also causes a slowing of the heart action, increasing both the heart phase and pause. Valerian has no influence in this respect. The author discusses the therapeutic application of these various drugs, as deduced from their effects on the electrocardiam curve. The experiments were carried out with dogs and rabbits. S. B. S.

The Relationship between Heart Drugs and the Physiological Action of Cations. ARTUR VON KONSCHEGG (*Arch. expt. Path. Pharm.*, 1913, **71**, 251—260).—If a frog's heart is perfused with Ringer's solution free from calcium, the stoppage so produced can be counteracted by strophanthine; but if the solution is free from both potassium and calcium, strophanthine has not the power to resuscitate the heart. A heart poisoned with potassium again beats when strophanthine is applied. If a heart is stopped by a calcium-free solution, adrenaline and camphor cause weak contractions of the sinus, but caffeine has no effect. W. D. H.

The Depressor Effect of Adrenaline on Arterial Pressure. WALTER B. CANNON and HENRY LYMAN (*Amer. J. Physiol.*, 1913, **31**, 376—398).—Stimulation of the cat's adrenal causes vaso-dilation and a fall of arterial pressure. Small doses of adrenaline have the same effect. After pithing, or extreme depression, the effect is pressor, but ergotoxine restores the depressor action. The effects are attributed to opposite actions of adrenaline according to the state of the muscle; relaxation occurs when the muscle is tonically shortened, and contraction when relaxed. W. D. H.

Adrenaline and Glycamia. HENRI BIERRY and (Mlle.) LUCIE FANDARD (*Compt. rend.*, 1913, **156**, 480—482).—After injection of adrenaline to the extent of 0·001 gram per kilo. of body-weight, either intravenously or into the peritoneal cavity, there is marked progressive hyperglycamia and also a considerable rise in the combined sugar of the blood, which, however, increases more slowly than the free sugar. W. G.

[Physiological] Action of Scopolamine. MAX CLOETTA (*Arch. expt Path. Pharm.*, 1913, **71**, 290—292).—Polemical remarks on the controversy between Hug and Cushny (compare A., 1912, ii, 790; this vol., i, 226). W. D. H.

The Action of Veratrine and Protoveratrine. RUDOLF BOEHM (*Arch. expt. Path. Pharm.*, 1913, **71**, 269—289).—The intensity of the action of protoveratrine on the frog's heart is much greater than that of veratrine; on nerve it is less active; on skeletal muscle

it is also less active, although its effects are substantially the same in kind. W. D. H.

The Behaviour in the Organism of 2 Phenylquinoline-4-carboxylic Acid (Atophan). W. SKÓRCZEWSKI and J. SOHN (*Bull. Acad. Sci. Cracow*, 1912, **9**, *A*, 885—887).—After administration of atophan, the urine gives the following reactions: (1) A yellow colour with concentrated hydrochloric acid. (2) A yellow precipitate with phosphotungstic acid. (3) A dark green colour with ammonium sulphate and ammonia. (4) A characteristic diazo-reaction with Ehrlich's reagent. These reactions are given neither by the drug itself nor by normal urine, but are due to an acid, which can be extracted from the concentrated urine by ether, and which after recrystallisation by ether and light petroleum has m. p. 231—232° after turning brown at 200°. Its formula, $C_{18}H_{11}O_3N$, corresponds with that of hydroxyphenylquinolinecarboxylic acid. The position of the hydroxyl group in this compound is not yet determined. S. B. S.

Action of Arseno-aromatic Compounds ("606" and Neo-salvarsan) on the Hæmoglobin of the Blood. R. DALIMIER (*Compt. rend.*, 1913, **156**, 629—631).—Salvarsan (diaminodihydroxyarsenobenzene) has no action on hæmoglobin either *in vitro* or *in vivo*. Neo-salvarsan (sodium diaminodihydroxyarsenobenzene-methylenesulphenate), on the other hand, produces marked hæmolysis and reduction of the oxyhæmoglobin when acting *in vitro*. On injection into the ear-vein of the rabbit, only a fugitive hæmolysis is noticeable, there being no reduction of the oxyhæmoglobin.

W. G.

Chemistry of Vegetable Physiology and Agriculture.

Protein and Phosphorus Content of Azotobacter Cells. CONRAD HOFFMANN (*Centr. Bakt. Par.*, 1913, ii, **36**, 474—476. Compare Abstr., 1910, ii, 988).—During the course of earlier investigations the author found the protein content of *Azotobacter* cells to vary from 8·3—12·0%, and the phosphorus content to be 2·51—2·97%. These amounts vary considerably from those found by Stoklasa (A., 1911, ii, 429), and it is suggested that the differences are possibly due to differences in the methods employed in preparing the samples for analysis. The relatively high content (61·25—71·87%) found by Stoklasa might be attributed to removal of carbohydrates during washing, whereas the material used by the author was obtained, without washing, from agar cultures. If this were the case, the protein: phosphorus ratio ought to be the same in the two sets of results, but such agreement does not appear to exist. H. B. H.

The Chemical Composition of Tubercle bacilli. TADEUSZ KOŹNIEWSKI (*Bull. Accad. Sci. Cracow*, 1913, **10**, *A*, 942—947).—When the bacteria are extracted with cold 96% alcohol, a small quantity of extract is obtained, which contains lipoids, colouring matter, and other substances. If the bacteria are extracted after alcohol treatment with hot acetone, relatively large quantities (20—24% of the dried bacteria) of a white, waxy substance are obtained, which is only slightly soluble on heating in most organic solvents, and is insoluble in mineral acids. On prolonged boiling with alcoholic potassium hydroxide, it yields a soap. Its formula agrees approximately with that of substance $C_{12}H_{24}O$, and the saponification number found was 125·2. The substance is probably an ester. When the bacteria are treated with 3—5% hydrochloric acid, a reducing sugar appears to pass into solution, which, even in concentrations of 2%, is optically inactive. The solution of sugar ferments with yeast. The author failed, in other experiments, to isolate glucosamine, from which he draws the conclusion that the bacteria do not contain chitin. S. B. S.

Proteus vulgaris Considered as a Producer of Indole. ALBERT BERTHELOT (*Compt. rend.*, 1913, **156**, 641—643. Compare Herter and Broeck, A., 1911, ii, 758).—Numerous observers having obtained varying results as to the production of indole by different specimens of *Proteus vulgaris*, Hauser, the author has made a careful study of the question, and finds that, in the case of the fifty-seven specimens examined, all the *Proteus vulgaris* are capable of attacking tryptophan, giving either indole or indoleacetic acid, or more generally, a mixture of these two substances, and that there is no reason for distinguishing a species *Bacillus proteus anindologenes*, as distinct from the *Proteus*-giving indole. The action of the microbe is variable not only with different specimens, but for the same race at different ages and under different conditions. W. G.

Influence of Cæsium, Rubidium, and Lithium Salts on Yeast as Compared with Potassium and Ammonium. THOMAS BOKORNY (*Bied. Zentr.*, 1913, **42**, 141—142; from *Allgem. Brauer-Hopfenzeit.*, 1912, **52**, 1469).—Addition of rubidium and cæsium sulphates to a nutritive solution containing sucrose (10), asparagine (0·1), peptone (0·025), monopotassium phosphate (0·1), and magnesium sulphate (0·025%) increased the yield of yeast, whilst lithium chloride and sulphate were injurious rather than beneficial. Potassium is essential; as much as 4·0% of monopotassium phosphate may be present without injurious effects. Ammonium salts up to 2% may be employed without injuring yeast. N. H. J. M.

Biochemical Synthesis of Alkyl Glucosides (α-Glucosides) by means of α-Glucosidase: α-Methyl Glucoside. Destruction of the α-Glucosidase in a Strongly Alcoholic Medium. ÉMILE BOURQUELOT, HENRI HÉRISSEY, and MARC BRIDEL (*Compt. rend.*, 1913, **156**, 491—493; *J. Pharm. Chim.*, 1913, [vii], **7**, 233—236).—The authors have synthesised α-methyl glucoside by the action of

α-glucosidase, obtained from bottom yeast (compare this vol., i, 323), on a solution of dextrose in dilute methyl alcohol. The glucoside is readily hydrolysed in aqueous solution by the enzyme. Both the synthesising and the hydrolysing influence of α-glucosidase are destroyed by contact for forty-eight hours at 15—18° with 60% methyl alcohol. With 35% alcohol slow destruction also takes place. W. G.

Action of Boron Compounds on the Growth of Plants. EMIL HASELHOFF (*Landw. Versuchs-Stat.*, 1913, **79–80**, 399—429. Compare Peligot, *Compt. rend.*, 1876, **83**, 686; Morel, A., 1892, 651; Loew, *Flora*, 1892, 374; Hotter, A., 1890, 1338; Nakamura, *Bull. Coll. Agric. Tokyo*, 1903, **5**, 509; Agulhon, A., 1910, ii, 236).—Small amounts of borax in water cultures (1 mg. per litre) acted favourably on the growth of plants, although the appearance of the plants indicated some injurious action. The same amount of boron in the form of borax diminished the yield. Both beans and maize are injured by 1·15 mg. per litre of boron.

In soil culture experiments, 0·125 mg. of boron (as borax) per kilo. of soil was not injurious to beans, whilst the same amount as boric acid is toxic. In some cases very small amounts (less than 0·1 per million of soil) seemed to have a stimulating effect.

The boron taken up by plants is deposited in the straw, and not in the seed. Although the production of spots on the leaves, under the influence of boron, seems to be the same in all kinds of plants, the effect on growth seems to vary with different plants.

N. H. J. M.

The Value of the Chlorophyll Coefficients and their Relation to the Real Respiratory Coefficients. LÉON MAQUENNE and ÉM. DEMOUSSY (*Compt. rend.*, 1913, **156**, 506—512).—The authors have determined the respiratory quotient and the chlorophyll coefficient of some thirty-two species of plants, and as a result of this and previous work (compare A., 1912, ii, 1201) put forward a number of conclusions as to the conditions governing respiration and assimilation in the plant. In the case of green plants the normal respiratory quotient is generally greater than one during the total period of growth, but diminishes as the leaves grow older, its excessive diminution being a sign of decay or damage of the organs under observation. Leaves, with a respiratory quotient greater than one, increase the pressure of the air in which they breathe and vice versa. Certain species, particularly those rich in organic acids, are sensitive to prior conditions of light and temperature, exposure to strong light tending to diminish the respiratory quotient, but there is a particular state of equilibrium for each of such conditions, and to this, by adaptation, the plant tends to come. For a plant in equilibrium with external conditions there exists a simple relation between its apparent and real respiratory quotients and the composition of the medium in which it breathes and its coefficient of absorption for carbon dioxide, the cellular juice in a leaf sheltered from light being supersaturated with respect to the latter. The apparent chlorophyll-coefficient is generally intermedi-

ate between the respiratory quotient and unity, the real coefficient being very near to unity. Changes in the ratio hydrogen : oxygen in the composition of the vegetable tissues are due mainly, if not entirely, to respiration, and but little to assimilation. The variations of the real respiratory quotient, due to changes in temperature, arise from changes in the chemical composition of the vegetable tissues under the given conditions, the chlorophyll-coefficient being unaffected. W. G.

Absorption of Oxygen by the Respiratory Chromogens of Plants. VLADIMIR I. PALLADIN and Z. N. TOLSTAJA (*Bull. Acad. Sci. St. Pêtersbourg*, 1913, 93—108*).—Experiments with etiolated stems of *Vicia faba* and with zymin give the following results.

The protoplasm in which the respiratory chromogens effect absorption of oxygen possesses an alkaline reaction. These chromogens may be extracted from plants by means of methyl alcohol, and, in alkaline solution, are found to absorb oxygen eagerly from the air, with formation of a cinnamon-red pigment; peroxydases or hydrogen peroxide likewise cause oxidation of the chromogens. Aqueous extracts of plants also contain chromogens able to fix atmospheric oxygen, the power to do this being weakened or completely annulled by boiling the extracts.

Chromogens extracted by means of methyl alcohol undergo scarcely any oxidation in the air, but those obtained from plants subjected for some days to autolysis in an oxygen-free medium rapidly absorb oxygen from the air with development of pigments; the addition of hydrogen peroxide prevents the formation of pigment, the liquid remaining colourless. The chromogen modified by autolysis is hence termed "reducing." Autolysis with yeast converts ordinary chromogen into the reducing modification.

Plants which, after autolysis in absence of oxygen, give a chromogen rapidly blackening in the air, give no trace of pigment when the autolysis proceeds in presence of oxygen.

The respiratory chromogen from beans is probably catechol or some derivative of it.

Alcoholic fermentation is accompanied by the formation of a substance, which readily removes hydrogen from the respiratory chromogen, and oxidises it, by means of atmospheric oxygen, to water; this withdrawal of hydrogen from the chromogen is not prevented by boiling the products of fermentation.

Thus, the respiratory chromogen, $\mathbf{R{\cdot}H_2}$, like leuco-compounds, gives up its hydrogen to the absorbed oxygen with formation of pigment, **R**, and water.

Palladin's previous statement that, during respiration of plants the carbon is oxidised, not by the oxygen of the air, but by water, is completely confirmed by the results of Wieland's investigations (A., 1912, i, 348, 944), which showed that the oxidation of aldehydes (intermediate products of alcoholic fermentation) may proceed by removal of oxygen from water with preliminary formation of hydrates. The removal of the hydrogen formed by the decomposi-

* and *Biochem. Zeitsch.*, 1913, **49**, 381—397.

tion of the water, which in Wieland's experiments was effected by means of methylene-blue or quinonoid compounds, is brought about in the case of plants by the respiratory chromogens; according to Bach, the decomposition of the water is a result of the action of reducases.

It is quite probable that, in the oxidation of chromogen to pigment, water is not immediately formed, but that the first product is either hydrogen peroxide (compare Manchot, A., 1901, i, 565, 574; ii, 93) or an organic peroxide (Bach's oxygenase).

T. H. P.

The Migration of Mineral Constituents and the Displacement of These Constituents in Leaves Immersed in Water. GUSTAVE ANDRÉ (*Compt. rend.*, 1913, **156**, 564—566).—The author has estimated the mineral constituents in the dry matter of chestnut leaves plucked at various times during the summer of 1912. The figures, whilst varying in the same direction, differ considerably from the results obtained for 1911 (compare this vol., i, 233). The total nitrogen and phosphorus diminish with increase in age of the leaf, whilst the sulphur, calcium, magnesium, and potassium increase as the leaf grows older, the increase in sulphur and calcium being probably largely due to the accumulation of calcium sulphate in the leaf.

The figures for the percentage loss of mineral matter during immersion in water for one month are of the same order as those obtained for leaves grown in 1911 (*loc. cit.*), calcium being the most resistant to exosmosis.

W. G.

The Germination of Seeds which have been Chemically Treated and Exposed to Light. FRIEDRICH SIMON (*Biochem. Zeitsch.*, 1913, **48**, 410—417).—Seeds of various plants (cress, oats, radishes) were allowed to germinate after treatment with ferric and uranyl sulphates, both when kept in the dark after the action of the reagent, and when exposed to sunlight. The percentage of the number of plants which germinated after five days was determined and compared with the number of seedlings obtained from seeds which had not been chemically treated, some of which had been exposed to light, and others kept in the dark. The results are tabulated, and it was found that in some cases (but by no means all) the seeds which had been exposed to light germinated more than those which had been kept in the dark. The action of the light and chemicals differed, however, in the different varieties of seed.

S. B. S.

Alleged Constant Occurrence of Iodine in Cells. JOHANNA BABIY (*Ber. deut. bot. Ges.*, 1913, **31**, 35—47).—The examination of numerous plants for iodine gave negative results invariably. Further experiments were made to ascertain whether plants absorb iodine from solutions containing potassium iodide. The results were negative.

The conclusion drawn by Justus (A., 1902, ii, 311) that iodine

is always present in the cell nucleus, animal and vegetable, is therefore incorrect. N. H. J. M.

Formation of Carbamide by Higher Plants. ROBERT FOSSE (*Compt. rend.*, 1913, **156**, 567—568. Compare A., 1912, ii, 1203).—Carbamide has been found in wheat, barley, maize, peas, clover, and beans, germinated under conditions excluding the presence of carbamide in the medium. Its presence has been proved in the seed during germination; but with the seed in a state of repose a negative result was obtained in the case of the white lupin and the bean, and a positive result with wheat, maize, and peas. In the case of the bean, after six weeks' germination no carbamide could be detected in the cotyledon, but it was found in the plumule to the extent of 0·112 gram per kilo. of fresh material. It was also present in the embryo of the haricot. Finally, its presence has been proved in the plumule of maize, aseptically germinated, and in the adult plant developed on a sterile, nutritive liquid according to Mazé's method. W. G.

Presence of Callose in the Membrane of the Marine Siphonaceous Algæ [Siphonates]. ROBERT MIRANDE (*Compt. rend.*, 1913, **156**, 475—477).—The membrane of the *Caulerpa* contains no true cellulose, but is composed of two substances, one belonging to the group of pectins and the other to the calloses. This holds good for all the *Siphonates* with the exception of the *Vaucheriaceae*, which possess a celluloso-pectic membrane. The *Siphonates* thus form a distinct group, not only by reason of their anatomic characteristics, but by the chemical constitution of their membrane. W. G.

Influence of Temperature on the Development of Active Principles in Some Medicinal Plants. JAMES BURMANN (*Bull. Soc. chim.*, 1913, [iv], **13**, 246—248. Compare A., 1912, ii, 379).—By a comparison of the quantities of active principles present in colchicum, digitalis (*D. ambigua* and *D. purpurea*), aconite, and belladonna plants gathered under the same conditions each year from 1907–11 with the mean temperature prevalent during each year, the author is led to the conclusion that the alkaloidal or glucosidic content of a plant is a function of the mean temperature of the year during which it was grown. H. W.

Production of Oxalic Acid by Aspergillus niger. CARL WEHMER (*Centr. Bakt. Par.*, 1913, ii, **37**, 31—33).—Polemical against Buromski (this vol., i, 230), with special reference to the methods used for the estimation of oxalic acid in cultures. H. B. H.

Calotropis procera. A New Digitalis-like Drug. LOUIS LEWIN (*Arch. expt. Path. Pharm.*, 1913, **71**, 142—156).—A full botanical account is given of the plant, one of the Asclepiadeæ. The active principle is called calotropin, but it has not yet been prepared pure for chemical analysis. The main fact is expressed in the title, namely, that it belongs to the drugs which act on the heart like digitalis. W. D. H.

Enzyme Action. IV. Occurrence of a Urease in Castor Beans. K. GEORGE FALK (*J. Amer. Chem. Soc.*, 1913, **35**, 292—294. Compare Falk and Nelson, A., 1912, i, 523, 593; Falk and Hamlin, this vol., i, 303).—In continuation of a study of the enzymes of the castor bean, the presence of a urease has been demonstrated, which is rendered inactive by heat. E. G.

Constituents of the Seeds of Croton tiglium. ERNST WINTERSTEIN and M. A. JEGOROV (*Landw. Versuchs-Stat.*, 1913, **79–80**, 535—539).—The seeds examined contained 5—10% of nitrogen as proteins, and 0·19 and 0·19% of nitrogen as bases and amino-acids respectively. The proteins yield the usual cleavage products. When the seeds, freed from fat, are kept for sixteen days at 37—40° in presence of toluene, chloroform, and some sodium fluoride, xanthine bases, arginine and lysine are produced. The solution from the lead acetate precipitate contained the following amounts of nitrogen: as bases, 1·437; as ammonia, 0·3514; and as amino-acids, 1·7648 grams (from 500 grams of seeds). N. H. J. M.

The Acids of Fungi. E. HERRMANN (*Chem. Zeit.*, 1913, **37**, 206).—Oxalic, fumaric, and malic acids are widely distributed in fungi, and usually occur as calcium salts. Oxalic acid, supposed to be derived by oxidation of carbohydrate, is the commonest. Malic acid is sometimes found as potassium salt. Fatty acids also occur in fungi, particularly palmitic acid. Formic, acetic, and butyric acids are characteristic of individual species. Ergotic and sclerotic acids are characteristic of ergot. Telephoric acid, present in the cuticle of some fungi, is a pigment. E. F. A.

Composition of Some Fungi, and the Products of Their Autolysis. ERNST WINTERSTEIN, C. REUTER, and R. KOROLEV (*Landw. Versuchs-Stat.*, 1913, **79–80**, 541—562).—The fat of *Boletus edulis* contains 0·52% of a cholesterol, m. p. 160°; $[\alpha]_D$ −133° in 5% chloroform solution. The following substances were obtained from the fungus: inactive alanine, valine, phenylalanine, small amounts of amino-acids and trimethylamine, guanine, adenine, hypoxanthine, trimethylhistidine, and tetramethylenediamine.

In the autolysis of *Boletus*, 80—90% of the total dry matter becomes soluble; the insoluble portion contains little nitrogen. The solution contained small amounts of guanine, some hypoxanthine, but no adenine or histidine. Trimethylhistidine, much tetramethylenediamine and *iso*amylamine, and a great deal of ammonia were found.

Agaricus campestris, *Cantharellus cibarius*, and *Craterellus cornucopioides* were also subjected to autolysis.

The results show that the proteins of fungi are to a great extent decomposed into their simple crystalline cleavage products, and probably peptones and polypeptides as well. It is probable that autolytic processes occur in the symbiosis of root-nodules (compare Shibata, *Jahrb. wiss. Bot*, **37**, 643). N. H. J. M.

The Presence of Gentiopicrin, Gentianose, and Sucrose in the Fresh Roots of Gentiana punctata. MARC BRIDEL (*Compt. rend.*, 1913, **156**, 627—629; *J. Pharm Chim.*, 1913, [vii], **7**, 289—292. Compare this vol., i, 149).—The author has isolated in a pure, crystalline state, and characterised, gentiopicrin, gentianose, and sucrose from the fresh roots of *Gentiana punctata*, and has also obtained evidence of the presence of a supposed new sugar. W. G.

Formation of Acetaldehyde during the Anaërobic Respiration of Poplar Blossom. S. KOSTYTSCHEV, ELISE HÜBBENET, and A. SCHELOUMOV (*Zeitsch. physiol. Chem.*, 1913, **83**, 105—111. Compare Palladin and Kostytschev, A., 1906, ii, 696).—Considerable quantities of freshly gathered poplar blossoms were kept in a stream of hydrogen, and the carbon dioxide, alcohol, and other volatile products formed were measured. The ratio of CO_2 : C_2H_6O during respiration varied from 100 : 35 to 100 : 55, and differed from that obtained in alcoholic fermentation. In addition, acetaldehyde is formed. The amount of sugar in the fresh flowers is not large, and it is almost entirely used up during the experiment. The excess of carbon dioxide formed over that produced during alcoholic fermentation is attributed to the decomposition of other substances. The formation of acetaldehyde is considered to be due to the oxidation of active hydrogen attached to reductase and consequent partial retardation of the reduction of acetaldehyde to alcohol (compare this vol., i, 323). E. F. A.

A New Rhubarb from Altai. ALEXANDER TSCHIRCH and M. RUSZKOVSKI (*Arch. Pharm.*, 1913, **251**, 121—136. Compare A., 1905, ii, 851; 1907, ii, 501; and Tutin and Clewer, T., 1911, **99**, 946).—A proximate analysis of roots from an unidentified species of rheum collected at Altai shows that it belongs to the "rhaponticum" group. The constituents observed are rhaponticin, chrysophanol, emodin methyl ether, emodin, dextrose, tannoglucosides, and anthraglucosides; the last two groups of substances yield respectively rheum-red and rheonigrin on hydrolysis by acids. Rhein is absent. T. A. H.

The Oil Seed of Ximenia Americana, L. F. SCHRÖDER (*Arb. Kais. Gesund.* 1912, **43**, 454—474).—An account of the constituents is given. The seeds consist of 32·3% shell, and 67·6% kernel; the latter contains 2·99% moisture, 66·0% fat, 15·2% proteins, 3·0% crude fibre, 2·19% ash, and 10·46% nitrogen free extract. No saponin, alkaloid, or cyanogenetic glucoside was found. The kernels also contain about 1% of a caoutchouc-like substance, which yields a tetrabromide. The oil varies a little in physical properties depending on the method of preparation; it is yellow, semi-solid, possesses a sharp after-taste, and has the following constants: D^{15} 0·9205 to 0·9220; saponification number, 173·2 to 177·0; iodine number, 80·3 to 85·05; Hehner number, 93·9 to 94·8; Reichert Meissl number, 1·61 to 2·45; Polenske number, 0·12 to 0·21; unsaponifiable matter, 0·46 to 0·55%. The viscosity in Engler degrees varied from 19·2 to 37·1 at 25°, and from 6·6 to 11·3 at 50°, the

highest value in each case being for oil extracted by ether, and the lowest for oil extracted by acetone. The total fatty acids included 75% of liquid fatty acids, and 10% of arachidic acid.

The shell contained 1·07% moisture, 5·9% fat, 9·05% proteins, 24·83% crude fibre, 12·78% ash, and 46·32% nitrogen-free extract.

T. A. H.

Biochemistry of Sea Weeds. HARALD KYLIN (*Zeitsch. physiol. Chem.*, 1913, **83**, 171—197).—Fucosan, the constituent of the bladders of the *Fucoideæ* which is coloured red by vanillin and hydrochloric acid, has strong reducing properties; it is precipitated by lead acetate and in acid solution by gelatin solutions. Its solutions have an adstringent taste resembling tannin. On oxidation, phycophæin is obtained. No sugar is eliminated on boiling fucosan with dilute sulphuric acid.

Mannitol has been found in several *Fucus* and *Laminaria* species The sweet-tasting, white substance, which often covers the whole thallus of *Laminaria* on drying, is mannitol.

Dextrose or lævulose were found in small quantity in four of the *Fucoideæ* investigated, but in none of the *Florideæ*. Several of the *Fucoideæ* contain also a dextrin-like polysaccharide, laminarin, which is regarded as a reserve material built up from dextrose and corresponding with starch in the higher plants.

Two species, *Ascophyllum nodosum* and *Fucus vesiculosus*, which contain fat, contained very little laminarin.

The *Florideæ* contain starch, which gives dextrose when boiled with dilute acids, and is quickly hydrolysed by malt diastase.

The seaweeds are rich in slimy cell-wall constituents. Algin and fucidin, obtained from the *Fucoideæ*, are described briefly, as well as similar products from the *Florideæ*. E. F. A.

Nutrition of Green Plants with Ammonium Salts. ENRICO PANTANELLI and G. SEVERINI (*Bied. Zentr.*, 1913, **42**, 98; from *Staz. sper. agrar. ital.*, 1911, **44**, 873).—Sand-culture experiments in which wheat and mustard were supplied with different ammonium salts under sterilised conditions. Sodium nitrate was also employed.

The greatest amounts of leaf were obtained with sodium nitrate, whilst ammonium salts produced the greatest amount of seed.

The only injurious effects were observed when ammonium chloride was employed, and in the case of mustard, with ammonium citrate. The best results with wheat were obtained with the organic ammonium salts, then the insoluble ammonium magnesium phosphate, and next with sodium nitrate. Mustard developed most quickly under the influence of sodium nitrate. N. H. J. M.

Changes of Phosphoric Acid in Plants at Different Periods of Growth and with Different Phosphorus Manures. LEOPOLD SEIDLER (*Landw. Versuchs-Stat.*, 1913, **79–80**, 563—610).—Pot experiments in which barley and oats were grown in different soils, without phosphorus and with superphosphate, bone meal, and basic slag respectively.

The result obtained by Staniszkis with millet, indicating that the nitrogen increases in the parts above ground to the end, was partly confirmed. In the roots, however, there is a diminution in the amount of nitrogen. The amount of phosphoric acid taken up is not always in proportion to the production of dry matter. Inorganic phosphates which, at first, are taken up in considerable amounts are, as vegetation proceeds, to a great extent converted into organic phosphorus compounds. In barley the organic phosphorus is chiefly in the forms of protein and lecithins, whilst in oats phytin frequently predominates. The phosphoric acid of phytin, which generally forms only a fraction of the total phosphoric acid, increases in the whole plant to the end of the vegetative period; in the roots it generally diminishes.

As regards the relation between the inorganic and organic phosphorus, the latter increases in barley, and generally in oats, as vegetation proceeds; in oats, however, the amount of organic phosphorus generally remains less than the inorganic phosphorus.

N. H. J. M.

The Significance of the Lime-Magnesia Ratio in Soil Analyses. P. L. Gile and C. N. Ageton (*J. Ind. Eng. Chem.*, 1913, **5**, 33—35).—Loew has put forward the hypothesis that plants make their maximum growth, other factors being favourable, only when the available lime and magnesia are present in a ratio which may vary from 1 : 1 to 4 : 1. The authors have made observations on Porto Rican soils, and obtained very conflicting results, finding that soils with lime-magnesia ratios varying from 30 : 1 to 500 : 1 are productive pineapple soils; that one soil with the ratio 25 : 1 is an exceptionally productive soil for citrus fruits and pineapples; that another soil, where the ratio varies from 22 : 1 to 1461 : 1 is an exceptionally productive soil for sugar cane.

It may be that the apparently confirmatory results arrived at by some investigators are to be attributed rather to alterations in the soil reaction than to the lime-magnesia ratio. It would appear that in analyses of ordinary soils the above ratio is of no significance, but in analyses of the soluble salts of alkali soils the ratio may be exceedingly important. T. S. P.

Weathering of Soil. G. H. Leopold (*Chem. Weekblad*, 1913, **10**, 70—86).—An investigation of the conditions affecting the formation of various types of soil by weathering, based on a large number of analyses of dark grey and red loams. A. J. W.

Two Volcanogenic Loams from Japan. Toyotaro Seki (*Landw. Versuchs-Stat.*, 1913, **79–80**, 871—890).—Analyses of two loams from Tokio and from North-East Japan. The soils possess only a slight plasticity when kneaded with water, and are friable when dry. The soils do not contain zeolites, and their deficient plasticity is attributed to the absence of aluminium hydroxides and to the presence of allophanoids. N. H. J. M.

Organic Chemistry.

Some Data of the Solubility of Metallic Copper in the Different Fractions Obtained by the Distillation of Crude Petroleum. CONSTANTIN I. ISTRATI and C. TEODORESCU (*Bull. Acad. Sci. Roumaine*, 1912/3, **1**, 19—25).—The requisite petroleum was obtained by fractionating crude petroleum taken from the Moreni reservoir. Eight fractions were collected, the extreme values of the b. p. being 100° and 300° respectively, each fraction having a range of b. p. of 25°. The separate fractions were placed in sunlight after addition of an excess of purely divided metallic copper. In general, the amount of copper salt formed increased with increasing b. p. of the fraction, the values observed varying from 0·022 gram per 100 c.c. for fraction b. p. 100—125° to 3·499 grams per 100 c.c. for fraction b. p. 275—300°. A notable exception to this regularity occurs with the portion of b. p. 250—275°, which dissolves less copper than either the preceding or succeeding fraction. Determination of the acidity of these fractions, whether by extraction with alcohol or by direct estimation with alcoholic potassium hydroxide, shows that this factor increases regularly with increasing b. p. of the fractions. The authors are led to the conclusion that this apparent anomaly is due to the presence of a larger proportion of lactones in the fraction b. p. 250—275°, which, although capable of neutralising alkali, are unable to attack metallic copper. This view is confirmed by the fact that a greater quantity of lactones can be extracted by means of alcohol from the fraction b. p. 250—275°, which has been treated with metallic copper, than from a similarly treated fraction, b. p. 225—250°. H. W

The Composition of Illuminating Gas. PAUL LEBEAU and A. DAMIENS (*Compt. rend.*, 1913, **156**, 797—799).—Combining the ordinary methods of gas analysis with their own methods for analysing mixtures of gaseous hydrocarbons (this vol., ii, 253), the authors have made very complete analyses of three different samples of illuminating gas, and their results, which are tabulated, establish the presence of higher homologues of methane. Their values for carbon monoxide are somewhat lower than the generally accepted figure for that constituent. W. G.

Mechanism of the Transformation of Stereoisomeric Ethylene Compounds. RICHARD STOERMER (*Chem. Zentr.*, 1913, i, 693—694; from *Sitzungsber. Abh. Naturforsch. Ges. Rostock*, 1912, **4**, 35—43).—The transformation of stable ethylene compounds into labile stereoisomerides by means of ultraviolet light (A., 1911, i, 295) cannot be explained by the theories of Wislicenus, Nef, or Aschan. Only Werner's conception of the carbon atom offers any assistance, and this has now been developed so as to include *cis-trans*-isomerism in ring compounds. J. C. W.

Elimination of Water from Pinacolyl Alcohol and on Tertiary Butylethylene. W. FOMIN and N. SOCHANSKI (*Ber.*, 1913, **46**, 1219. Compare this vol., i, 331).—The hexylene which Delacre obtained by the action of sodium on the chloride, $CMe_3\cdot CCl:CH_2$ (A., 1906, i, 476), was also *tert.*-butylethylene ($\gamma\gamma$-dimethyl-Δ^{α}-butylene). The hydrocarbon, "pseudo-butylethylene," b. p. 56—58°, which accompanied the $\beta\gamma$-dimethyl-Δ^{β}-butylene (Couturier, A., 1893, i, 244) had in the meantime been identified as $\beta\gamma$-dimethyl-Δ^{α}-butylene. J. C. W.

Preparation of $\beta\gamma$-Dimethyl-$\Delta^{\alpha\gamma}$-butadiene. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 256717).—It is found that the yield of $\beta\gamma$-dimethyl-$\Delta^{\alpha\gamma}$-butadiene obtained from pinacone or pinacolin (A., 1911, i, 829) can be increased to 80% if the operation is carried out at 450° and under reduced pressure. F. M. G. M.

Preparation of Diolefines. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 255519).—When monohalogenated olefines, dihalogenated paraffins or halogenated alcohols are heated at 300—500° at ordinary or reduced pressures with catalytic agents, such as barium chloride, nickel chloride, lead chloride or aluminium hydroxide, they furnish satisfactory yields of the corresponding diolefines, and the preparation of isoprene by this method from the following substances is now recorded.

From (1) $\beta\gamma$-dibromo*iso*pentane, $CMe_2Br\cdot CHBrMe$, (2) $\beta\gamma$-dichloro*iso*pentane, (3) $\alpha\gamma$-dibromo*iso*pentane, $CMe_2Br\cdot CH_2\cdot CH_2Br$, (4) $\alpha\beta$-dibromo*iso*pentane, $CHMe_2\cdot CHBr\cdot CH_2Br$, (5) γ-bromo-β-methyl-Δ^{β}-butylene, $CMe_2:CMeBr$, (6) β-chloro-β-methylbutan-γ-ol, $CMe_2Cl\cdot CHMe\cdot OH$, (7) from the acetate of γ-bromo-β-methylbutan-α-ol,

$$OAc\cdot CH_2\cdot CHMe\cdot CHBrMe,$$

whilst $\beta\gamma$-dibromobutane, $CHMeBr\cdot CHBrMe$, furnishes divinyl, hexylene dibromide gives rise to hexadiene, b. p. 68—77°, and dichloro-*n*-pentane yields $\Delta^{\alpha\gamma}$-pentadiene, b. p. 38—45°. F. M. G. M.

The Action of Monosodioacetylene on the Alkyl Iodides. Preparation of True Acetylenic Hydrocarbons. PAUL LEBEAU and MARIUS PICON (*Compt. rend.*, 1913, **156**, 1077—1079).—Monosodioacetylene, prepared by the action of acetylene on sodium dissolved in liquid ammonia, when dissolved in the same solvent readily reacts with the alkyl iodides, giving the corresponding acetylene hydrocarbons, in nearly theoretical yield. The ammonia is removed by absorption with water, the last traces being eliminated by dilute sulphuric acid. By this method the authors have prepared allylene and hexinene.
W. G.

Preparation of Primary Alcohols by Reduction of the Esters with Absolute Alcohol and Sodium-ammonia. E. CHABLAY (*Compt. rend.*, 1913, **156**, 1020—1022).—Sodium in liquid ammonia reacts with esters of monobasic acids according to the equation: $3R\cdot CO_2R' + 4NH_3Na = 2R\cdot CONH_2 + R\cdot CH_2\cdot ONa + 3R'\cdot ONa + 2NH_3$ (compare A., 1912, i, 244). Coupling this with the action of absolute alcohol on the sodium, giving nascent hydrogen, the

amide in its turn is converted into the corresponding primary alcohol, the whole of the acid being thus reduced to primary alcohol: $2R\cdot CO\cdot NH_2 + 4H_2 = 2R\cdot CH_2\cdot OH + 2NH_3$.

The ester dissolved in absolute alcohol is poured on to the solution of sodium in ammonia at $-80°$. When the action is complete, the residue is decomposed by water, distilled in steam, and the mixture of alcohols separated by fractionation. The corresponding alcohols have thus been prepared from the esters of a number of the higher fatty acids. The esters of dibasic acids are similarly reduced, giving dihydroxy-alcohols; methyl sebacate gives decane-$\alpha\kappa$-diol, m. p. 71·5°. Ethyl phenylacetate gives phenylethyl alcohol, whilst methyl cinnamate gives, not cinnamyl alcohol, but the saturated phenylpropyl alcohol. W. G.

New Methods of Spirit Rectification. HUGO MASING (*Chem. Zeit.*, 1913, **37**, 329—330).—It has hitherto been usual to dilute the raw spirit with water before submitting it to the process of rectification. It has been found in Russia, however, that better results are obtained when the undiluted spirit is used. In order to find out the reason, the author has constructed a special still-head, a modification of the Le Bel and Henninger form, in which there are taps to the side-tubes so that the liquid flowing from any one of the bulbs can be collected for analysis.

The results show that the strength of the spirit collecting in the bulbs increases more slowly than according to Gröhning's tables (compare A., 1908, i, 751), the slowest rate of increase being with the very dilute spirit. The Russian method of rectification is therefore justified. T. S. P.

$\beta\gamma$-Dimethylbutan-α-ol. ALEXANDER I. GORSKI (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 167—169).—*Ethyl $\alpha\beta$-dimethylbutyrate*, $C_8H_{16}O_2$, has b. p. 148—150°/745 mm., $D_4^{17.5}$ 0·8719, $D_4^{25.3}$ 0·8647, n_D^{18} 1·4048.

$\beta\gamma$-Dimethylbutan-α-ol, $C_6H_{14}O$, obtained by reducing the above ester by means of sodium in alcoholic solution, is a viscous liquid, b. p. 144—145°/761 mm., $D_4^{20.5}$ 0·8297, $n_D^{20.5}$ 1·4195, and forms a *urethane*, $C_{13}H_{19}O_2N$, m. p. 28—29°. T. H. P.

New Data Concerning the Oxide of Pentamethylene Glycol. NICOLAI J. DEMJANOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 169—173).—Since the action of nitric acid on pentamethylenediamine gives, in addition to pentamethylene glycol, a small proportion of an isomeric glycol, it is probable that the oxide obtained by the author (A., 1892, 1292) by heating pentamethylenediamine nitrite and by the action of sulphuric acid on the glycol prepared from pentamethylenediamine, and also that obtained by Hochstetter (A., 1903, i, 305) by the action of water on the bromide corresponding with the glycol from pentamethylenediamine, are not chemical individuals. Further, it is possible that the action of sulphuric acid on pure pentamethylene glycol may be accompanied by isomeric change, with formation of the oxide, $O{<}\begin{matrix}CHMe\cdot CH_2\\ CH_2—CH_2\end{matrix}$.

The author has therefore prepared the pure oxide by heating pentamethylene bromide in a sealed tube. This oxide, $C_5H_{10}O$, is a liquid, b. p. 86·5—87·5°/743 mm., $D_0^{18·5}$ 0·883, D_0^0 0·900, $n_D^{18·5}$ 1·4195, and on oxidation with nitric acid yields mainly succinic acid, its structure being thus confirmed. These properties agree closely with those given by Harries (A., 1911, i, 798) for his 3-methyltetrahydrofuran, and it may be that in the formation of this compound by the reduction of ethyl pyrotartrate, isomeric change occurs. T. H. P.

Development of Heat on Mixing Ether and Chloroform. (Mme.) MARCELET and H. MARCELET (*Chem. Zentr.*, 1913, i, 229; from *Bull. Sci. Pharmacol.*, 1912, **19**, 676—677).—Heat is developed when ether and chloroform are mixed, the maximum effect resulting from equal volumes; 25 c.c. of each liquid give a rise in temperature from 16·6° to 30·3°. J. C. W.

The Constitution of Sulphurous Acid. WILHELM STRECKER (*Verh. Ges. deut. Naturforsch. Aerzte*, 1913, 126).—In continuation of previous investigations (A., 1910, i, 532), the sulphoxides have been prepared from symmetrical diethyl sulphite, and investigated optically. No details are given, but the conclusion arrived at from the optical results is, that there is no change in valency of the sulphur when a sulphoxide is oxidised into the sulphone; this is not in accordance with the chemical behaviour of these compounds. T. S. P.

Decomposition of Formates. WILLIAM ŒCHSNER DE CONINCK and ALBERT RAYNAUD (*Rev. Gen. Chim. pure appl.*, 1912, **15**, 455—456).—When sodium formate is heated, a complex mixture of substances is evolved containing aqueous vapour, aldehydes (among which acraldehyde has been identified, A., 1912, i, 527), oily substances, formic acid, and small quantities of carbon dioxide. The residue contains sodium carbonate, sodium hydroxide, and carbon.

Sodium, calcium, barium, potassium, and lead formates are decomposed to a greater or less extent when treated with pure methyl alcohol at its b. p. Formic acid was detected by distilling a portion of the alcohol and testing with silver nitrate solution after addition of water. When ethyl alcohol is substituted for methyl alcohol, very little decomposition is observed in the cases of sodium and calcium formates, whilst barium, potassium, and lead formates are rather more sensitive to the decomposing action of this reagent.

Solutions of lead formate, when exposed to diffused light during four months, are partly decomposed with the liberation of formic acid. Under similar conditions, uranium formate is completely decomposed in methyl-alcoholic solution within three months (compare this vol., i, 333). H. W.

Catalytic Esterification in Dilute Solutions: Preparation of Ethyl Acetate. FERNAND BODROUX (*Compt. rend.*, 1913, **156**, 1079—1081. Compare Senderens and Aboulenc, A., 1911, i, 600, 637; ii, 1080; 1912, i, 694).—By distilling mixtures of ethyl alcohol and acetic acid diluted with water containing varying quantities of sulphuric

acid, ethyl acetate is obtained, the yield of the ester from given quantities of alcohol and acid varying with the amount of sulphuric acid in the water. With 10% sulphuric acid, a yield of 92% of ethyl acetate is obtained. The sulphuric acid can be replaced by numerous other acids as catalysts, but they are less effective. W. G.

The Hydrolysis of Fats. JULIUS MARCUSSON (*Zeitsch. angew. Chem.*, 1913, **26**, 173—176).—It is now generally accepted that the hydrolysis of fats in a homogeneous system takes place in steps with intermediate formation of diglycerides and monoglycerides (Fortini, A., 1912, i, 826; Grün and Corelli, A., 1912, i, 409; Fanto and Stritar, A., 1908, i, 499, and others). The present state of knowledge of the process of hydrolysis in a heterogeneous system, for example, by alkali, is not so satisfactory (compare Marcusson, A., 1906, i, 924; 1907, i, 674). Kellner (A., 1909, i, 357, 548, 759) obtained indications of a graded hydrolysis by superheated steam, but unfortunately used natural palm-kernel oil, which, as a mixture of triglycerides, might give misleading results. The author has investigated the hydrolysis of simple triglycerides, such as tribenzoin, tristearin, and tripalmitin, by heating with water in an autoclave; after this treatment the triglyceride had a m. p. several degrees lower, and in the case of the two latter fats, treatment with acetic anhydride (during which "acetolysis" did not occur; Willstätter and Madinaveitia, A., 1912, ii, 1104) gave a product which showed a considerably higher saponification number than the original triglyceride. Palm-kernel oil exhibited similar behaviour. From these results it appears that the hydrolysis of fats by water, and therefore presumably also by acids and enzymes, is a bimolecular process.

The author favours the view that the exceptional behaviour of alkali, which appears to hydrolyse directly to glycerol, is due to hydrolysis occurring mainly at the contact surface of fat and aqueous liquid; on account of the slow rate of diffusion of the intermediate diglycerides and monoglycerides, and the relatively great rapidity of their hydrolysis, no appreciable quantity of these substances can escape into the main body of fat again. In the above autoclave experiments, however, the elevated temperature increases the velocity of diffusion of the substances, whilst the hydrolysis is relatively much slower, so that the escape of the intermediate products from immediate further hydrolysis is facilitated. D. F. T.

Glycerides of Fats and Oils. IV. The Mixed Glycerides of Palmitic and Stearic Acids Obtained from Lard. ALOIS BÖMER (*Zeitsch. Nahr. Genussm.*, 1913, **25**, 321—353. Compare A., 1912, i, 600).—By repeated fractionation from ether, pure glycerides of saturated fatty acids were isolated from lard; the least soluble glyceride so obtained was found to be a palmityldistearin, and not heptadecyldistearin as stated by Kreis and Hafner. Tristearin is not present in lard. The palmityldistearin separated from lard had m. p. 68·5° (corr.), and differed in this respect and also in its crystalline form from the similar glyceride separated from mutton fat; the former is probably α-palmityldistearin, whilst that from mutton fat is β-palmityl-

distearin. The lard under examination contained about 3% of α-palmityldistearin, and about 2% of another saturated glyceride, namely, stearyldipalmitin, m. p. 58·2° (corr.). W. P. S.

Glycerides of Fats and Oils. V. Nomenclature of Mixed Glycerides and the Synthesis of α-Distearin and β-Palmityldistearin. ALOIS BÖMER and R. LIMPRICH (*Zeitsch. Nahr. Genussm.*, 1913, **25**, 354—366).—It is suggested that, in the case of mixed glycerides, where different fatty acid radicles are combined with the same glycerol molecule, the position of the fatty acid radicles should be denoted by the letters α, β, and γ respectively. In the preparation of α-distearin from α-dichlorohydrin and potassium stearate (compare A., 1903, i, 788) considerable quantities of tristearin are also formed; again, tristearin and possibly stearyldipalmitin are produced together with β-palmityldistearin when the latter is prepared from α-distearin and palmitic acid. α-Distearin has m. p. 78·5° (corr.), and β-palmityldistearin has m. p. about 63°, and is identical with the palmityldistearin separated from mutton fat. W. P. S.

China Oil. SERGEI A. FOKIN (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 283—285).—The polymerisation of this oil when heated, the increased refraction, and the transformation of the elæomargaric acid under the influence of light into a product with a higher melting point are explainable on the assumption that the acid contains either conjugated double linkings or, as in allene, a carbon atom with two double linkings. The products obtained when the acid is oxidised with alkaline permanganate solution indicate its structure to be:

$$CH_3\cdot[CH_2]_3\cdot CH\colon CH\cdot CH\colon CH\cdot[CH_2]_9\cdot CO_2H.$$ T. H. P.

Behaviour of Certain Unsaturated Acids Towards Selenious Acids. SERGEI A. FOKIN (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 285—286).—Various unsaturated aliphatic acids and, more especially, the oils containing them as glycerides, undergo marked changes when heated with concentrated solutions of selenious acid at 100° under the ordinary pressure. This action is most characteristic in the case of castor oil. After one to three hours' heating, the oil becomes converted into a caoutchouc-like mass of a faint red colour. This product is insoluble in alcohol, ether, benzene, pyridine, etc., but it dissolves with decomposition in boiling acetic acid, and is saponified and darkened by alcoholic potassium hydroxide. When treated with alcohol or ether, it swells to a jelly, which can be readily pounded to a paste and, after evaporation of the alcohol or ether in the cold, reduced to powder. After being washed to remove any excess of selenious acid or castor oil, the powder has the iodine number 59·0 and the saponification number 168·5, the corresponding numbers for castor oil being 86 and 180 respectively. The substance contains selenium, and the presence of double linkings and the small difference between its saponification number and that of the original oil indicate it to be different from the "factis" obtained by the action of sulphur di- or tetra-chloride on linseed and other oils. T. H. P.

Formation, Decomposition, and Transformation of Glycollic Acid. EMIL BAUR (*Ber.*, 1913, **46**, 852—863).—It is found that the reduction of oxalic acid to glycollic acid which can be effected by electrolytic reduction with lead, or less well with platinum, cathodes (A., 1908, i, 600), also occurs to some extent when a solution of oxalic acid with formic acid is submitted to the action of finely divided rhodium (Schade, A., 1908, i, 136; Blackadder, this vol., ii, 36) or of platinised platinum foil. The metal causes the decomposition of the formic acid into hydrogen and carbon dioxide, the former of which effects a reduction of the oxalic acid through glyoxylic acid to glycollic acid. Small quantities of the two last substances can be detected in the final mixture.

In the presence of coloured metallic salts, glycollic acid is affected by exposure to the light of a quartz mercury lamp, being partly converted into formaldehyde and formic acid. The following salts, copper sulphate, uranic and uranous sulphates, and ferric sulphate all exerted this effect, but the first-named was least active and the last-named most.

When tubes of quartz glass containing an aqueous solution of calcium glycollate or of a mixture of calcium glycollate and calcium malate are submitted to the light of a quartz-mercury lamp for one hundred and forty hours, a certain amount of calcium citrate is formed (compare Ciamician and Silber, A., 1911, i, 513, 650); the same condensation to citric acid occurs when saturated solutions of calcium glycollate or calcium malate, mixed with one and a-half times their bulk of saturated lime-water, are kept for a few days. Although it was not possible to prove the presence of a malate in the solution of calcium glycollate after exposure to light, the accidental growth of a mould in a solution of calcium glycollate caused the formation of minute crystals of calcium malate.

In connexion with his view that oxalic acid is the first product of assimilation of carbon dioxide in plants (A., 1908, ii, 780), the author draws attention to the manner in which the above results render oxalic acid a possible origin of the common vegetable acids; further, by its scission into formaldehyde and formic acid, glycollic acid may possibly be the source of the sugars. D. F. T.

Method of Preparing Ethyl γ-Chloroacetoacetate. DIMITRI K. ALEXANDROV (*Ber.*, 1913, **46**, 1021—1024).—By the interaction of magnesium powder with ethyl α-chloroacetate, a condensation product of two molecules, $CH_2Cl\cdot C(OEt)(O\cdot MgCl)\cdot CH_2\cdot CO_2Et$, is formed, which is decomposed by water into ethyl γ-chloroacetoacetate. This is a colourless oil, b. p. 107°/14 mm., giving a red coloration with ferric chloride, D_4^{20} 1·2157, n_D^{17} 1·4546. The copper salt crystallises in thin, matted, pale green needles, m. p. 168—169° (decomp.). E. F. A.

Action of Oxalyl Chloride on Several Organic Derivatives. HERMAN J. TAVERNE (*Chem. Weekblad*, 1913, **10**, 214—223. Compare Graebe and Liebermann, *Ber.*, 1869, **2**, 678; Staudinger, A., 1908, i, 938; 1909, i, 796, 905; 1912, i, 567; Jones and Tasker, T., 1909, **95**, 1904; Liebermann and Zsuffa, A., 1911, i, 202;

Liebermann, A., 1911, i, 656; 1912, i, 464; Bornwater, A., 1911, i, 616).—A summary of work on the reactions of oxalyl chloride previously published. A. J. W.

Solubility of Thorium Oxalate. A. COLANI (*Compt. rend.*, 1913, **156**, 1075—1076. Compare Wirth and Hauser, A, 1912, i, 827).—A study of the solubility of thorium oxalate, alone or in the presence of oxalic acid, in hydrochloric acid at 17° and 50°. For varying concentrations of hydrochloric acid, the amount of oxalate dissolved is independent of the amount in contact with the liquid. With moderately strong acid, the oxalate is converted into chloro-oxalate with the elimination of oxalic acid, which consequently diminishes the solubility of the chloro-oxalate. The solubility of the thorium oxalate in hydrochloric acid is greatly diminished by the presence of small amounts of oxalic acid. W. G.

Preparation and Properties of the Ammonium Salts of Some Organic Acids. LEROY MCMASTER (*Amer. Chem. J.*, 1913, **49**, 294—301).—Keiser and McMaster (this vol., i, 248) have described a method for the preparation of normal ammonium salts of dibasic organic acids. In continuation of this work, ammonium *malonate*, succinate, *malate*, *tartrate*, phthalate, and iso*phthalate* have been prepared. The method has also been used for obtaining the salts of certain monobasic acids, and ammonium *propionate*, iso*butyrate*, *palmitate*, *benzoate*, and *cinnamate* are described. E. G.

Crystalline Form and Optical Properties of Magnesium Malate. O. I. MOROSCHKINA (*Bull. Acad. Sci. St. Pétersbourg*, 1913, 225—230).—Magnesium malate, $MgC_4H_4O_5.5H_2O$, crystallises in hemihedral forms of the rhombic system: $a:b:c=0{\cdot}7476:1:0{\cdot}4096$ (compare Traube, A., 1899, i, 484). The etched figures and optical properties are described. T. H. P.

Tetrolaldehyde (Δ^{α}-Butinal) and Some of Its Derivatives. PAUL L. VIGUIER (*Ann. Chim. Phys.*, 1913, [viii], **28**, 433—536).—A résumé of the work accomplished, and already abstracted, on this subject since 1908. T. A. H.

Catalytic Hydrogenation of Acetone. A. LASSIEUR (*Compt. rend.*, 1913, **156**, 795—797. Compare Haller and Lassieur, A., 1910, i, 355).—The hydrogenation of acetone by the method of Sabatier and Senderens at temperatures above 200° yields neither *iso*propyl alcohol nor a pinacone, but the principal product is methyl *iso*butyl ketone, together with a small quantity of valerone and some still more highly condensed products. W. G.

Migration of the Chlorine in the Halogenated Ketones. EDMOND E. BLAISE (*Compt. rend.*, 1913, **156**, 793—795. Compare this vol., i, 11).—By the chlorination of methyl ethyl ketone in the presence of water and marble a mixture of three chlorinated ketones is obtained. The smallest fraction is dichloromethyl ethyl ketone, b. p. 31°/

33—34 mm. The second and largest fraction is chloromethyl α-chloroethyl ketone, b. p. 165° (compare Vladesco, A., 1892, 424). The third constituent is methyl α-dichloroethyl ketone (compare Favorski and Desbout, A., 1895, 497). On heating dichloromethyl ethyl ketone with a mixture of hydrochloric and acetic acids on a water-bath for six hours, 50% of it is converted into chloromethyl α-chloroethyl ketone, one of the chlorine atoms having migrated. Increase in the amount of hydrochloric acid in the mixture facilitates the migration. W. G.

Reduction of Acetobromoglucose and Similar Substances. EMIL FISCHER and KARL ZACH (*Sitzungsber. K. Akad. Wiss. Berlin.* 1913, 311—317).—On reduction of acetobromoglucose by means of zinc dust and acetic acid at the ordinary temperature, a crystalline compound, $C_{12}H_{16}O_7$, is obtained, together with a molecule of acetic acid. The new compound, *acetoglucal*, takes up two atoms of bromine. On hydrolysis three molecules of acetic acid are eliminated, and *glucal*, $C_6H_8O_3$, a soluble viscid syrup, b. p. 170—185°/0·2 mm. pressure, is obtained. This behaves as an aldehyde, and forms oily hydrazones, but no osazones. It decolorises bromine in aqueous solution, and is decomposed by acids, giving an intense green pine-splinter reaction when heated with hydrochloric acid.

Provisionally the formula $\begin{matrix} CH\cdot CH(CH_2\cdot OH) \\ \| \\ CH\text{———}CH(CHO) \end{matrix}\!\!>\!O$ is suggested.

Acetobromogalactose and acetobromolactose behave similarly when reduced, but only oily products were obtained.

Acetoglucal has m. p. 54—55°, $[\alpha]_D^{20} - 13{\cdot}02°$. E. F. A.

Phytin. R. H. ADERS PLIMMER and HAROLD J. PAGE (*Biochem. J.*, 1913, **7**, 157—174).—Inorganic phosphates in phytin can be estimated by precipitation with ammonium molybdate in semi-normal nitric acid at room temperature. The calcium can be estimated by precipitation as calcium sulphate, but not as oxalate. The magnesium can then be estimated as pyrophosphate. There is great difficulty in removing the calcium from phytin in the preparation of phytic acid. The yield of inositol on hydrolysis of the latter is not quantitative; there is possibly another organic constituent in phytin. W. D. H.

Transformation of *l*-Arabinose into *l*-Ribose. WILLIAM ALBERDA VAN EKENSTEIN and JAN J. BLANKSMA (*Chem. Weekblad*, 1913, **10**, 213—214).—Heating with dilute aqueous sodium hydroxide partly converts *l*-arabinose into *l*-ribose, the presence of the latter in the mixture being proved by oxidising the two pentoses to arabonic acid and ribonic acid, converting these acids into their phenylhydrazides, and separating the hydrazides by fractional crystallisation.

A. J. W.

Action of Hydrogen Peroxide and Ferric Chloride on Starch. O. DURIEUX (*Bull. Soc. chim. Belg.*, 1913, **27**, 90—97. Compare Neuberg and Miura, A., 1911, i, 935; Gerber, A., 1912, i, 538).—Hydrogen peroxide solution does not hydrolyse soluble starch prepared by Fernbach's method at the ordinary temperature, and the

same is true of colloidal solutions of iron or of mixtures of these two products. Similarly, a solution of ferric chloride does not hydrolyse starch, but when used along with hydrogen peroxide it causes hydrolysis at an appreciable rate, which increases with the quantity of ferric chloride employed. The results of experiments designed to test the influence of various factors on the reaction show that the quantity of reducing substances formed depends on the quantity of peroxide used, and that the acidity of the mixture increases with the quantity of reducing substances formed. The hydrogen peroxide is decomposed, but no oxygen is evolved unless the peroxide is present in excess. The iron remains in the ferric state until hydrolysis is complete, when it suffers reduction, the reducing substances disappearing at the same time. Measurements of the rate of hydrolysis show that the reaction does not follow the logarithmic law for a unimolecular reaction. Hydrogen peroxide reduces the rate of hydrolysis of starch by diastase and does not undergo decomposition itself. T. A. H.

Starch of Glutinous Rice and Its Hydrolysis by Diastase. YOSHIO TANAKA (*J. Ind. Eng. Chem.*, 1912, **4**, 578—581).—The starch of glutinous rice is characterised by giving a red coloration with iodine; the microscopic characteristics of these starch granules and the hydrolysed products do not apparently differ in any way from those of common rice starch. The starch of glutinous rice does not contain amylodextrin, erythrodextrin, or the special proteins which have previously been considered to be the cause of the red iodine coloration; nor does it contain any of the common starch, which gives a blue colour with iodine.

Glutinous rice starch is, moreover, rapidly hydrolysed by diastase to dextrin with the production of a less amount of maltose than in the case of equal quantities of potato or common rice starch; the author considers that glutinous rice starch contains a larger amount of amylopectin, or some analogous constituent which produces a dextrin that hydrolyses more slowly with diastase than does that from ordinary starch.

It is probable that there are many other cereals in Nature containing a similar variety of starch, its presence having been noted in glutinous millet, glutinous *Panicum miliaceum*, L., and in *Andropogon Sorghum*. The separation of glutinous from common rice starch is comparatively simple, as the former is opaque, the latter translucent.

F. M. G. M.

The Acetolysis of Cellulose to Dextrose Acetate. HERMANN OST (*Verh. Ges. deut. Naturforsch. Aerzte.*, 1913, 124—125).—The end-product of the acetylation of cellulose is cellobiose octa-acetate (compare A., 1912, i, 680), which is readily obtained in a pure crystalline condition when a mixture of 5 grams of cellulose with 25 c.c. of acetic anhydride and 2·5 grams of concentrated sulphuric acid is kept at the room temperature for some days, or even weeks; the yield is 33%. The reaction proceeds farther on warming. For example, a mixture of 5 grams of cellulose, 25 c.c. of acetic anhydride, 25 c.c. of glacial acetic acid, and 5 grams of concentrated sulphuric acid when heated

for three days at 45° no longer gives cellobiose octa-acetate; by extraction with ether, a syrup consisting of a mixture of dextrose penta-, tetra-, and tri-acetates is obtained, which by further acetylation can be transformed into dextrose α-penta-acetate, m. p. 112°, and a rotation of +101·7°. The same product can be obtained directly from cellobiose octa-acetate.

The results confirm the conclusion already drawn by Ost and Wilkening that the cellulose molecule is built up exclusively from dextrose residues. T. S. P.

Nitrocellulose. H. TEDESCO (*Zeitsch. ges. Schiess-Sprengstoffwesen*, 1912, 7, 474—477).—An account of numerous experiments on various methods of preparing nitrocellulose, with special regard to the varying nitrogen content and stability of the products obtained under different conditions, such as varying the relative concentrations of the acids employed, the time allowed, and the temperature at which nitration is carried out, and employing different forms of cellulose for the experiments. F. M. G. M.

Soil Humus. SHERMAN LEAVITT (*J. Ind. Eng. Chem.*, 1912, 4, 601—604).—Two methods of preparing samples of humus are fully described, and the following facts are emphasised.

(1) Two methods were employed for the removal of clay: (*a*) Mooers and Hampton's method; (*b*) mechanical separation, without evaporation to dryness.

(2) Indications were obtained of the relative behaviour of ferric iron, ferrous iron, and calcium in the retention of humus from water solution.

(3) Protein or protein-like substances were present in the humus examined.

(4) A starch-like substance was present which can be hydrolysed by acids, acted on by diastase with subsequent acid hydrolysis, and both processes gave reducing sugars in comparable amounts in all samples of humus examined.

(5) One of these reducing sugars was obtained in crystalline form, but has not yet been fully identified.

(6) Pentosans were present in appreciable amounts in all samples of humus examined.

(7) Nitrogen, present probably as an amino-acid, was found in the 1% hydrochloric acid extract in all soils examined by the official method. F. M. G. M.

Action of Hypochlorous Acid on Tertiary Amines. JAKOB MEISENHEIMER (*Ber.*, 1913, 46, 1148—1161).—Willstätter and Iglauer (A., 1900, i, 458) have shown that dialkylchloroamines are formed by the action of hypochlorous acid on tertiary amines (compare also Hantzsch and Graf, A., 1905, i, 575). The authors have applied the reaction to simple tertiary amines, and are led to the conclusion that a trialkylamine dichloride is first formed, which rapidly decomposes with elimination of hydrogen chloride according to the scheme for trimethylamine: (i) $N(CH_3)_3 + Cl_2 = N(CH_3)_3Cl_2$;

$$\text{(ii) } N(CH_3)_3Cl_2 = N(CH_3)_2(\colon CH_2)Cl + HCl.$$

Dimethylmethylene ammonium chloride becomes transformed into formaldehyde and dimethylamine hydrochloride, the latter finally reacting with excess of hypochlorite, yielding dimethylchloroamine. This explanation differs from that given by Willstätter or Hantzsch in that two molecules of hypochlorous acid are required for each molecule of amine instead of one, and thus accounts for the fact that Willstätter and Iglauer obtained the best yields of chloronortropidine only by the use of two or more molecules of hypochlorous acid. Further, it involves the formation of aldehydes instead of alcohols as secondary products, and the production of large quantities of formaldehyde or acetaldehyde during the action of sodium or calcium hypochlorite on trimethylamine or triethylamine has been experimentally proved. Such aldehydes must be directly formed, since, under the conditions employed, alcohols are not oxidised to aldehydes. The assumption of the primary addition of chlorine appears at first sight to be improbable, since free chlorine does not convert tertiary amines into dialkylchloroamines to an appreciable extent. This is explained by the fact that two molecules of a tertiary amine are converted by one molecule of chlorine into a mixture of the hydrochlorides of the tertiary and secondary amines:

$$2N(CH_3)_3 + Cl_2 + H_2O = NMe_2H_2Cl + NMe_3HCl + CH_2O,$$

and that free chlorine does not react with salts of amines in the same manner as with the free amines.

No action occurs when the hydrochlorides of trimethylamine or triethylamine are mixed with aqueous solutions of free hypochlorous acid. With the free amines, dialkylchloroamines are formed in small quantity. Good yields of the latter substances can only be obtained by employing sodium hypochlorite or, better, bleaching powder.

An aqueous solution of trimethylamine hydrochloride was added to a cooled suspension of bleaching powder in water. On distillation, a mixture of dimethylchloroamine and methyldichloroamine was obtained, the latter being derived from decomposition of the former. Formaldehyde remained chiefly in the residue, and was identified by precipitation with *p*-nitrophenylhydrazine. Good yields of chloroamine were only obtained when a large excess of bleaching powder was used. Employment of sodium hypochlorite led to similar results. The yields, however, were uniformly less, and the best experimental conditions less readily ascertained. Nitrogen, nitric acid, and tetramethylammonium chloride were not formed.

Triethylamine hydrochloride in aqueous solution was similarly converted by an aqueous suspension of bleaching powder into a mixture of diethylchloroamine and ethyldichloroamine, which possibly contained a small quantity of chloroform. A large excess of bleaching powder was necessary, since, otherwise, the yields of chloroamine became very small. On the other hand, a portion of the triethylamine became then converted into diethylamine as was shown in experiments with sodium hypochlorite.

Triethylamine hydrochloride did not react with chlorine water, which, however, was decolorised by dimethylamine hydrochloride.

The reaction between triethylamine and chlorine water has been investigated. When the former was distilled into the latter, smaller

quantities of diethylamine hydrochloride and acetaldehyde were obtained than are required by the equation:

$$2NEt_3 + Cl_2 + H_2O = NEt_3HCl + NEt_2H_2Cl + C_2H_4O.$$

The authors consider that acid is formed in by-reactions which converts the tertiary amine into the corresponding salt, which is not acted on by chlorine. In a subsequent experiment, in which the amine was added in one portion to the chlorine water, a somewhat larger amount of aldehyde was detected. H. W.

Preparation of Betaine from Molasses Residues. KARL URBAN (*Zeitsch. Zuckerind. Böhm.*, 1913, **37**, 339—341).—To obtain betaine the evaporated molasses residues are mixed with an equal volume of concentrated hydrochloric acid. After cooling, the alkali chlorides which have separated are removed by filtration, and the filtrate is evaporated in a porcelain dish. The volatile organic acids and hydrochloric acid pass away, and humus substances are precipitated. These are also filtered off, and the residue further evaporated to a thick syrup. This is dissolved in water, filtered, decolorised by means of charcoal, and concentrated, when betaine hydrochloride separates out in a nearly pure state. E. F. A.

Chemical Reactions Brought About by Sunlight. DOMENICO GANASSINI (*Chem. Zentr.*, 1913, i, 153—154; from *Giorn. Farm. Chim.*, 1912, **61**, 439—444, 481—491).—Aqueous solutions of some mono- and di-basic amino-acids have been exposed to sunlight for three or four days, then treated with an excess of magnesium oxide, and left with red litmus paper. This soon became blue, whereas solutions which had been kept in the dark were without action. It was shown that glycine, alanine, asparagine, aspartic acid, and glutamic acid gradually decomposed into the corresponding aldehyde, ammonia, and carbon dioxide. J. C. W.

Synthesis of the Natural Hydroxyproline Present in Proteins. Pyrrolidine Derivatives. IV. HERMANN LEUCHS and JOSEPH F. BREWSTER (*Ber.*, 1913, **46**, 986—1000).—The preparation of hydroxyproline has been improved by treating $\alpha\delta$-dichlorovalerolactone with ammonia instead of δ-chloro-α-bromovalerolactone.

γ-Hydroxyproline-(a)-phenylcarbimide is resolved by means of quinine. The synthetic l-γ-hydroxyproline derivative has $[\alpha]_D^{20}$ $-37{\cdot}0°$, whereas the natural product has $[\alpha]_D^{20}$ $-37{\cdot}2°$. This synthesis confirms the γ-position of the hydroxy-group and the structure assumed for the natural hydroxyproline.

The phenylcarbimide of hydroxyproline-(b) is also resolved by means of quinine, the ammonium salt having $[\alpha]_D$ $\pm 45°/d$. The active acid could not be obtained crystalline, but the corresponding hydantoins crystallise without difficulty.

To convert the γ-hydroxyproline-phenylcarbimide into the corresponding amino-acid, heating with concentrated hydrochloric acid in a sealed tube at 95° is necessary, but the product has lost its optical activity. To preserve this, the heating is carried out at 95° with aqueous ammonia, when γ-hydroxyproline and phenylcarbamide are

obtained. The synthetic *l*-hydroxyproline has $[\alpha]_D^{20}$ $-76{\cdot}3°$, whereas the only value available for the natural acid is $-81°$.

The *quinine* salt of *hydroxyproline-phenylcarbimide* crystallises in needles or thin prisms, m. p. 206—209° (decomp.), $[\alpha]_D$ $-37{\cdot}2°$.

The corresponding *hydantoin* also crystallises in needles or thin prisms, m. p. 122—123°, $[\alpha]_D^{20}$ $-50{\cdot}4°$.

l-γ-*Hydroxyproline-phenylcarbimide*-(a) has m. p. 175°.

The corresponding derivative of γ-hydroxyproline-(*b*) does not crystallise, but the *hydantoin* forms lustrous, oblique prisms, m. p. 156—158°, $[\alpha]_D^{20}$ $-55{\cdot}2°$. E. F. A.

A New Amino-acid of the Composition $C_6H_{13}O_2N$ Obtained by the Total Hydrolysis of the Proteins of the Nerve Substance. EMIL ABDERHALDEN and ARTHUR WEIL (*Zeitsch. physiol. Chem.*, 1913, **84**, 39—59. Compare A., 1912, ii, 1191).—The leucine fraction of the products of the complete hydrolysis of nerve proteins contains an amino-acid, $C_6H_{13}O_2N$, differing from either leucine,

$$CHMe_2{\cdot}CH_2{\cdot}CH(NH_2){\cdot}CO_2H,$$

or *iso*leucine, $CHMeEt{\cdot}CH(NH_2){\cdot}CO_2H$, which is regarded as *d*-α-aminohexoic acid, $CH_3{\cdot}[CH_2]_3{\cdot}CH(NH_2){\cdot}CO_2H$, and termed caprine. The existence of this isomeride in the nerve proteins was suggested by Thudichum, who did not determine its constitution. It is probable that it is present in other proteins. The ester of *d*-caprine has b. p. 91°/12 mm. d-*Caprine* itself has decomp. 285°, $[\alpha]_D^{20}+6{\cdot}53°$ in water, and $+14{\cdot}1°$ in 20% hydrochloric acid, and tastes faintly sweet. The corresponding *hydroxy-acid* crystallises in long, four-angled plates, m. p. 57°, $[\alpha]_D^{20}-4{\cdot}68°$. The same acid prepared from the synthetic amino-acid forms slender, needle-shaped prisms, m. p. 60°, $[\alpha]_D^{20}-2{\cdot}17°$, whereas the corresponding hydroxy-acid from *l*-leucine has m. p. 71°, $[\alpha]_D^{20}-16{\cdot}37°$. E. F. A.

Compounds of Guanylcarbamide and Guanylguanidine with Dextrose. LEOPOLD RADLBERGER (*Chem. Zentr.*, 1912, ii, 1963—1964; from *Österr. ung. Zeitsch. Zucker-Ind. Landw.*, 1912, **41**, 745—750).—Guanylcarbamide (dicyanodiamidine) forms a *chloride*, $C_2H_7ON_4Cl,\frac{1}{2}H_2O$, which is obtained in thin, colourless leaflets by evaporating the solution in concentrated hydrochloric acid over lime. The aqueous solution is neutral, and when rendered alkaline and boiled with a few drops of copper sulphate solution, develops a violet colour and deposits a rose-red *powder*, $C_4H_5O_2N_4Cu$, on cooling. Guanylguanidine (biguanide), may be purified by recrystallisation from alcohol (compare Bamberger and Dieckmann, A., 1892, 737). The chloride has the formula

$$C_2H_9N_5Cl_2.$$

The chlorides condense with dextrose in alcoholic solution. *Guanylcarbamide-dextrose*,

$$OH{\cdot}CH_2{\cdot}[CH{\cdot}OH]_4{\cdot}CH{:}N{\cdot}C(NH){\cdot}NH{\cdot}CO{\cdot}NH_2,HCl,$$

forms slender, microscopic needles, m. p. 107° (decomp.), $\alpha_D^{20}+0{\cdot}2°$ (2% solution in alcohol, 2-dcm. tube), which reduce Fehling's solution and respond to the above test for guanylcarbamide. *Guanylguanidine-dextrose*, $OH{\cdot}CH_2{\cdot}[CH{\cdot}OH]_4{\cdot}CH{:}N{\cdot}C(NH){\cdot}NH{\cdot}C(NH){\cdot}NH_2,2HCl$, forms small needles which sinter at 116°, have a bitter taste, reduce

Fehling's solution, and give red needles of cuprobiguanide sulphate with ammoniacal copper sulphate. A 2% alcoholic solution in a 2-dcm. tube gives $\alpha_D^{20}+0.5^\circ$. J. C. W.

Action of Sulphuric Acid on Dicyanodiamide Correction. HJALMAR LIDHOLM (*Ber.*, 1913, **46**, 1218. Compare this vol., i, 252).—The formula for dicyanodiamide was suggested by Bamberger (A., 1883, 907) and not by Pohl, and the reduction to guanidine was accomplished by Bamberger and Seeberger (A., 1893, 494).
J. C. W.

Colour Changes in Solutions of Cobaltous Thiocyanate. RAÚL WERNICKE (*Anal. Soc. Chim. Argentina*, 1913, **1**, 8—32).—Pure cobaltous thiocyanate was obtained by the action of an excess of the sulphate on alcoholic potassium thiocyanate, and repeated extraction and crystallisation of the cobalt salt by alcohol. Data of the conductivity and viscosity are given. The phenomena of colour-change are in general similar to those shown by the chloride. G. D. L.

Reduction of Sodium Nitroprusside by Hydrogen Sulphide. DOMENICO VENDITORI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 162—167. Compare A., 1906, i, 486).—The reduction was effected by the action of an excess of hydrogen sulphide on a 10% solution of sodium nitroprusside kept on a water-bath for five or six hours. Hydrogen cyanide is evolved, and ultimately there results a solution (of nitrosulphide and ferrocyanide) and a precipitate (of sulphur and complex iron cyanogen compounds). As to the soluble products, 100 parts of nitroprusside yield about 13 parts of the nitrosulphide, $NaFe_4(NO)_7S_3$, and about 42 parts of sodium ferrocyanide. The yellowish-white precipitate becomes blue on exposure to the air; the yield of it is about 33% of the nitroprusside taken. When it is treated with warm concentrated hydrochloric acid, a blue powder remains undissolved, whilst the solution contains a green substance which can be re-precipitated with water. It is uncertain whether the acid effects a separation or induces a further reaction. The original crude precipitate seems to have a constant composition. R. V. S.

Vinyl*cyclo*propane and its Derivatives. NICOLAI J. DEMJANOV and M. DOJARENKO (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 176—184).—By various methods Gustavson (A., 1896, i, 669) obtained from vinyltrimethylene an alcohol, b. p. 115—118°. This alcohol is of tertiary character, and from the value of its optical exaltation and from the fact that its boiling point exceeds that of dimethylethylcarbinol by 15°, which is also the difference between the boiling points of β-methylbutyl alcohol and *cyclo*butylcarbinol, the authors conclude that it is probably 1-methyl*cyclo*butan-1-ol,

$$CH_2{<}{}^{CH_2}_{CH_2}{>}CMe{\cdot}OH,$$

and not 1-ethyl*cyclo*propan-1-ol.

The alcohol is converted by the action of hydriodic acid, first into the iodide, C_5H_9I, b. p. 50°/22 mm., 53°/30 mm., D_4^{18} 1·603, and

subsequently into the iodide, $C_5H_{10}I_2$. Reduction of the iodide C_5H_9I, by means of zinc dust and acetic acid yields (1) *ethyl*cyclo*propane*, $\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!>\!CHEt$, b. p. 34—35°/753 mm., D_0^0 0·6973, D_4^0 0·6971, D_4^{17} 0·6805, n_D^{17} 1·3814, which is also obtained on reducing vinyl*cyclo*propane by means of hydrogen in presence of platinum black, and (2) an ester, $C_7H_{14}O_2$, of the original alcohol and acetic acid.

T. H. P.

Terpenes and Ethereal Oils. CXIV. Alicyclic Unsaturated Hydrocarbons. OTTO WALLACH (*Annalen*, 1913, **396**, 264—284).—4-Methyl*cyclo*hexan-1-one and magnesium methyl iodide yield by the usual method 1 : 4-dimethyl*cyclo*hexan-1-ol, which is converted by boiling dilute sulphuric acid into 1 : 4-dimethyl-Δ^1-*cyclo*hexene, b. p. 127—128°, $D^{19.5}$ 0·8020, n_D 1·4459. By oxidation with 1% potassium permanganate at 0°, the latter is converted into 1 : 4-*dimethyl*cyclo*hexane*-1 : 2-*diol*, m. p. 77°, which yields 1 : 4-dimethyl*cyclo*hexan-2-one by treatment with dilute sulphuric acid. 1 : 4-Dimethyl-Δ^1-*cyclo*hexene forms a *nitrosochloride*, m. p. 83—84°, which is easily volatile with steam, forms a *nitrolpiperidide*, $C_5NH_{10}\cdot CMe<\begin{matrix} C(:NOH)\cdot CH_2 \\ CH_2\text{———}CH_2 \end{matrix}>CHMe$, m. p. 169—170°, and is converted into 1 : 4-dimethyl-Δ^6-*cyclo*hexen-2-oneoxime by loss of hydrogen chloride.

i-1 : 3-Dimethyl*cyclo*hexan-3-ol is converted by boiling dilute sulphuric acid into 1 : 3-*dimethyl*-Δ^3-cyclo*hexene*, b. p. 127·5—128·5°, D^{21} 0·8025, n_D^{21} 1·4466, which forms a *nitrosochloride* (the *nitrolpiperidide* has m. p. 130—131°) extremely slowly, and is oxidised to 1 : 3-dimethyl*cyclo*hexane-3 : 4-diol by 1% potassium permanganate.

By careful fractional distillation with an efficient column, it can be shown that the liquid obtained by the auto-condensation of methylheptenone in the presence of zinc chloride or phosphoric oxide, and hitherto regarded as pure dihydro-*m*-xylene, contains 1 : 3-dimethyl-Δ^3-*cyclo*hexene. Also when methylheptenone is treated with 75% sulphuric acid, the product is shown to be a mixture of 1 : 3-dimethyl-Δ^3-*cyclo*hexene and *m*-xylene.

1 : 2-Dimethyl*cyclo*hexan-1-ol and boiling dilute sulphuric acid yield 1 : 2-dimethyl-Δ^1-*cyclo*hexene, b. p. 135—137° (Sabatier gives 132°), D^{20} 0·824, n_D^{20} 1·4587, which forms a *nitrosochloride*, m. p. 58—60°, colourless when solid, blue when liquid, from which an oxime cannot be obtained. The unsaturated hydrocarbon forms a *dibromide*, m. p. 154—156°, and a *glycol*, m. p. about 38—39°, by oxidation.

[With L. AUGSPURGER.]—By warming with dilute sulphuric acid, 4-methyl-1-ethyl*cyclo*hexan-1-ol yields chiefly 4-*methyl*-1-*ethyl*-Δ^1-cyclo*hexene*, b. p. 153—154°, D^{22} 0·8145, n_D 1·4514, which forms a *nitrosochloride* consisting of two stereoisomeric modifications, one having m. p. 103—104° and being sparingly soluble in acetone or petroleum, the other having m. p. 98—99° and being easily soluble. Both modifications yield the same *nitrolpiperidide*, m. p. 134°, and by loss of hydrogen chloride the same *oxime*, m. p. 59—60°. By oxidation with dilute potassium permanganate, 4-methyl-1-ethyl-Δ^1-*cyclo*hexene is

converted into 4-*methyl*-1-*ethyl*cyclo*hexane*-1 : 2-*diol*, m. p. 76—77°, the constitution of which is proved by its conversion into 4-methyl-1-ethyl*cyclo*hexan-2-one.

[With HANS SCHLUBACH.]—1 : 3 : 5-*Trimethyl*cyclo*hexan*-1-*ol*, b. p. 181°, prepared from 3 : 5-dimethyl*cyclo*hexan-1-one and an excess of magnesium methyl iodide, is converted by boiling 50% sulphuric acid into 1 : 3 : 5-*trimethyl*-Δ^1-cyclo*hexene*, b. p. 142·5—143·5°, D^{21} 0·7965, n_D^{21} 1·4447, which forms a *nitrosochloride*, m. p. 134° (*nitrolpiperidide*, m. p. 122—123°), and is oxidised to 1 : 3 : 5-*trimethyl*cyclo*hexane*-1 : 2-*diol*, m. p. 104°, by cold dilute potassium permanganate. C. S.

Preparation of Partly Hydrogenised Cyclic Hydrocarbons.

BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 255538. Compare this vol., i, 349).—When dichloro*cyclo*hexane is heated at 350—450° and 15—20 mm. in the presence of potassium hydroxide, it gives rise to *cyclo*hexadiene, whilst 1 : 2-dibromo*cyclo*hexane furnishes $\Delta^{1:3}$-*cyclo*-hexadiene and chloro*cyclo*pentane yields *cyclo*pentene. F. M. G. M.

Derivatives of Phenylacetylene, Methoxyphenylacetylene, and Allied Compounds.

FRANZ KUNCKELL [with KURT ERAS, EMIL MÜLLER, and ALFRED HILDEBRANDT] (*Ber. Deut. Pharm. Ges.*, 1913, **23**, 188—227).—A recapitulation and extension of previous work on the preparation of derivatives of phenylacetylene from aryl chloromethyl ketones (A., 1897, i, 282, 522; 1901, i, 75, 552, 638; 1903, i, 413).

p-Tolylacetylene combines with bromine to form a *dibromide*, a pale yellow oil, b. p. 139—143°/13 mm., D^{17} 1·669, and a yellow, viscid, oily *tetrabromide*; with ammoniacal silver nitrate it yields a white, gelatinous *silver* salt, which forms an explosive grey powder when dry. The *copper* salt is light yellow, and is oxidised by aqueous potassium ferricyanide in the presence of potassium hydroxide to *di*-p-*tolylbutadi-inene*, $C_7H_7\cdot C⋮C\cdot C⋮C\cdot C_7H_7$. This crystallises in white needles, m. p. 183°, and yields a *dibromide*, m. p. 148°, *tetrabromide*, m. p. 163°, and an *octabromide*, m. p. 156—157°.

p-Ethylphenylacetylene gives a yellow oily *dibromide*, b. p. 168—172°/20 mm., D^{18} 1·598, a *tetrabromide*, and greenish-grey *silver* salt; the *copper* salt forms a light yellow powder, and is oxidised by alcoholic potassium ferricyanide to *di*-p-*ethylphenylbutadi-inene*, white needles, m. p. 72°.

αβ-Dichloro-2-*bromo*-5-*methoxystyrene*, $OMe\cdot C_6H_3Br\cdot CCl⁚CHCl$, prepared from 2-bromo-5-methoxyphenyl chloromethyl ketone and phosphorus pentachloride, forms a yellowish-brown oil, b. p. 210—215°/25 mm., D^{18} 1·3610. When heated with phosphorus pentachloride on the water-bath, 3 : 4-dichloroacetyl-1-methoxybenzene gives rise to 1-*methoxy*-3 : 4-*bis*-*αβ*-*dichlorovinylbenzene*, $OMe\cdot C_6H_3(CCl⁚CHCl)_2$, a pale yellow liquid, b. p. 160—170°/17 mm., D^{21} 1·461; if the reaction is carried out at a higher temperature, 2 : 5-*dichloro*-1-*methoxy*-3 : 4-*bis*-*αβ*-*dichlorovinylbenzene*, $OMe\cdot C_6HCl_2(CCl⁚CHCl)_2$, a yellow oil, b. p. in vacuum 170—180°, D^{19} 1·570, is produced.

αβ-2 : 5-Tetrachloro-4-methoxystyrene, $OMe\cdot C_6H_2Cl_2\cdot CCl:CHCl$, prepared by boiling *p*-methoxyphenyl chloromethyl ketone with excess of phosphorus pentachloride, is a yellow liquid of aromatic odour, b. p. 165—175°/18 mm., D^{17} 1·44; the prolonged action of phosphorus pentachloride gives rise to *αβ-2 : 3 : 5-pentachloro-4-methoxystyrene*, a yellow oil which has b. p. 180—190°/20 mm., D^{18} 1·6100, and solidifies when kept.

*αβ-Dichloro-*p*-ethoxystyrene*, prepared from *p*-ethoxyphenyl chloromethyl ketone, is a brownish-yellow liquid of disagreeable odour, b. p. 170—180°/26 mm., D^{20} 1·243.

5-Methoxy-*o*-tolyl chloromethyl ketone gives rise to *αβ-dichloro-5-methoxy-2-methylstyrene*, $OMe\cdot C_6H_3Me\cdot CCl:CHCl$, a pale yellow oil, b. p. 160°/20 mm., D^{18} 1·2520; *chloro-5-methoxy-*o*-tolylacetylene* has b. p. 145—150°/15 mm., D^{18} 1·166. *5-Methoxy-*o*-tolylacetylene* is a pale yellow liquid of ethereal odour, b. p. 110—120°/18 mm., D^{17} 1·011.

2 : 4-Dimethoxyphenyl chloromethyl ketone, prepared from resorcinol dimethyl ether and chloroacetyl chloride, crystallises in yellow leaflets, m. p. 104°, and yields with phosphorus pentachloride, *αβ-dichloro-2 : 4-dimethoxystyrene*, a reddish-yellow liquid which has a sweet odour and becomes crystalline when kept, b. p. 160—165°/18 mm.

Resorcinol diethyl ether and chloroacetyl chloride yield *4 : 4(?)-dichloroacetyl-1 : 3-diethoxybenzene*, $C_6H_2(OEt)_2(CO\cdot CH_2Cl)_2$, small, yellow needles, m. p. 106°.

*Di-*p*-chloroacetyldiphenyl ether*, $O(C_6H_4\cdot CO\cdot CH_2Cl)_2$, prepared from diphenyl ether and chloroacetyl chloride, forms greenish granules, m. p. 111°, and gives rise to *di-*p*-αβ-dichlorovinyldiphenyl ether*, $O(C_6H_4\cdot CCl:CHCl)_2$, a viscid liquid having a green shimmer, b. p. 225°/20 mm.

2 : 6-Dichloroacetylmesitylene, from chloroacetyl chloride and mesitylene, forms large, lustrous crystals, m. p. 134—135° (compare Meyer, A., 1897, i, 55), and yields *1 : 3 : 5-trimethyl-2 : 6-bis-αβ-dichlorovinylbenzene*, $C_6HMe_3(CCl:CHCl)_2$, a colourless oil, b. p. 180—181°/12 mm., D^{18} 1·3106. When impure, the last-named substance gradually loses hydrogen chloride on exposure to air, yielding a white *substance*, m. p. 95°.

2 : 4 : 6-Triethylphenyl chloromethyl ketone, prepared from 2 : 4 : 6-triethylbenzene, is a strongly refractive liquid, b. p. 207—215°/20 mm., and yields *αβ-dichloro-2 : 4 : 6-triethylstyrene*, which forms a golden-yellow oil of aromatic odour, b. p. 175°/18 mm., D^{18} 1·1447; *2 : 4 : 6-triethylphenylchloroacetylene*, a yellow oil, b. p. 155°/18 mm., D^{18} 1·0236; *2 : 4 : 6-triethylphenylacetylene*, a colourless liquid, b. p. 124—126°/14—16 mm., D^{21} 0·9004, which forms a yellow, amorphous *copper* salt.

2 : 6-Dichloroacetyl-1 : 3 : 5-triethylbenzene, $C_6HEt_3(CO\cdot CH_2Cl)_2$, crystallises in transparent, hexagonal plates, m. p. 71—72°, and gives rise to *1 : 3 : 5-triethyl-2 : 6-di-αβ-dichlorovinylbenzene*, $C_6HEt_3(CCl:CHCl)_2$, a golden-yellow oil, b. p. 210—215°/17—18 mm., D^{15} 1·245.

2 : 4-Di-chloroacetyl-6-acetyl-1 : 3 : 5-triethylbenzene,

$$COMe\cdot C_6Et_3(CO\cdot CH_2Cl)_2,$$

from 2 : 4 : 6-triethylphenyl methyl ketone and chloroacetyl chloride, crystallises in stout, transparent needles, m. p. 72°. F. B.

Preparation of Sulphonic Acids of the Benzene and Naphthalene Series. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 255724. Compare Friedländer and Lucht, A., 1894, i, 138). —When an electric current is passed through an alkaline solution of an aniline-, naphthylamine- or naphthol-polysulphonic acid in the presence of sodium amalgam a sulphonic group is eliminated.

The reduction of the following compounds is described: aniline-3:6-disulphonic acid to aniline-3-sulphonic acid; α-naphthylamine-4:8-disulphonic acid to α-naphthylamine-4-sulphonic acid; β-naphthylamine-4:8-disulphonic acid to the corresponding -8-sulphonic acid; β-naphthylamine-5:7-disulphonic acid to β-naphthylamine-7-sulphonic acid; α-naphthylamine-3:5:7-trisulphonic acid to α-naphthylamine-3:7-disulphonic acid; α-naphthylamine-2:4:6-trisulphonic acid to α-naphthylamine-2:4-disulphonic acid; α-naphthylamine-2:5:7-trisulphonic acid to α-naphthylamine-2:7-disulphonic acid; α-naphthol-3:8-disulphonic acid to α-naphthol-3-sulphonic acid; α-naphthol-2:4:8-trisulphonic acid to α-naphthol-2:4-disulphonic acid, and β-naphthol-3:6:8-trisulphonic acid to β-naphthol-3:6-disulphonic acid.

F. M. G. M.

Δ^1-Dihydronaphthalene. FRITZ STRAUS (*Ber.*, 1913, **46**, 1051—1055).—By the exhaustive methylation of tetrahydro-β-naphthylamine, Willstätter and King (this vol., i, 353) have obtained a dihydronaphthalene which they consider to be identical with the Δ^2-dihydronaphthalene, described by Bamberger (A., 1896, i, 99).

The author points out, however, that the properties of Willstätter and King's dihydro-compound show such complete agreement with those of the Δ^1-dihydronaphthalene (this vol., i, 256) that there can be no doubt as to the identity of the two hydrocarbons.

Δ^2-Dihydronaphthalene forms a dibromide differing very little in m. p. from that of the Δ^1-isomeride. The removal of bromine by means of zinc in alcoholic solution yields in each case the original hydrocarbon. The statement of Willstätter and King that their dihydronaphthalene can be obtained by the removal of bromine from the dibromide of Bamberger's Δ^2-dihydro-compound is, therefore, erroneous.

F. B.

Halogen Compounds of Anthracene. KURT H. MEYER and KARL ZAHN (*Annalen*, 1913, **396**, 166—180).—The halogen additive compounds of anthracene are derivatives of 1:2:3:4-tetrahydroanthracene. Attempts to replace the halogen atoms by hydroxyl, amino-, and other groups have been unsuccessful, but a new case of isomerism has been observed.

Graebe and Liebermann have shown that the action of bromine vapour on anthracene yields 9:10-dibromoanthracene tetrabromide. This yields 1:3:9:10-tetrabromoanthracene by treatment with alcoholic potassium hydroxide, 2:9:10-tribromoanthracene by heating, and 9:10-dibromoanthracene by reduction with zinc and acetic acid.

By treating anthracene moistened with chloroform with bromine (4 mols.) in chloroform, a *substance*, $C_{14}H_8Br_6$, m. p. 134—135° (decomp.), colourless needles, is obtained, which reacts like the older isomeride towards alcoholic potassium hydroxide, heating, and reducing agents. The two isomerides, therefore, are structurally alike. It is suggested that the two are stereoisomeric, the new compound, which is called α-9 : 10-*dibromoanthracene tetrabromide*, having the four homonuclear bromine atoms in *cis*-positions, whilst in the older (β-) compound they are alternately *cis* and *trans*. These configurations are in harmony with a property which is characteristic of the α-, but not of the β-isomeride. α-9 : 10-Dibromoanthracene tetrabromide in boiling benzene is decomposed into bromine and 9:10-dibromoanthracene by exposure to sunlight or to the light of a mercury lamp; the change is not reversible in boiling benzene in darkness.

α-9:10-*Dichloroanthracene tetrabromide*, $C_{14}H_8Cl_2Br_4$, m. p. 141—142° (decomp.), colourless, hexagonal prisms, prepared from dichloroanthracene and bromine (2 mols.) in chloroform, exhibits a similar photochemical decomposition in benzene, whilst the long-known β-isomeride does not.

The 9:10-dichloroanthracene tetrachloride obtained by Hammerschlag by passing chlorine into a benzene solution of anthracene is the β-isomeride, since it is photochemically inactive and does not liberate iodine from potassium iodide. The α-isomeride has not been obtained. The β-isomeride yields 1 : 3 : 9 : 10-tetrachloroanthracene (the constitution of which is proved by its conversion into 1 : 3-dichloroanthraquinone) by treatment with alcoholic potassium hydroxide, 2 : 3 : 9 : 10-*tetrachloroanthracene*, m. p. 240—241°, yellow needles (yielding 2 : 3-dichloroanthraquinone by oxidation), by heating above its m. p., and 9 : 10-dichloroanthracene by reduction with zinc and acetic acid.

9 : 9 : 10 : 10-Tetrachloroanthracene, m. p. 170° (Schwarzer gives 149—150°), obtained together with 9 : 10-dichloroanthracene tetrachloride by passing chlorine into a chloroform solution of anthracene at 0°, yields the *dianil*, $NPh:C<\substack{C_6H_4\\C_6H_4}>C:NPh$, m. p. 201—202°, golden-yellow leaflets, with aniline in boiling alcohol, and the *tetramethylacetal*, $C(OMe)_2<\substack{C_6H_4\\C_6H_4}>C(OMe)_2$, m. p. 161—162°, colourless crystals, with boiling methyl alcohol and sodium carbonate.

C. S.

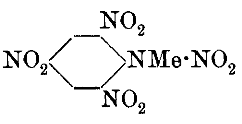
Preparation of *o*-Substituted Derivatives of Acetoacetanilide and Their Homologues. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 256621).—3-*Chloroacetoaceto*-o-*toluidide*, colourless needles, m. p. 120°, is obtained in 66% yield when a solution of ethyl acetoacetate in chlorobenzene is added to a hot solution of 3-chloro-*o*-toluidine in the same solvent.

o-*Chloroacetoacetanilide* is prepared in 75% yield in a similar manner from *o*-chloroaniline.

Acetoaceto-o-*anisidide*, a colourless, crystalline powder, has m. p. 84°,

whilst the analogous *compounds* from 3-amino-*p*-tolyl ethyl ether and from *phenyl* o-*aminophenyl ether* have m. p. 80° and 61° respectively.
F. M. G. M.

The Manufacture of Tetranitromethylaniline. F. LANGENSCHEIDT (*Zeitsch. ges. Schiess-Sprengstoffwesen*, 1912, **7**, 445—447).—2 : 4 : 6-N-*Tetranitromethylaniline* ("Tetril") (annexed formula), m. p. 129—130°, is obtained in 87% yield when pure methyl- or dimethyl-aniline is dissolved in 10 parts of concentrated sulphuric acid (pure and free from lead), thoroughly cooled, and slowly added to 4·3 parts of nitric acid (47° Be′) at 40°, 44° being the utmost limit to which the temperature may rise in the early stages of the operation; later, when the violence of the action decreases, it is allowed to rise to, and maintained at, about 53—55°, and after about eleven hours the nitration is completed. The product is purified by crystallisation from benzene.



F. M. G. M.

[Preparation of 4-Chloro-2 : 6-diaminophenol.] FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 256794).—4-*Chloro*-2 : 6-*diaminophenol*, obtained by the reduction of 4-chloro-2 : 6-dinitrophenol, crystallises from hot water in needles, has m. p. 88—89°, and furnishes crystalline *salts*.

3 : 5-*Diamino*-p-*cresol*, m. p. 146°, is prepared by the reduction of the corresponding 3 : 5-dinitro-*p*-cresol.
F. M. G. M.

Preparation of Dialkylaminoformic Esters. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 255942).—When halogen formic esters are treated with trialkylamines the following reaction takes place: $ClCO_2R + NMe_3 = NMe_3Cl \cdot CO_2R$, and the compounds so obtained when heated give rise to dialkylaminoformic esters of the general formula: $NMe_3Cl \cdot CO_2R = NMe_2 \cdot CO_2R + MeCl$ (R may be alkyl, aryl, or alkylaryl).

Phenyl dimethylaminoformate, $NMe_2 \cdot CO_2Ph$, colourless needles, m. p. 44—45°, b. p. 134—135°/16 mm., is obtained in quantitative yield when a cooled benzene solution of trimethylamine is slowly treated with phenyl chloro-formate; the intermediate *compound*, $NMe_3Cl \cdot CO_2Ph$, separates as a colourless, crystalline precipitate, and, on subsequently boiling, the reaction mixture is slowly converted into the foregoing ester.

Tolyl dimethylaminoformate, $NMe_2 \cdot CO_2 \cdot C_6H_4Me$, a viscid, colourless oil, b. p. 145—195°/15 mm., consisting of a mixture of the ortho-, meta-, and para-isomerides, is prepared in a similar manner from the mixture of *tolyl chloroformates*, b. p. 85—105°/18 mm., obtained by the action of carbonyl chloride on a freshly distilled benzene solution of crude cresol (b. p. 190—206°) in the presence of dimethylaniline.

β-Naphthyl chloroformate, colourless prisms, m. p. 57° (prepared from carbonyl chloride and β-naphthol), when treated with trimethylamine furnishes the *compound*, $NMe_3Cl \cdot CO_2 \cdot C_{10}H_7$, as a colourless, crystalline precipitate, and on boiling is converted into *β-naphthyl dimethylamino-formate*, $NMe_2 \cdot CO_2 \cdot C_{10}H_7$, colourless crystals, m. p. 92°.

iso*Amyl dimethylaminoformate*, $Me_2N\cdot CO_2\cdot C_5H_{11}$, a colourless oil, b. p. 194—197°, and *phenyl diethylaminoformate*, $NEt_2\cdot CO_2Ph$, a colourless oil, b. p. 142—146°/13 mm., are prepared in a similar manner.

F. M. G. M.

Preparation of Aromatic Selenocyano-compounds. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 255982).—An account of the preparation of compounds previously described by Bauer (this vol., i, 263); the m. p. of *o*-nitrophenyl selenocyanate is given as 144—145° (*loc. cit.*, 142°). F. M. G. M.

Iron Compounds of Phenols. IV. RUDOLF F. WEINLAND and KARL BINDER (*Ber.*, 1913, **46**, 874—885).—The dark blue substance obtainable from catechol and ferric acetate, which dissolves in water to a green solution, was provisionally regarded as having the structure $Fe_3(C_6H_4O_2)_4\cdot OH,7H_2O$ (A., 1912, i, 445), but it is now shown to yield acetic acid when warmed, and to contain actually one atomic weight of iron to a molecular weight of acetic acid and of catechol; it is obtained when two molecular proportions of ferric acetate are mixed with 1—2 of catechol in aqueous solution. If, however, four times the above quantity of catechol is used the violet acid, $H\left[\begin{matrix}Fe(C_6H_4O_2)_2\\ H_2O\end{matrix}\right],H_2O$ (*loc. cit.*), is obtained. It is therefore a probable conclusion that the substance which yields a green solution is a complex salt containing as components the above violet acid and the hexa-acetotriferric base (Weinland and Gussmann, A., 1910, i, 457), the constitution accordingly being:

$$[Fe_3(OAc)_6][Fe(C_6H_4O_2)_2]_3,12H_2O.$$

The view is confirmed by the production of a green colour on the addition of the red solution of ferric acetate to a solution of an alkali salt of the above violet acid, or on the addition of a little catechol to ferric acetate solution. It is suggested that the green coloration produced by ferric chloride solution with catechol may be due to the formation of some analogous complex salt. The green colour of the solutions of the above complex salt is not due to the mere superposition of the colours of the acid and metallic radicles, but the possibility is not excluded that some decomposition may occur during the process of solution with formation of still unknown complexes.

The preparation of the violet acid can be effected without the addition of sodium acetate (compare A., 1912, i, 445), provided that sufficient catechol is added to decompose all the ferric acetate.

As ferric chloride is soluble in certain organic solvents, the reaction of this substance with catechol was examined in other solvents than water. In ethereal solution the reaction product was a crystalline, blackish-brown *substance*, $Fe(O\cdot C_6H_4\cdot OH)Cl_2,Et_2O$ (compare A., 1912, i, 850), which may possibly be an oxonium salt of ether with the acidic portion of the substance; it is very sensitive to moisture, and soon becomes decomposed in the air; in alcohol it gives a blue solution. The reaction in acetophenone solution yields a product which when precipitated by pyridine forms bluish-black, microscopic leaflets of a

substance which may be regarded as a pyridine salt of the acid present in the last substance, that is, $(C_5H_5N)_5,[HFe(C_6H_4O_2)Cl_2]_4$. In pyridine solution a bluish-black, crystalline powder consisting of microscopic leaflets is obtained; the structure of this substance may be that of a salt of the red acid, $H_3[Fe^{III}(C_6H_4O_2)_3]$ (A., 1912, i, 445), with complex bases, and the formula $Fe(C_6H_4O_2)_3<\begin{matrix}[Fe(C_5H_5N)_4Cl,H_2O] \\ [Fe(C_5H_5N)_3Cl_2,H_2O]\end{matrix}$ is suggested.

The potassium salt of the violet acid retains its molecule of water in a vacuum over sulphuric acid for six months, and the potassium salt of the red acid holds its $2H_2O$ equally tenaciously; the sodium salt of the latter acid, however, yields 8 of its 9 H_2O under similar treatment.

D. F. T.

Some Additive Products of Styphnic Acid. CLAUDIO AGOSTINELLI (*Gazzetta*, 1913, **43**, i, 124—128).—The additive compound of 3 : 5-*dimethylpyrazole* and styphnic acid,

$$C_5H_8N_2,C_6H_3O_8N_3,$$

crystallises in golden-yellow scales, m. p. 203—204°. The compound from *antipyrine*, $C_{11}H_{12}ON,C_6H_3O_8N_3$, crystallises in canary-yellow laminæ, m. p. 204°. The compound from *pyramidone*,

$$C_{13}H_{17}ON_3,C_6H_3O_8N_3,$$

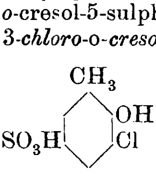
forms thin, yellow needles, m. p. 191°. The compound from *camphorphenylhydrazone*, $C_{10}H_{16}:N\cdot NHPh,C_6H_3O_8N_3$, crystallises in green, woolly needles, m. p. 150—151°. The compound from *acetonephenylhydrazone*, $C_3H_6:N\cdot NHPh,C_6H_3O_8N_3$, crystallises in yellowish-green scales, m. p. 104—106°. The compound from *cinnamaldehydephenylhydrazone*, $C_{15}H_{14}N_2,(C_6H_3O_8N_3)_2$, forms minute, pale green needles, m. p. 137—138°. The compound from *benzylideneaniline*, $C_{13}H_{11}N,C_6H_3O_8N_3$, crystallises in pale yellow scales, m. p. 193°. The compound from *cinnamylideneaniline*,

$$C_{15}H_{13}N,C_6H_3O_8N_3,$$

crystallises in bright red laminæ, m. p. 178°. The compound from *benzylideneazine*, $C_{14}H_{12}N_2,C_6H_3O_8N_3$, forms yellow needles, m. p. 152°. The compound from *cinnamylideneazine*, $C_{18}H_{16}N_2,C_6H_3O_8N_3$, crystallises in orange-yellow needles, m. p. 176°.

R. V. S.

Preparation of 2 : 3-Dihydroxytoluene. SACCHARIN-FABRIK AKTIENGESELLSCHAFT VORM. FAHLBERG, LIST & CO. (D.R.-P. 256345).—2 : 3-Dihydroxytoluene, m. p. 68°, b. p. 241° or 112°/3 mm., as obtained by Limpach (A., 1892, 447) had m. p. 47°, and the following method of preparation is now described. *o*-Cresol is sulphonated, and the *o*-cresol-5-sulphonic acid so obtained, chlorinated, when it yields 3-*chloro*-o-*cresol*-5-*sulphonic acid* (annexed formula); this when



heated at 130° with dilute sulphuric acid gives rise to 3-*chloro*-o-*cresol*, m. p. 185°, or if fused for 8—10 hours at 160—170° with sodium hydroxide and again subsequently heated at 200° with water under pressure, it yields 2 : 3-dihydroxytoluene in glistening, colourless leaflets.

F. M. G. M.

Some New Polymerides of the Phenols with Propenylic Side-chains. ERNESTO PUXEDDU (*Gazzetta*, 1913, **43**, i, 128—133).—The author has obtained new polymerides of *iso*safrole and anethole by methods based on the employment of an anhydrous ethereal solution of ferric chloride.

When an anhydrous ethereal solution of *iso*eugenol and ferric chloride is treated with dry hydrogen chloride for three hours, the di*iso*eugenol already known is produced.

If an absolute ethereal solution of *iso*safrole and ferric chloride is treated with dry hydrogen chloride for five days, a new *polymeride* of *iso*safrole is produced; it crystallises in spherical nodules, m. p. 92°, and reacts with bromine with evolution of hydrogen bromide and formation of an oily product.

Anethole, when treated in a manner similar to that described in the two preceding cases, yields a new *polymeride*, which, however, is better prepared by simply mixing anhydrous ethereal solutions of anethole and ferric chloride; the mixture deposits a white powder, which does not melt at 340°. R. V. S.

Action of Nitrous Acid on Ethyl*iso*eugenol. ERNESTO PUXEDDU (*Gazzetta*, 1913, **43**, i, 133—138. Compare A., 1912, i, 186).—The paper deals with the ethyl*iso*eugenol peroxide previously described (*loc. cit.*) with a view to showing its analogy to similar substances investigated by Angeli and others (A., 1893, i, 261, 263; 1894, i, 72; 1895, i, 35). When the peroxide is boiled with alcoholic potassium hydroxide for a few minutes, it is converted into a *substance*, $C_{12}H_{14}O_4N_2$, which crystallises in long, yellow, prismatic needles, which become red at 170°, m. p. 180° (decomp.).

Reduction of the peroxide with tin and hydrochloric acid yields a furazan derivative, $C_{12}H_{14}O_3N_2$, m. p. 116°. When the reduction is effected by zinc and acetic acid in certain conditions, *ethyl*iso*eugenol-α-dioxime*, $C_{12}H_{16}O_4N_2$, is produced; it forms lustrous scales, m. p. 150°. On heating at 150° for some hours, it yields the *β-dioxime*, which forms prismatic crystals, m. p. about 190°. R. V. S.

Some Derivatives of Hydroxyquinol. IX. GUIDO BARGELLINI (*Gazzetta*, 1913, **43**, i, 164—175. Compare Bargellini and Avrutin, A., 1911, i, 68).—The paper deals with the constitution of two substances obtained by the action of zinc chloride on triacetylhydroxyquinol, and described in the paper cited.

The red substance of m. p. 200—202° is 2:4:5-*trihydroxyacetophenone*, for it is formed by the saponification of the white substance of m. p. 165—166°, and it also results from the action of potassium persulphate on resacetophenone in alkaline solution (compare Bargellini and Aureli, A., 1911, i, 855). Benzoyl chloride yields 2:4:5-*tribenzoyloxyacetophenone* with both substances; it forms colourless needles, m. p. 131—133°. Acetyl chloride gives with both red and white compounds a substance of the empirical formula C_2H_2O, m. p. 110—111°, which is 2:4:5-*triacetoxyacetophenone*. Both red and white compounds yield diacetyl-β-methylæsculetin (Bargellini and Martegiani, A., 1912, i, 292) when heated with acetic anhydride and

sodium acetate; the formation of another substance, which begins to decompose at 245°, was also observed. The reactions above described, taken in conjunction with the results of the molecular weight determination and of the estimation of saponifiable acetic acid in the compound, show that the white substance is a *hydroxydiacetoxyacetophenone.*

The reaction between zinc chloride and triacetylhydroxyquinol thus results in a migration of one of the acetyl groups to a carbon atom of the nucleus. Other similar reactions are known. R. V. S.

Behaviour of Individual Organo-magnesium Compounds Towards Aromatic Ethers. VLADIMIR V. TSCHELINCEV and B. V. PAVLOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 289—300. Compare A., 1906, ii, 334, 335; A., 1907, i, 499; A., 1908, i, 254; Štadnikov, and also Stadnikov and Kuzmina-Aron, A., 1912, i, 971).—The authors have investigated the products formed and the thermal changes involved in the action of magnesium propyl iodide on (1) benzyl ethyl ether; (2) diphenylmethyl ethyl ether, and (3) triphenylmethyl ethyl ether. The products are (1) phenylbutane, *s*-diphenylethane, benzene, and ethyl alcohol; (2) diphenylbutane and *s*-tetraphenylethane, and (3) triphenylmethane and ethyl alcohol. The heat effects observed also indicate, not merely a combination of the ether with the organo-magnesium compound, but a more profound interaction.

These results show that when ethers of the aromatic series, which are less stable than the corresponding ones of the aliphatic series, react with organo-magnesium compounds, they are partly divided at the junction of the aromatic radicle with the oxygen of the alkoxy-group. This division leads to the formation of aromatic hydrocarbons of two types: (1) CH_2PhPr, $CHPh_2Pr$, CPh_3Pr, and (2) $CH_2Ph{\cdot}CH_2Ph$, $CHPh_2{\cdot}CHPh_2$, $CPh_3{\cdot}CPh_3$. These hydrocarbons are produced in accordance with the scheme advanced by Erlenmeyer, jun.: (1) $R{\cdot}OEt + IMg{\cdot}Pr = R{\cdot}Pr + OEt{\cdot}MgI$, and (2) $2R{\cdot}OEt + 2IMg{\cdot}Pr = R{\cdot}R + Pr{\cdot}Pr + 2OEt{\cdot}MgI$.

Since these hydrocarbons represent the actual products of the interaction of organo-magnesium compounds and ethers, and are not formed only after the action of water on these products, any attempt to draw conclusions concerning the structure of the ethereal complexes of organo-magnesium compounds on the basis of experimental results of this kind is pure speculation.

Further, no certain conclusions can be deduced from consideration of the products obtained by decomposition of the complexes by means of carbon dioxide (compare Stadnikov and Kuzmina-Aron, A., 1912, i, 971), since such decomposition is not quantitative, especially when molecular proportions of the ether and organo-magnesium compound are taken, and at the same time there is no exclusion of the possibility of formation from undecomposed magnesium alkyl iodide of the corresponding fatty acid, and hence of, for example, triphenylacetic acid.

In deciding between the two structures: $R_2:O(MgR)I$ and $R_2:O(MgI)R$, it must be borne in mind that ethereal complexes of this type are obtained, not only with such compounds as MgRI, but also with magnesium iodide, and in the latter case the only possible structure is $R_2:OI\cdot Mg\cdot OI:R_2$. T. H. P.

Reduction by means of Organo-magnesium Compounds. ALEXANDER I. GORSKI (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 163—166).—The author has previously (A., 1912, i, 622) expressed the opinion that the formation of triphenylmethane by the interaction of triphenylmethyl ethyl ether, propyl iodide, and magnesium in an indifferent solvent is due to hydrolytic decomposition of the ether into triphenylmethyl iodide and reduction of the latter to the corresponding hydrocarbon. As alkyl iodides and magnesium, however, react in absence of an ether or other catalyst, it may be that in the above case no etherate of the type Pr·Mg·OEt is formed, but that these reactions take place between the individual organo-magnesium compounds and the ether.

In order to test the accuracy of this view, experiments were made in which the triphenylmethyl ethyl ether was replaced by other oxygenated compounds, such as ketones. The reaction between β-benzopinacolin and magnesium propyl iodide in toluene solution proceeds in the same direction as the reaction with triphenylcarbinol in presence of ethyl ether, giving a compound apparently identical with benzopinacolin alcohol. Similarly, benzophenone yields benzhydrol and other compounds. It is known that the action of organozinc compounds on aldehydes and on ketones may, under certain experimental conditions and with certain radicles in the organometallic compounds, result in the reduction of the aldehydes to primary, and of the ketones to secondary, alcohols; hence the reaction with β-benzopinacolin may be represented by the equation: $CPh_3\cdot COPh + MgPrI = CPh_3\cdot CHPh\cdot OMgI + C_3H_6$.

That the reaction between nascent organo-magnesium compounds and ketones is not generally limited to such a reduction is, however, rendered evident by the fact that the secondary alcohol is not the sole final product.

These considerations indicate the possibility that the reaction between triphenylmethyl ethyl ether and magnesium propyl iodide may be one of direct reduction, without intermediate formation of iodide: $CPh_3\cdot OEt + MgPrI = CHPh_3 + OEt\cdot MgI + C_3H_6$. T. H. P.

Phenylethanolamines, Phenylnitroethanols, and their Hydroxy-derivatives. KARL W. ROSENMUND (*Ber.*, 1913, **46**, 1034—1050. Compare A., 1910, i, 106; 1911, i, 34).—An account of a preparation of a number of β-hydroxy-β-arylethylamines, $OH\cdot CHR\cdot CH_2\cdot NH_2$, by the reduction of the corresponding nitro-alcohols, $OH\cdot CH\cdot CHR\cdot CH_2\cdot NO_2$. The latter compounds are obtained in good yield by decomposing the sodium salts, produced by the condensation of aromatic aldehydes with nitromethane in the presence of sodium methoxide, with acetic acid. On treatment with mineral acids or when heated, the nitro-alcohols

lose water with the formation of the corresponding nitrostyrenes, $R\cdot CH\colon CH\cdot NO_2$. They dissolve in alkalis, yielding colourless solutions from which acetic acid liberates the nitro-alcohols unchanged, whilst mineral acids give rise to β-nitrostyrenes.

When dissolved in alkalis and the solutions acidified with acetic acid, the β-nitrostyrenes combine with water to form nitro-alcohols.

A similar addition of alcohol, resulting in the formation of nitro-ethers of the type $OEt\cdot CHR\cdot CH_2\cdot NO_2$, may be effected by treating the nitrostyrenes with alcoholic alkali hydroxides and subsequently acidifying with acetic acid.

Although hydroxybenzaldehydes do not directly condense with nitromethane, the preparation of the corresponding nitrostyrenes and nitro-alcohols may be readily accomplished by the method illustrated in the following example: *p*-hydroxybenzaldehyde is converted into *p*-ethylcarbonatobenzaldehyde (I), $CO_2Et\cdot O\cdot C_6H_4\cdot CHO$, which instantly reacts with nitromethane in the presence of alkali, yielding the salt $CO_2Et\cdot O\cdot C_6H_4\cdot CH(OH)\cdot CH\colon NO\cdot OK$; on treatment with hydrochloric or acetic acid this yields the compounds (II)

$$CO_2Et\cdot O\cdot C_6H_4\cdot CH\colon CH\cdot NO_2$$

and (III) $CO_2Et\cdot O\cdot C_6H_4\cdot CH(OH)\cdot CH_2\cdot NO_2$ respectively. If excess of alkali is employed and the reaction mixture allowed to remain for one to two minutes, the carbethoxy-group is removed and subsequent acidification yields (IV) $OH\cdot C_6H_4\cdot CH\colon CH\cdot NO_2$ or (V)

$$OH\cdot C_6H_4\cdot CH(OH)\cdot CH_2\cdot NO_2,$$

accordingly as hydrochloric or acetic acid is employed.

β-Nitro-α-phenylethyl alcohol, $OH\cdot CHPh\cdot CH_2\cdot NO_2$, prepared by condensing benzaldehyde with nitromethane in alcoholic solution by means of sodium methoxide below 8° and acidifying the aqueous solution of the resulting sodium salt with dilute acetic acid, is a yellow oil, b. p. 163—165°/15 mm. On treatment with sodium methoxide in methyl-alcoholic solution, β-nitrostyrene yields a colourless solution, from which the successive addition of acetic acid and water liberates *β-nitro-α-phenylethyl methyl ether*, $OMe\cdot CHPh\cdot CH_2\cdot NO_2$, as a pale yellow oil, b. p. 140—141°/15 mm.

*β-Nitro-α-*p*-methoxyphenyl ethyl alcohol*, $OMe\cdot C_6H_4\cdot CH(OH)\cdot CH_2\cdot NO_2$, prepared by acidifying with acetic acid an aqueous solution of the *sodium* salt, obtained by the condensation of anisaldehyde and nitromethane with sodium methoxide, is a yellow oil, which partly decomposes on distillation or on treatment with mineral acids into β-nitro-*p*-methoxystyrene.

*β-Nitro-α-*p*-methoxyphenylethyl methyl ether*,

$$OMe\cdot C_6H_4\cdot CH(OMe)\cdot CH_2\cdot NO_2,$$

is a yellow oil.

p-Benzyloxybenzaldehyde condenses with nitromethane, yielding *β-nitro-*p*-benzyloxystyrene*, $C_7H_7\cdot O\cdot C_6H_4\cdot CH\colon CH\cdot NO_2$, m. p. 120°, from which *β-nitro-α-*p*-benzyloxyphenylethyl methyl ether*,

$$C_7H_7\cdot O\cdot C_6H_4\cdot CH(OMe)\cdot CH_2\cdot NO_2,$$

m. p. 105—106°, is obtained in the usual manner.

p-*Benzoyloxybenzaldehyde*, prepared by the successive addition of the theoretical amount of potassium hydroxide and benzoyl chloride to an alcoholic solution of *p*-hydroxybenzaldehyde, yields with nitromethane

β-nitro-p-*benzoyloxystyrene*, which crystallises in slender, pale yellow needles, m. p. 153—155°. *β-Nitro-α*-p-*benzoyloxyphenylethyl alcohol* forms almost white, lustrous scales, m. p. 127—130°, and yields a white *sodium* salt. p-*Ethylcarbonatobenzaldehyde* (I), prepared from *p*-hydroxybenzaldehyde and ethyl chloroformate in the presence of alkali, is a colourless oil, b. p. 170—172°/13 mm., and yields *β-nitro*-p-*ethylcarbonatostyrene* (II), crystallising in slender, pale yellow needles, m. p. 112—113°.

β-Nitro-α-p-*ethylcarbonatophenylethyl alcohol* (III) forms yellow needles, m. p. 91·5°. *β-Nitro*-p-*hydroxystyrene* (IV), prepared by hydrolysing its acyl derivatives with cold aqueous potassium hydroxide, crystallises in stout, long needles, m. p. 154—160° (decomp.). *β-Nitro-α*-p-*hydroxyphenylethyl alcohol* (V) is a yellow syrup.

4-*Benzoyloxy*-3-*methoxybenzaldehyde*, prepared by benzoylating vanillin by the pyridine method, has m. p. 75—76°, and condenses with nitromethane, yielding *β-nitro*-4-*benzoyloxy*-3-*methoxystyrene*, which forms slender, pale yellow needles, m. p. 152—155°, and is hydrolysed by alcoholic potassium hydroxide to vanillylidenenitromethane (A., 1905, i, 65).

4-*Ethylcarbonato*-3-*methoxybenzaldehyde*, prepared from vanillin and ethyl chloroformate, has m. p. 71° and loses CO_2, at 135°, yielding 3-methoxy-4-ethoxybenzaldehyde; with nitromethane it yields *β-nitro*-4-*ethylcarbonato*-3-*methoxystyrene*, m. p. 125°, and *β-nitro-α*-4-*ethylcarbonato*-3-*methoxyphenylethyl alcohol*, which crystallises in stout needles, m. p. 84—86°.

3 : 4-*Dibenzoyloxybenzaldehyde*, prepared from protocatechualdehyde in a similar manner to that given for *p*-benzoyloxybenzaldehyde, separates from alcohol in rosettes of white needles, m. p. 96—97°, and gives rise to *β-nitro*-3 : 4-*dibenzoyloxystyrene*,

$$C_6H_3(OBz)_2\cdot CH\colon CH\cdot NO_2,$$

which forms slender, pale yellow needles, m. p. 143—144°, and is hydrolysed by alcoholic potassium hydroxide to *β-nitro*-3 : 4-*dihydroxystyrene*, crystallising in yellow needles or leaflets, m. p. 155—157°, with previous darkening at 145—148° (decomp. 160°).

3 : 4-*Diethylcarbonatobenzaldehyde*, obtained from ethyl chloroformate and protocatechualdehyde, is a colourless oil, b. p. 215—217°/13 mm., and yields with nitromethane, *β-nitro*-3 : 4-*diethylcarbonatostyrene*, yellow needles, m. p. 72°.

Acidification of the products, resulting from the condensation of 3 : 4-diethylcarbonato- and 3 : 4-dibenzoyloxy-benzaldehyde with nitromethane in the presence of sodium methoxide, with acetic acid yields *β-nitro-α*-3 : 4-*diethylcarbonatophenylethyl alcohol* and *β-nitro*-3 : 4-*dibenzoyloxyphenylethyl alcohol*, as yellow oils. If excess of sodium methoxide is used, *β-nitro*-3 : 4-*dihydroxyphenylethyl alcohol* is formed. *Alkyl ethers* of the last-mentioned compound have also been prepared, but these resemble the previously-mentioned nitro-alcohols derived from 3 : 4-dihydroxybenzaldehyde in being too unstable to allow of their isolation in a state of purity. Their constitution was therefore established by reduction to the corresponding amino-alcohols and ethers.

β-Hydroxy-*β*-phenylethylamine is obtained by reducing *β*-nitro-*α*-

phenylethyl alcohol with sodium amalgam and acetic acid in aqueous alcoholic solution; it is accompanied by a substance of feeble basic properties, m. p. 217—218°.

β-Methoxy-β-phenylethylamine hydrochloride,

$$OMe\cdot CHPh\cdot CH_2\cdot NH_2,HCl,$$

obtained by reduction of β-nitro-α-phenylethyl methyl ether in a similar manner, crystallises in white needles, m. p. 158—159°.

Successive treatment of β-nitro-*p*-methoxystyrene with alcoholic potassium hydroxide and acetic acid gives rise to *β-nitro-α-*p*-methoxyphenylethyl ethyl ether.*. On reduction this yields *β-ethoxy-β-*p*-methoxyphenylethylamine*, $OMe\cdot C_6H_4\cdot CH(OEt)\cdot CH_2\cdot NH_2$, as a syrup which slowly crystallises and yields a hydrochloride, m. p. 173—175° (decomp. 182°).

*β-Methoxy-β-*p*-methoxyphenylethylamine*, obtained from β-nitro-α-*p*-methoxyphenylethyl methyl ether, forms a *hydrochloride*, crystallising in white needles, m. p. 166—166·5° (decomp. 186—187°).

*β-Hydroxy-β-*p*-methoxyphenylethylamine hydrochloride* has m. p. 171—172°.

β-Nitro-β-3 : 4-dimethoxyphenylethyl methyl ether, obtained as a yellow oil by dissolving β-nitro-3 : 4-dimethoxystyrene (A., 1911, i, 34) in methyl-alcoholic sodium methoxide, is reduced by sodium amalgam and acetic acid to β-methoxy-β-3 : 4-dimethoxyphenylethylamine, identical with the arterenol trimethyl ether of Mannich and Neumann (A., 1910, i, 413).

The condensation of veratraldehyde and nitromethane with sodium methoxide yields the *sodium* salt of *β-nitro-α-3 : 4-dimethoxyphenylethyl alcohol*, which on decomposition with acetic acid and subsequent reduction is converted into *β-hydroxy-β-3 : 4-dimethoxyphenylethylamine*, $C_6H_3(OMe)_2\cdot CH(OH)\cdot CH_2\cdot NH_2$, the *hydrochloride* of which crystallises in leaflets, m. p. 163°.

β-Hydroxy-3 : 4-dihydroxyphenylethylamine is obtained in an impure condition by the reduction of β-nitro-α-3 : 4-dihydroxyphenylethyl alcohol; the *hydrochloride* gives an intense catechol reaction with ferric chloride. F. B.

Action of Sulphuric Acid on Tetramethyldiaminobenzhydrol. The Pinacone of Michler's Ketone. S. Fischl (*Monatsh.*, 1913, **34**, 337—350).—The observation of Rosenstiehl (A., 1895, i, 541) and of Weil (A., 1894, i, 419; 1895, ii, 145), that tetramethyldiaminobenzhydrol is converted into hexamethyltriaminotriphenylmethane by warming with dilute sulphuric acid is confirmed, and it is further shown that by the action of sulphuric acid, Michler's ketone is formed, which then condenses with some of the unchanged hydrol producing a substance of the formula:

$$CH(C_6H_4\cdot NMe_2)_2\cdot C_6H_3(NMe_2)\cdot CO\cdot C_6H_4\cdot NMe_2.$$

Tetramethyldiaminobenzhydrol, when dissolved in sulphuric acid and gently warmed, furnishes Michler's ketone (tetramethyldiaminobenzophenone), together with a *substance*, $C_{34}H_{40}ON_4$, m. p. 212—213°, crystallising from methyl alcohol in slender, silky needles, or from benzene on addition of light petroleum in short colourless prisms; it is readily soluble in benzene, less so in acetone, and must have the

constitution given above, since it is also formed by the condensation of Michler's ketone with tetramethyldiaminobenzhydrol in presence of sulphuric acid. It is unaffected by acids or alkalis, but on oxidation furnishes a greenish-blue dye. The reactions of the substance indicate that the ·CO· group is in the ortho-position to the methane residue.

Tetramethyldiaminobenzophenone is not affected by zinc and acetic acid, but may be reduced electrolytically or by zinc with sulphuric or hydrochloric acid, giving the corresponding pinacone,

$$OH\cdot C(C_6H_4\cdot NMe_2)_2\cdot C(C_6H_4\cdot NMe_2)_2\cdot OH,$$

m. p. 195° (compare Escherich and Moest, A., 1903, i, 89). This is somewhat soluble in benzene, but almost insoluble in alcohol; its solution in acetic acid is colourless in the cold, but becomes blue on warming. It dissolves in sulphuric acid, forming a deep red solution, which on heating at 115—120° gives rise to the corresponding *pinacolin*,

$$C_{34}H_{40}ON_4,$$

m. p. 232—233°, which crystallises with one mol. of benzene in glandular masses of glancing prisms. On heating with alcoholic potassium hydroxide, the pinacone is converted into a mixture of the ketone and the hydrol. T. A. H.

1 : 1-Dimethylol*cyclo*butane. NICOLAI D. ZELINSKI and M. N. UJEDINOV (*Ber.*, 1913, **46**, 1093—1094).—A solution of ethyl tetramethylenedicarboxylate in absolute alcohol was added to sodium covered with dry ether, and, after the first vigorous action had subsided, the product was heated at 130—140° until the sodium was completely dissolved. After addition of water, the alcohol was removed by distillation and the residue poured into water and saturated with potassium carbonate. The oil which separated was removed, united with a portion obtained by extracting the aqueous liquor with ether, and fractionated. Thereby, cyclo*butylcarbinol*, $C_4H_7\cdot CH_2\cdot OH$, b. p. 142—144°/760 mm., was obtained, together with 1 : 1-*dimethylol*cyclo*butane*, $C_4H_6(CH_2\cdot OH)_2$, a viscous, pale yellow oil, b. p. 145—147°/20 mm. H. W.

The Iodohydrin of the Glycol Derived from Cinnamyl Methyl Ether. HENRI BEAUFOUR (*Bull. Soc. chim.*, 1913, [iv], **13**, 349—353. Compare A., 1912, i, 621).—The iodohydrin obtained by treating cinnamyl methyl ether with iodine and mercuric oxide (*loc. cit.*) may have the formula $OH\cdot CHPh\cdot CHI\cdot CH_2\cdot OMe$ or

$$CHPhI\cdot CH(OH)\cdot CH_2\cdot OMe.$$

The results recorded in this and the next abstract support the first formula.

On treatment with powdered potassium hydroxide the iodohydrin (D_{19}^{19} 1·500) furnishes the corresponding *oxide*, $CHPh{<}\overset{O}{\underset{CH\cdot CH_2\cdot OMe}{|}}$, D_0^0 1·0714, b. p. 127—128°/14 mm., a mobile, colourless liquid with a pungent odour; it does not combine with bromine, but reacts energetically with hydriodic acid, forming an iodo-derivative which probably has the second formula quoted above.

With dimethylamine the iodohydrin yields *ω-methoxymethylephedrine*,

$OH\cdot CHPh\cdot CH(NMe_2)\cdot CH_2\cdot OMe$, m. p. 76°, b. p. 152—153°/12 mm., which crystallises in colourless needles, and furnishes a *hydrochloride*, m. p. 170°, *hydriodide* m. p. 102—103°, *methiodide*, m. p. 160°, *picrate*, m. p. 152—153°, and with ethyl chloroacetate a *morpholone*, m. p. 168°. The *hydrochloride* of the *benzoyl* derivative, m. p. 118°, crystallises in spangles, has a bitter taste, and has a slow but distinct numbing action on the tongue. T. A. H.

Alkyliodohydrins Derived from Cinnamyl Methyl Ether. HENRI BEAUFOUR (*Bull. Soc. chim.*, 1913, [iv], **13**, 354—358. Compare A., 1912, i, 621, and preceding abstract).—The methyl- and ethyl-iodohydrins, $OR\cdot CHPh\cdot CHI\cdot CH_2\cdot OMe$, already described differ from the simple iodohydrin (preceding abstract) in being more stable. The methyliodohydrin, D_0^0 1·5070, b. p. 160—161°/15 mm., does not react with potassium hydroxide, except in alcohol, and then furnishes at 100°, the *ether*, $OMe\cdot CPh{:}CH\cdot CH_2\cdot OMe$, D_0^0 1·0483, b. p. 243°/760 mm., 128—129°/13 mm., a strongly-smelling liquid, which combines vigorously with bromine, reduces potassium permanganate solution, and when treated with steam in presence of sulphuric acid yields *phenyl vinyl ketone*, $COPh\cdot CH{:}CH_2$, b. p. 110—115°/15 mm., which readily polymerises, and yields a *dibromide*, m. p. 56°, crystallising in colourless needles.

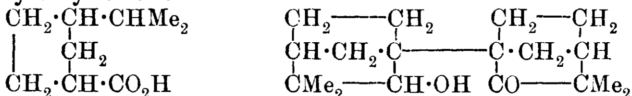
The methyliodohydrin reacts only feebly with dimethylamine at 120°, giving the *amine*, $OMe\cdot CHPh\cdot CH(NMe_2)\cdot CH_2\cdot OMe$, b. p. 132—133°/11 mm., whilst at higher temperatures, tarry products result.

The ethyliodohydrin (D_0^0 1·4568) behaves like its lower homologue, and with potassium hydroxide in alcohol yields the ethylenic *ether*, $OEt\cdot CPh{:}CH\cdot CH_2\cdot OMe$, D_0^0 1·0428, b. p. 137—139°/15 mm., whilst with dimethylamine it is even less reactive. T. A. H.

Preparation of Aromatic Amino-alcohols. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 256750).—The previously described reduction of amino-ketones in the presence of colloidal metals of the platinum group (this vol., i, 361) is found to proceed equally satisfactorily if the metal is in a state of very fine division, and the preparation of 3 : 4-dihydroxyphenyl-α-propanolamine and of 3 : 4-dimethoxyphenyl-α-propanolamine in the presence of finely-divided palladous chloride are described. F. M. G. M.

1-Methyl*cyclo*pentane-1-carboxylic Acid. ALEXEI E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 184—188).—*cyclo*Pentanone (compare Aschan, A., 1912, i, 536) was converted into 1-methyl*cyclo*pentan-1-ol (compare Zelinski and Nametkin, A., 1902, i, 672), this into 1-methyl-1-chloro*cyclo*pentane, and the latter, by the action of magnesium in ethereal solution and then of carbon dioxide, into 1-*methyl*cyclo*pentane*-1-*carboxylic acid*, $\begin{array}{l}CH_2\cdot CH_2\\ |\\ CH_2\cdot CH_2\end{array}\!\!>CMe\cdot CO_2H$, which is an unpleasant smelling liquid, b. p. 219—219·5°, D_4^{20} 1·0218, D_4^0 1·0392. Its *silver* and *cadmium* salts were analysed. The *methyl* ester, $C_8H_{14}O_2$, b. p. 159·5°/721 mm., D_4^{20} 0·9641, D_4^0 0·9850, $D_4^{18\cdot 5}$ 0·9657, $n_D^{18\cdot 5}$ 1·43727, and the *amide*, $C_7H_{13}ON$, m. p. 124—125° were prepared. T. H. P.

Dihydrocamphoceic Acid (Camphenilolic Acid) and the Action of Sodium on Camphenilone. S. V. HINTIKKA (*Chem. Zentr.*, 1913, i, 625; from *Ann. Acad. Sci. Fennicae*, 1913, **9**, 1—7).—*Camphenilolic acid*, $C_{18}H_{15}\cdot CO_2H$, is obtained by heating camphenilone with powdered potassium hydroxide, as an oil, b. p. 140—141°/15 mm., D_4^{20} 0·9820, n_D 1·45650. It forms a *chloride*, b. p. 112—114°/10 mm., a *methyl* ester, mobile oil, b. p. 203—204°/762 mm., D_4^{21} 0·9392, n_D 1·44441, and an *anilide*, $C_8H_{15}\cdot CO\cdot NHPh$, in radiating needles, m. p. 89—90°. If the acid had Wallach's formula (I) it should give a hydroxy-acid on oxidation, which should further yield the lactone, dimethylnorcampholide. It undergoes extensive decomposition, however, and the products include acetic acid and probably butyric acid.



(I.) (II.)

When boiled with sodium in xylene, camphenilone yields a yellow, viscous *oil*, $C_{18}H_{28}O_2$ (II?), b. p. 172—174°/12 mm., D_4^{20} 1·0601, n_D 1·51547. J. C. W.

Direct Hydrogenation of the Hydrocinnamic Esters: Preparation of β-*cyclo*Hexylpropionic Acid. PAUL SABATIER and MARCEL MURAT (*Compt. rend.*, 1913, **156**, 751—753).—The esters of β-phenylpropionic acid like those of phenylacetic acid (compare this vol., i, 362) readily undergo direct hydrogenation in the presence of active nickel at 170—185°, giving the corresponding esters of β-*cyclo*hexylpropionic acid in a pure state. The following have been prepared:

Methyl β-cyclo*hexylpropionate*, b. p. 222—224° (corr.), D_0^0 0·9705, D_0^{16} 0·9603, n_D^{16} 1·453.

Ethyl β-cyclo*hexylpropionate*, b. p. 231° (corr.), D_0^0 0·9512, D_0^{17} 0·9383, n_D^{17} 1·452.

Propyl β-cyclo*hexylpropionate*, b. p. 251—252° (corr.), D_0^0 0·9467, D_0^{15} 0·9322, n_D^{15} 1·455.

iso*Butyl* β-cyclo*hexylpropionate*, b. p. 260° (corr.), D_0^0 0·9368, D_0^{15} 0·9281, n_D^{15} 1·456.

Whilst the densities decrease with increase in molecular weight the refractive indices remain practically constant. All these esters are readily saponified by warming with alcoholic potassium hydroxide, and with dilute sulphuric acid yield β-*cyclo*hexylpropionic acid (compare Ipatiev, A., 1909, i, 472). W. G.

Influence of the Nature and Position of Substituents on the Stability of the Carboxyl Group in Substituted Benzoic Acids. FRANZ VON HEMMELMAYR (*Monatsh.*, 1913, **34**, 365—388. Compare Cazeneuve, A., 1895, i, 57).—The relative stability of the carboxyl group in various substituted benzoic acids was determined by boiling the acids in solution in water or aniline and estimating the proportion decomposed in a certain time. The results, which are tabulated in detail and fully discussed, show that it is difficult to draw general conclusions as to the influence of the position of substituents on the stability of the carboxyl group. The four substituents

investigated are arranged in the following descending order as regards their effect on the stability of the carboxyl group: $\cdot OH$, $\cdot NO_2$, $\cdot Br$, $\cdot NH_2$. T. A. H.

Preparation of Nuclear Nitroso-derivatives of Phenylglycine-*o*-carboxylic Acids, their Acids and Neutral Esters. J. D. RIEDEL (D.R.-P. 256461. Compare A., 1887, 729, 1114; 1909, i, 794, 645).—When a cold concentrated hydrochloric acid solution of phenylglycine-*o*-carboxylic acid (5 parts) is treated with sodium nitrite, it furnishes p-*nitrosophenylglycine*-o-*carboxylic acid hydrochloride*, decomp. about 100°; the free *base*, a green powder, condenses with *p*-nitrobenzonitrile to furnish an *azomethine*, red needles, m. p. 256—258°, and with benzonitrile to give a yellow *compound*.

Dimethyl p-*nitrosophenylglycine*-o-*carboxylate* has m. p. 164—165°, and the *diethyl* ester, m. p. 131°.

p-*Nitroso*-o-*carbomethoxyphenylglycine ethyl* ester is a green, crystalline compound, m. p. 125°, and p-*nitroso*-o-*carboxyphenylglycine ethyl* ester has m. p. 115—116°. F. M. G. M.

Preparation of Derivatives of Arylalkyloxyacetic Acids. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 256756. Compare McKenzie, T., 1899, **75**, 755).—*α-Ethoxy-α-phenylacetamide*, $OEt\cdot CHPh\cdot CO\cdot NH_2$, colourless needles, m. p. 90°, is obtained when ethyl ethoxyphenylacetate, b. p. 145—147°/20 mm., is shaken with saturated ammonium hydroxide; the following derivatives have been obtained in an analogous manner.

α-Methoxyphenylacetamide, m. p. 110—111°, from *ethyl α-methoxyphenylacetate*, b. p. 148—152°/22 mm.

p-*Tolyloxyethylacetamide*, m. p. 130—131°, from *ethyl* p-*tolyloxyethylacetic acid*, b. p. 160—165°/25 mm.

o-*Chlorophenoxyallylacetamide*, a colourless oil, b. p. 171—174°/21 mm., from *ethyl* o-*chlorophenoxyallylacetate*, b. p. 166—170°/25 mm.

Phenoxyallylacetamide, m. p. 77—78°, from *ethyl phenoxyallylacetate*, b. p. 163—164°/24 mm.

Phenoxyphenylacetamide, $OPh\cdot CHPh\cdot CO\cdot NH_2$, colourless needles, m. p. 154—155°, from phenoxyphenylacetic acid; the *carbamide*,

$$OPh\cdot CHPh\cdot CO\cdot NH\cdot CO\cdot NH_2,$$

colourless needles, has m. p. 193°. F. M. G. M.

Stereoisomeric *iso*Fenchocamphoric Acids. A. E. SANDELIN (*Annalen*, 1913, **396**, 285—335).—The constitution,

$$\begin{matrix} CMe_2\cdot CH(CO_2H) \\ | \\ CH_2\cdot CMe(CO_2H) \end{matrix} \!\!>\! CH_2,$$

of *iso*fenchocamphoric acid has been proved by Aschan. Theoretically, six stereoisomerides are possible, four active and two racemic. Wallach has prepared the *cis-d-* and *l*-acids, and has shown that by mixture they produce the *cis-dl*-acid, which has been obtained by Aschan. The latter has also shown that the *cis-dl*-acid is partly changed to the *trans-dl*-acid by warming with glacial acetic and hydrochloric acids. The *trans-d-* and *l*-acids hitherto have been unknown, but have now been prepared by the author. A large

number of derivatives of all the acids have also been prepared for comparative purposes. The two active *cis*-acids behave alike chemically and physically, except in the sign of the rotation; the same is true of the active *trans*-acids. The fact that the *cis*-acid can be changed to the *trans*-acid, and vice versa proves that the two are geometrical isomerides.

trans-d- and l-iso*Fenchocamphoric acids* are prepared by heating the corresponding *cis*-acids for twenty-four hours at 180—200° with a mixture of equal parts of glacial acetic acid and hydrochloric acid, D 1·20. The product, which consists of approximately equal quantities of the *trans*- and the *cis*-acids (the same product is obtained by treating the pure *trans*-acid in the same manner), is treated with acetyl chloride, and the resulting mixture of *cis*-anhydride and *trans*-acid is extracted in a Soxhlet apparatus with carbon tetrachloride, in which the *trans*-acid is insoluble. Another method of partly changing the *cis*- to the *trans*-acid is the hydrolysis of the acid chloride.

cis-*d*- and *l*-*iso*Fenchocamphoric acids crystallise in prisms, have m. p. 158—159°, K 0·00492, $[\alpha]_D^{20}$ +14·58° and −14·54° respectively in alcohol, and solubility (that is, amount dissolved by 100 grams of water at 25°) 1·409 and 1·412 grams respectively; *cis*-*dl*-*iso*fenchocamphoric acid crystallises in leaflets, and has m. p. 174—175°, K 0·00491, and solubility 0·224. *trans*-*d*- and *l*-*iso*Fenchocamphoric acids crystallise in prisms, and have m. p. 149—150·5°, K 0·00419 and 0·00421 respectively, $[\alpha]_D^{20}$ +4·19° and −4·16° respectively, and solubility 0·460 and 0·458 respectively; *trans*-*dl*-*iso*fenchocamphoric acid crystallises in leaflets, and has m. p. 173—174°, K 0·00420, and solubility 0·180.

cis-d- and l-iso*Fenchocamphoric anhydrides* crystallise in prisms, and have m. p. 98° and $[\alpha]_D^{20}$ +13·33° and −13·46° respectively in benzene; *cis*-*dl*-*iso*fenchocamphoric anhydride has m. p. 95—96°. These anhydrides are easily hydrolysed by water.

All the *iso*fenchocamphoric acids are readily esterified by the necessary alcohol and sulphuric acid, and yield, contrary to expectation, mainly the normal esters. *Methyl* cis-d-iso*fenchocamphorate* has b. p. 253—255°/764 mm, D_4^{20} 1·0484, n_D^{19} 1·45166, and $[\alpha]_D^{21}$ +19·17°; the *l*-ester has b. p. 253—255°/780 mm., D_4^{20} 1·0470, n_D^{12} 1·45388°, and $[\alpha]_D^{12}$ −19·06°. *Methyl* cis-dl-iso*fenchocamphorate* has b. p. 252—253°/760 mm., D_4^{20} 1·0490, n_D^{20} 1·45206. *Methyl* trans-d-iso*fenchocamphorate* has b. p. 248—249°/757 mm., D_4^{20} 1·0467, n_D^{15} 1·45267, $[\alpha]_D^{15}$ −1·14°; the l-*ester* has the same b. p., D_4^{20} 1·0471, n_D^{16} 1·45186, $[\alpha]_D^{16}$ +1·18. *Methyl* trans-dl-iso*fenchocamphorate* has b. p. 247—248°/757 mm., D_4^{20} 1·0448, $n_D^{15\cdot5}$ 1·45176. *Ethyl* cis-d-iso*fenchocamphorate* has b. p. 269—271°/764 mm., D_4^{20} 1·0067, n_D^{20} 1·44656, $[\alpha]_D^{20}$ +11·52°; the l-*ester* has b. p. 270—272°/780 mm., D_4^{20} 1·0073°, n_D^{12} 1·44926, and $[\alpha]_D^{12}$ −11·16°. *Ethyl* trans-d-iso*fenchocamphorate* has b. p. 266—267°/750 mm., D_4^{20} 1·0057, n_D^{16} 1·44656, $[\alpha]_D^{20}$ −1·05°; the l-*ester* has the same b. p., D_4^{20} 1·0053, n_D^{20} 1·44646, and $[\alpha]_D^{20}$ +0·99°. *Ethyl* trans-dl-iso*fenchocamphorate* has b. p. 264—265°/750 mm., D_4^{20} 1·0035, n_D^{16} 1·44576.

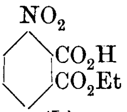
α-Alkyl hydrogen *iso*fenchocamphorates, $\begin{matrix} CMe_2\cdot CH(CO_2R) \\ | \\ CH_2\cdot CMe(CO_2H) \end{matrix}\!\!>CH_2$, are obtained as by-products in the esterification of the acids, and also by

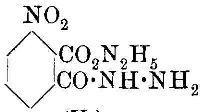
the action of sodium alkyloxides on the anhydrides; β-alkyl hydrogen esters are produced by the partial hydrolysis of the normal esters. These hydrogen esters are, almost without exception, viscous liquids which have not been obtained in a pure state. The dianilides of the *iso*fenchocamphoric acids are obtained from the acid chlorides and aniline in cold ether. cis-d- and l-iso*Fenchocamphordianilides* have m. p. 184—185°, and $[\alpha]_D^{18}$ +26·26° and −26·53° respectively in alcohol, and the dl-*anilide* has m. p. 142—144°. trans-d- and l-iso*Fenchocamphoranilides* have m. p. 190—191° and $[\alpha]_D$ −20·30° and +20·69° respectively in alcohol, whilst the dl-*anilide* has m. p. 185—187°. It is noteworthy that the replacement of the two chlorine atoms of the acid chloride by the anilino-group yields only one of the two possible, geometrically isomeric dianilides, whereas their replacement by hydroxyl gives both *cis*- and *trans*-*iso*fenchocamphoric acids.

Diamides of the *cis*-acids cannot be prepared. By passing dry ammonia into a cold solution of the respective acid chlorides in ethyl acetate, trans-d- and l-iso*fenchocamphordiamides*, $C_{10}H_{18}O_2N_2,H_2O$, m. p. 95—96° and 95—97° respectively, $[\alpha]_D^{17}$ −6·18° and +6·37° respectively in alcohol, and trans-dl-iso*fenchocamphordiamide*, $C_{10}H_{18}O_2N_2$, m. p. 202—204°, are obtained. cis-d- and l-iso*Fenchocamphorimides*, m. p. 120—121°, $[\alpha]_D^{18}$ −12·73° and +12·67° respectively in alcohol, and the dl-*imide*, m. p. 122—123°, are obtained by heating the ammonium salts of the corresponding acids at 180—200° for twenty-four hours. α-cis-l-iso-*Fenchocamphoramic acid*, $\begin{matrix}CMe_2\cdot CH(CO\cdot NH_2)\\ | \qquad\qquad \\ CH_2 — CMe(CO_2H)\end{matrix}\!\!>\!CH_2$, is prepared best by treating a cold ethereal solution of the *cis*-*l*-anhydride with dry ammonia and treating the concentrated aqueous solution of the product with hydrochloric acid. It has m. p. 220° (decomp.), decomposes when heated slowly, has $[\alpha]_D^{20}$ −11·18° in alcohol, and yields *cis*-*l*-*iso*fenchocamphoric anhydride above its m. p. α-cis-d-iso*Fenchocamphoramic acid*, m. p. 220° (decomp.), $[\alpha]_D^{20}$ +10·99° in alcohol, and the α-cis-dl-*isomeride*, m. p. 208° (decomp.), are prepared by similar methods. α-trans-d-, l-, and dl-iso*Fenchocamphoramic acids*, m. p. 210—211°, 210—211°, and 205° respectively, are obtained as by-products in the preparation of the diamides; the active acids have $[\alpha]_D^{18}$ +7·98° and −7·94° respectively in alcohol.

β-cis-d- and l-iso*Fenchocamphoramic acids*, $\begin{matrix}CMe_2 — CH(CO_2H)\\ | \qquad\qquad \\ CH_2\cdot CMe(CO\cdot NH_2)\end{matrix}\!\!>\!CH_2$, m. p. 180—181°, $[\alpha]_D^{18}$ +8·91° and −8·75° respectively in alcohol, and the cis-dl-*isomeride*, m. p. 194—195°, are prepared by boiling the respective imides with aqueous sodium hydroxide for two hours and acidifying. The yield is quantitative, and the acids are only very slowly attacked by boiling water, crystallising therefrom in well-formed needles. β-trans-d- and l-iso*Fenchocamphoramic acids*, m. p. 179—180°, $[\alpha]_D^{17}$ +9·71° and −9·57° respectively in alcohol, and the dl-*isomeride*, m. p. 155—156° (when crystallised from chloroform, the substance forms needles containing $CHCl_3$, m. p. 151—152°), are prepared by acidifying the solution obtained by boiling the respective diamides with the calculated amount of aqueous sodium hydroxide. C. S.

Behaviour of the 1-Ester of 3-Nitrophthalic Acid Towards Hydrazine. THEODOR CURTIUS and AUGUST SEMPER (*Ber.*, 1913, **46**, 1162—1171).—Miller's monoethyl 3-nitrophthalate (I) (A., 1882, 404), the constitution of which is ascertained in the present researches, has been converted into the hydrazine salt of *o*-nitrophthalic monohydrazide (II), and this into the acid hydrazide (III), and finally into the azoimide (IV).


(I.)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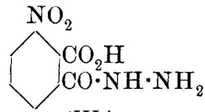
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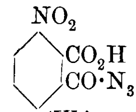
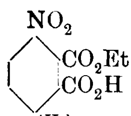

(IV.)

The latter substance loses hydrazoic acid when boiled with water or alcohol, forming *o*-nitrophthalic acid with water and the acid-ester (V) with alcohol. This isomeric acid-ester only gives a hydrazine salt with hydrazine, and, unlike the starting material, it is easily converted into the diethyl ester.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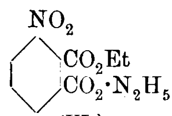
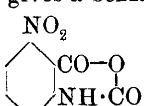
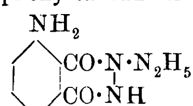
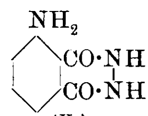

(VI.)

When the acid-azoimide is heated in benzene or chloroform, however, it slowly loses nitrogen and yields *o*-nitroisatoic anhydride (VII). The carbimide (VIII) might have been expected, but the substance gives, on boiling with water, not a carbamide, but 6-nitro-2-aminobenzoic acid, forms a urethane only on prolonged boiling with alcohol, and gives a benzanilide and not a phenylcarbamide with aniline.


(VII.)

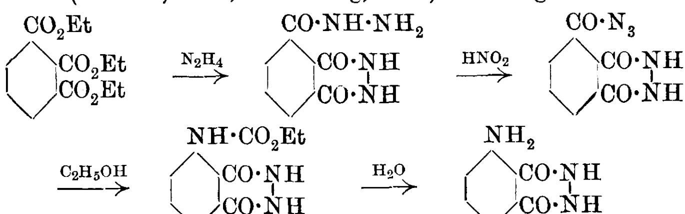

(VIII.)


(IX.)


(X.)

When heated with dilute sulphuric acid, the substance is also deprived of the carboxyl group and converted into *m*-nitroaniline.

If the initial acid-ester be boiled with an excess of hydrazine hydrate, the nitro-group is reduced, and water eliminated from the hydrazine salt of the monohydrazide, with the formation of the hydrazi-compound (IX), which is resolved into the aminohydrazide (X) by water. This compound was also obtained from triethyl *hemi*-mellitate (Schmitz, *Diss.*, Heidelberg, 1902) according to the scheme:



For the preparation of the *hydrazine* salt of o-*nitrophthalic acid monohydrazide* (II), Miller's ester, m. p. 110°, is triturated with hydrazine hydrate. It forms colourless needles, m. p. 157°, which yield the *benzylidene* compound of the acid-hydrazide,

$$CO_2H\cdot C_6H_3(NO_2)\cdot CO\cdot NH\cdot N:CHPh,$$

in small, colourless needles, m. p. 177°, and, with hydrochloric acid, the *acid hydrazide* (III), in flat needles, m. p. above 280°, from which the *azoimide* (IV) is obtained in colourless, shimmering scales by the addition of sodium nitrite to the suspension in concentrated hydrochloric acid. After prolonged boiling with absolute alcohol the azoimide is converted into the *acid-ester* (V), which forms yellow needles, m. p. 157°, but when heated in dry chloroform the product is o-*nitroisatoic anhydride* (VII), which crystallises in pale yellow, flat needles, m. p. 215°, and is isomeric with Kolbe's nitroisatoic anhydride (A., 1885, i, 666), which gave 5-nitro-2-aminobenzoic acid on boiling with water. It gradually dissolves in boiling absolute alcohol, forming the *urethane*, $C_{10}H_{10}O_6N_2$, in faintly yellow, flat needles, m. p. 187°, which yield *m*-nitroaniline with dilute acids. It also forms the *anilide*, $C_{13}H_{11}O_3N_3$, in slender, yellow needles, m. p. 137°.

The *hydrazine* salt of the cyclic *hydrazide* of o-*aminophthalic acid* (IX) results when the starting material is heated with an excess of hydrazine hydrate. The free *hydrazide* (X) is a yellow solid, which behaves as a monobasic acid, forming *barium*, *potassium*, and *sodium* salts. It is also soluble in dilute acids, and gives a blue fluorescence in hot glacial acetic acid (compare Schmitz, *loc. cit.*).

J. C. W.

Preparation of $\alpha\beta$-Diketonic Esters. André Wahl and M. Doll (*Bull. Soc. chim.*, 1913, [iv], **13**, 332—348. Compare A., 1904, i, 556; 1907, i, 217; 1911, i, 108; 1912, i, 536, 625).—This paper discusses in detail the mechanism of the reaction between "nitrous fumes" and acylacetic esters, by means of which the methylene group of the latter is converted into a carbonyl group, with the formation of $\alpha\beta$-diketonic esters. Examples of this reaction have been recorded already (*loc. cit.*). The reaction occurs in two stages: (1) the formation of an oximino-derivative of the acylacetate (A., 1904, i, 556; 1905, i, 409), and (2) the conversion of this oximino-derivative into the corresponding $\alpha\beta$-diketonic ester by the action of "nitrous fumes." The latter were obtained by treating "chamber crystals" with sodium nitrite, and as applied consisted chiefly of N_2O_3 and NO_2 (89·2%) with some NO (10%). The gas resulting from the second phase of the reaction was chiefly N_2 (54%), $N_2O_3+NO_2$ (29%), N_2O (10%), and NO (7%), so that this phase is not unilateral. The following new compounds were prepared.

Methyl benzoylglyoxylate, D_0^0 1·233, b. p. 146—149°/12 mm., is a mobile, orange-yellow liquid, which reduces Fehling's solution and ammoniacal silver nitrate, and yields a *hydrate*, $COPh\cdot CO\cdot CO_2Me,H_2O$, m. p. 65°, crystallising in stellate groups of pearly needles. *Propyl benzoylglyoxylate*, b. p. 155—158°/12 mm., D_0^0 1·159, combines with alcohol or water, but the products are not crystalline. iso*Butyl*

benzoylglyoxylate, D_0^0 1·124, b. p. 161—164°/12 mm., yields a crystalline *monohydrate*, m. p. 62—63°.

Ethyl valeroylglyoxylate, b. p. 100—125°/15 mm., was not obtained pure. T. A. H.

Synthesis of Orsellinic Acid and Everninic Acid. KURT HOESCH (*Ber.*, 1913, **46**, 886—892).—Attempts to synthesise orsellinic acid from orcinol by a process analogous to the salicylic acid synthesis yielded only the isomeric *p*-orsellinic acid. The synthesis could, however, be successfully effected by the oxidation of orcylaldehyde.

Orcylaldehyde, obtained from orcinol by the method of Gattermann (A., 1908, i, 28), was found to undergo oxidation more smoothly after converting the hydroxyl groups into methylcarbonato-groups (compare Fischer and Freudenberg, A., 1910, i, 265) by the action of methyl chlorocarbonate and sodium hydroxide. *Dimethylcarbonato-orcylaldehyde*, $CHO{\cdot}C_6H_2Me{\cdot}(O{\cdot}CO_2Me)_2$, crystallises in needles, m. p. 84—85°, which turn yellow on exposure to light; *methylcarbonato-orcylaldehyde*, $CHO{\cdot}C_6H_2Me(OH){\cdot}O{\cdot}CO_2Me$, obtained by the action of less methyl chlorocarbonate forms prisms, m. p. 79°. *Diethylcarbonato-orcylaldehyde*, needles, m. p. 60°, obtained analogously to the corresponding dimethylcarbonato-compound, behaves similarly to the latter towards oxidation; when treated in acetone solution at 40° with potassium permanganate, they are oxidised to dimethylcarbonato-orsellinic acid (compare Fischer and Hoesch, A., 1912, i, 859) and *diethylcarbonato-orsellinic acid*, prisms, m. p. 112° (decomp.) respectively. These acids are hydrolysed by *N*-sodium hydroxide solution at room temperature, giving satisfactory yields of orsellinic acid,

$$C_6H_2Me(OH)_2{\cdot}CO_2H.$$

If orcylaldehyde is cautiously methylated by methyl sulphate and 2*N*-sodium hydroxide in acetone solution, *everninaldehyde* (2-hydroxy-4-methoxy-6-methylbenzaldehyde) is obtained as needles, m. p. 65°. When heated with anhydrous sodium acetate and acetic anhydride in a sealed tube for five hours at 170—180°, everninaldehyde is converted into *7-methoxy-5-methyl-1 : 2-benzopyrone*, $OMe{\cdot}C_6H_2Me{<}\begin{matrix}CH{=}CH\\ O{-\!-\!-}CO\end{matrix}$, long needles, m. p. 146°, which dissolve in concentrated sulphuric acid, giving a blue fluorescence; the success of this synthesis confirms the structure already assumed for everninaldehyde (Fischer and Hoesch, *loc. cit.*). When an acetone solution of everninaldehyde is carefully treated with methyl chlorocarbonate and sodium hydroxide, *methylcarbonatoeverninaldehyde*, $OMe{\cdot}C_6H_2Me(O{\cdot}CO_2Me){\cdot}CHO$, needles, m. p. 77°, which redden in the light and are phototropic, is obtained. This is oxidisable by potassium permanganate with care to methylcarbonato-everninic acid, silky needles, which decompose near 100°, and can be hydrolysed by *N*-sodium hydroxide at the ordinary temperature to everninic acid, $OMe{\cdot}C_6H_2Me(OH){\cdot}CO_2H$. D. F. T.

Hydrogenation of Santonin. HEINRICH WIENHAUS and WOLFGANG FELIX VON OETTINGEN (*Annalen*, 1913, **397**, 219—246).—By reduction by the Paal-Amberger method, santonin absorbs four atomic proportions of hydrogen, and yields two stereoisomeric tetra-

hydrosantonins. Hence the formulæ of Cannizzaro and Andreocci and of Angeli and Marino, which contain only one ethylenic linking, are disproved. The formulæ of Cannizzaro and Gucci and of Francesconi and Cusmano (A., 1908, i, 272) are permissible, and of the two, the former, $\left.\begin{array}{l} \mathrm{CH_2{\cdot}CMe{:}C{\cdot}CH_2{\cdot}CH{-\!-\!-\!-}O} \\ \mathrm{CO{\cdot}CMe{=}C{\cdot}CH_2{\cdot}CH{\cdot}CHMe} \end{array}\right>\mathrm{CO}$, is preferable.

When the hydrogenation of santonin is discontinued after 1 mol. of hydrogen has been absorbed, it is found, in accord with Paal's experience with substances containing a conjugated system (A., 1912, i, 703), that the addition does not occur in the sense of Thiele's theory; in other words, one half of the santonin is completely reduced, the other half is unattacked.

Santonin is so readily reduced that 50 grams in methyl alcohol, in the presence of 1 gram of palladous chloride, absorbed 10 litres (at 15° and 745 mm.) of hydrogen in ten minutes; the reduction proceeds even with flocculent (non-colloidal) palladium. The products are α- and β-tetrahydrosantonins, the separation of which is effected by taking advantage of the very slight tendency of β-tetrahydrosantonic acid (see below) to lactone-formation.

α-Tetrahydrosantonin, $C_{15}H_{22}O_3$, m. p. 158°, colourless, rectangular leaflets, does not become yellow in light, is unchanged by the action of zinc-dust and warm acetic acid, and forms an *oxime*, m. p. 235—237°, and *semicarbazone*, m.p. 256—258° (decomp.). *β-Tetrahydrosantonin*, $C_{15}H_{22}O_3$, m. p. 105°, stout plates, forms an *oxime*, m. p. 182°, and *semicarbazone*, m. p. 248—250° (decomp.).

During the reduction of anhydrous santoninoxime by the Paal-Amberger method, the oximino-group is attacked, since ammonia and α-tetrahydrosantonin have been isolated from the products. The reduction of aqueous sodium santonate in a similar manner yields *α-tetrahydrosantonic acid*, $C_{15}H_{24}O_4,H_2O$, m. p. 115° (decomp.) (anhydrous, 135—145°), rhombohedral crystals (*sodium* salt, colourless needles or leaflets), and *β-tetrahydrosantonic acid*, $C_{15}H_{24}O_4$, m. p. 200° (decomp.), or 192° slowly heated, colourless plates, which form an *oxime*, $C_{15}H_{25}O_4N$, m. p. 218—220°.

By warming with aqueous sodium hydroxide or carbonate and then acidifying, α-tetrahydrosantonin is converted into α-tetrahydrosantonic acid, which is readily changed back to the lactone by heating, or by keeping its ethereal solution. In a similar manner, β-tetrahydrosantonin is converted into β-tetrahydrosantonic acid. This acid is more stable than the α-isomeride, but is re-converted into β-tetrahydrosantonin by heating at 200° under reduced pressure.

Attempts to convert α-tetrahydrosantonin or the acid into the corresponding β-compounds, and vice versa, have been unsuccessful.

Whilst santonin itself has $[\alpha]_D^{15}$ $-171{\cdot}70°$ in methyl alcohol, α-tetrahydrosantonin has a mean value $+17{\cdot}1°$ ($[\alpha]_D$ of the oxime in chloroform increases from $-38{\cdot}05°$ to $-53{\cdot}07°$ with increase of the concentration from 1·63% to 3·34%); β-tetrahydrosantonin has $[\alpha]_D+41{\cdot}08°$ when prepared directly from santonin and 9·27° when obtained from the β-acid; α-tetrahydrosantonic acid has $[\alpha]_D+20{\cdot}00°$, and the β-acid has $[\alpha]_D+2{\cdot}18°$ (both prepared from the sodium salts). C. S.

Santonin. XI. Tetrahydrosantonin. EDGAR WEDEKIND and E. BENIERS (*Annalen*, 1913, **397**, 246—254. Compare A., 1908, i, 183).—Many of the authors' results are identical with those obtained by Wienhaus and von Oettingen (preceding abstract). However, by the reduction of santonin in acetone by hydrogen ($1\frac{1}{4}$ atmospheres) in the presence of palladous chloride and gum arabic, they have been unable to isolate β-tetrahydrosantonin. The m. p. of α-tetrahydrosantoninoxime is given as 219—220°, and that of the *phenylhydrazone* as 205° (decomp.). α-Tetrahydrosantonin and nitric acid, D 1·4, yield *α-dinitrotetrahydrosantonin*, $C_{15}H_{20}O_7N_2$, decomp. 187°, large, colourless plates, $[\alpha]_D + 105·05°$ in alcohol and 90·22° in chloroform.

By bromination in chloroform at 35—40°, α-tetrahydrosantonin yields *α-bromotetrahydrosantonin*, $C_{15}H_{21}O_3Br$, decomp. 147°, colourless, prismatic needles, $[\alpha]_D + 9·09°$ in chloroform. C. S.

Preparation of 1-Aminoanthraquinone-2-carboxylic Acids and their Derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 256344. Compare A., 1912, i, 979).—*Ethyl* 1-op-*dichloroanilinoanthraquinone-2-carboxylate*, coppery-red needles, is obtained when *ethyl* 1-*chloroanthraquinone-2-carboxylate* (yellow leaflets, m. p. 142°) is boiled for five to six hours with *op*-dichloroaniline in nitrobenzene solution in the presence of cuprous chloride and sodium acetate; the free *acid* obtained by its hydrolysis (alcoholic potassium hydroxide) is a scarlet-red powder. *Methyl* 1-*chloroanthraquinone-2-carboxylate*, m. p. 164°, can also be employed in this reaction. *Ethyl* 1 : 1′-*anthraquinonylaminoanthraquinone-2-carboxylate* forms scarlet-red needles and the free *acid* a violet powder, whilst the isomeric *compounds* from ethyl 1-chloroanthraquinone-2-carboxylate with 2-aminoanthraquinone consist of orange-yellow leaflets and a red powder respectively. The *compound* from 1-amino-4-hydroxyanthraquinone and ethyl 1-chloroanthraquinone-2-carboxylate forms violet-blue needles.

Ethyl 1-*nitroanthraquinone-2-carboxylate*, yellow leaflets, m. p. 232—233°, when condensed with *op*-dichloroaniline gives rise to a *compound*, dark red needles; the free *acid* is a red powder.

F. M. G. M.

Esters of Polycinnamic Acid. CARL LIEBERMANN and M. KARDOS (*Ber.*, 1913, **46**, 1055—1066).—In continuation of previous work (A., 1911, i, 370) on the polymerisation of esters of cinnamic acid, the authors have investigated the two allyl polycinnamates described by Seeligmann (*Diss.*, Karlsruhe, 1906). These two esters, which are termed allyl polycinnamate *A* and *B*, are formed by heating allyl cinnamate in sealed tubes at 210°.

The ester *A* is obtained by heating for six hours, and isolated from the resulting liquid by dissolving in benzene and precipitating with a mixture of alcohol and ether. It separates in heavy, white flocks, sintering at 190—200°, but possesses no definite m. p.

The ester *B* is best prepared by heating allyl cinnamate for fifteen hours and extracting the product with benzene, when it is obtained as a white powder, which becomes brown and decomposes at abou

300°; it differs from the ester *A* in being insoluble in benzene and chloroform.

The two polymerides are hydrolysed by boiling with 25% alcoholic potassium hydroxide, but the amount of allyl alcohol produced is only 10—12% of that to be expected on the assumption that the polymerides are allyl esters of polycinnamic acid $(C_9H_8O_2)_x$. The conclusion is therefore drawn that the double linking of the allyl groups takes part in the polymerisation after the manner indicated in the following formula:

$$\begin{array}{l} CH_2\cdot CHMe\cdot CPh\cdot CH\cdot CO_2\cdot C_3H_5 \\ O\text{——}CO\text{——}CH\text{--}CHPh \end{array}.$$

This view is also confirmed by the behaviour of the ester *A* towards bromine. It combines with bromine very slowly, and after twenty-four hours yields a *bromo*-compound, $(C_{12}H_{12}O_2Br)_x$, the amount of bromine uniting with the ester being only half that which would have been combined had the allyl groups remained intact.

Both polymerides are hydrolysed by alcoholic potassium hydroxide to the corresponding *acids*, which form white, amorphous powders, sintering at 180—190° (decomp. 210—220°), and closely resemble one another

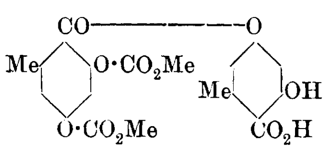
The above esters differ from that obtained by the polymerisation of allyl cinnamate by exposure to light, in solubility, and in being hydrolysed by alkalis.

Allyl cinnamate combines almost instantly with bromine (1 mol.) in chloroform solution, yielding *aβ-dibromopropyl cinnamate* as a viscid oil. Combination with a second molecule takes place more slowly, resulting in the formation of *aβ-dibromopropyl aβ-dibromopropionate*, which crystallises in white needles, m. p. 69—71°.

On exposure to light for nine months, allyl cinnamate yields a *polymeride*, which is precipitated by methyl alcohol in white flocks, m. p. above 300°, and is not hydrolysed by alcoholic potassium hydroxide.

The *polymerides* of benzyl cinnamate (decomp. 270°) and octyl cinnamate have been prepared in a similar manner. F. B.

Methylcarbonato-derivatives of Phenolcarboxylic Acids and their Use for Synthetic Operations. VIII. Derivatives of Orsellinic and α-Resorcylic [3 : 5-Dihydroxybenzoic] Acids. EMIL FISCHER and HERMANN O. L. FISCHER (*Ber.*, 1913, **46**, 1138—1148).—The difficulties attendant on the conversion of dimethylcarbonato-orsellinic acid (3 : 5-dimethylcarbonato-*o*-toluic acid) into its chloride have been overcome (compare A., 1912, i, 860). By coupling the latter with orsellinic acid, the authors have been able to prepare dimethylcarbonato - orsellinoylorsellinic acid (annexed formula), which, when hydrolysed, gives a diorsellinic acid identical with the natural lecanoric acid. A series of compounds has also been prepared from α-resorcylic acid.



Dimethylcarbonato-orsellinyl chloride, $C_6H_2Me(O\cdot CO_2Me)_2\cdot COCl$,

m. p. 53—54°, is obtained by the action of phosphorus pentachloride on dimethylcarbonato-orsellinic acid suspended in chloroform. In suitable circumstances it reacts readily with ethyl alcohol, the corresponding *ethyl* ester being probably formed. In alkaline acetone solution it condenses with *p*-hydroxybenzoic acid, forming 4-dimethylcarbonato-orsellinoyloxybenzoic acid,

$$C_6H_2Me(O{\cdot}CO_2Me)_2{\cdot}CO{\cdot}O{\cdot}C_6H_4{\cdot}CO_2H,$$

m. p. 203—205° (corr. decomp.), after previous softening at about 190°, which in aqueous alcoholic solution does not give a characteristic coloration with ferric chloride. The alkaline salts are sparingly soluble in water. When heated with ammonia, the didepside, 4-*orsellinoyloxybenzoic acid,* is obtained. Difficulty was experienced in obtaining the latter in the crystalline form until a nucleus of the crystalline acid was isolated by decomposition of the *pyridine* salt. The air-dried acid contains $1H_2O$. It has m. p. about 209° (corr. decomp.) after previous softening at about 180°, the value found depending greatly on the mode of heating.

Dimethylcarbonato-orsellinoylorsellinic acid, needles, m. p. 185—187° (corr. decomp.), is obtained by the gradual addition of a solution of dimethylcarbonato-orsellinoyl chloride in acetone to a well-cooled solution of orsellinic acid in acetone and *N*-sodium hydroxide. In aqueous alcoholic solution it gives an intense reddish-violet coloration with ferric chloride. By repeated treatment with methyl chloroformate and alkali in aqueous acetone solution, it yields a crystalline *product*, which gives no coloration with ferric chloride. This can be separated by means of potassium carbonate into a soluble portion, probably *trimethylcarbonatolecanoric acid,* and an insoluble portion which is being investigated. Aqueous sodium hydroxide slowly converts dimethylcarbonato-orsellinoylorsellinic acid into lecanoric acid, colourless needles, having no definite m. p. When quickly heated it softens at about 170°, and is completely melted at 175° with brisk evolution of gas. The air-dried acid contains $1H_2O$. Identity of this product with natural lecanoric acid was established by comparison of m. p., colorations with ferric chloride and bleaching powder, solubility, and crystal form of the two substances, and, further, by the transformation of each into the *trimethyl ether* of *methyl lecanorate,* $C_{20}H_{22}O_7$. The product from the synthetic acid had m. p. 147—148° (corr.), whilst that from the natural acid had m. p. 146—147° (corr.) after softening at 140°. A mixture of the two had m. p. 145—146·5°.

3 : 5-*Dimethylcarbonatobenzoic acid,* prepared by the action of methyl chlorocarbonate on a solution of 3 : 5-dihydroxybenzoic acid in *N*-sodium hydroxide, has m. p. 161—164° (corr.) after slight previous softening. Phosphorus pentachloride converts it into the corresponding *chloride,* colourless needles, m. p. 109—110° (corr.), which, when coupled with *p*-hydroxybenzoic acid in the usual manner, yields 4-(3 : 5-dimethylcarbonatobenzoyl)oxybenzoic acid, $C_6H_3(O{\cdot}CO_2Me)_2{\cdot}CO{\cdot}O{\cdot}C_6H_4{\cdot}CO_2H$, needles, m. p. 161—163° (corr.).

When treated with aluminium chloride and benzene during an hour at 70—75°, and then during forty-five minutes at 75—80°, 3 : 5-dimethylcarbonatobenzoyl chloride yields 3 : 5-*dihydroxybenzophenone,* which separates from water with $1H_2O$. The dry substance has m. p.

160—162° (corr.). If the temperature in the above process is maintained at 40—45° during five hours, no hydrogen chloride is evolved, and a pale yellow *oil* is subsequently obtained, which crystallises when brought into contact with light petroleum. The product, which has not yet been obtained in the pure state, contains the methylcarbonato-groups, and is transformed by alkali into 3 : 5-dihydroxybenzophenone. H. W.

Tannin and the Synthesis of Similar Substances. III. Compounds of High Molecular Weight. EMIL FISCHER and KARL FREUDENBERG (*Ber.*, 1913, **46**, 1116—1138).—The authors have continued their previous work (A., 1912, i, 471, 887), and describe a convenient method of preparing *m*-digallic acid in larger quantities. The properties of this acid resemble those of the digallic acid previously described as the para-compound (A., 1908, i, 893) so closely that the two substances are in all probability identical. It differs considerably, however, from the *m*-digallic acid described by Nierenstein (A., 1910, i, 265).

A series of compounds of high molecular weight has been obtained by the use of tribenzoylgallic acid; for example, hexa-(tribenzoylgalloyl)-mannitol. In the analysis of this and similar compounds, a difficulty is experienced in that the differences in the percentages of carbon and hydrogen are not sufficiently great to allow conclusions to be drawn with regard to the number of acyl groups present. This has been overcome by the introduction of halogen atoms into the molecule, and a series of substances has been prepared from 2 : 4 : 6-tribromophenol-*d*-glucoside and *p*-iodophenylmaltosazone, of which the most interesting is *hepta-(tribenzoylgalloyl)-*p*-iodophenylmaltosazone*,

$$C_{220}H_{142}O_{58}N_4I_2,$$

mol.-wt. 4021. The molecular weight of this and similar substances has been determined in bromoform solution, the observed values being found to agree with those theoretically required without greater divergence than is frequently encountered with much more simply constituted, crystalline substances.

Carbonylogallic acid (*4 : 5 - carbonato - 3 - hydroxybenzoic acid*), $OC{<}^{O}_{O}{>}C_6H_2(OH){\cdot}CO_2H$, is obtained by the addition of a solution of carbonyl chloride in toluene to a well-cooled mixture of gallic acid, acetone, and 2*N*-sodium hydroxide (3 mols.), and subsequent acidification of the product with hydrochloric acid. A full description of the apparatus employed is given. The acid has m. p. about 255° (corr. decomp.). It is sparingly soluble in cold water, and decomposed by hot water with regeneration of gallic acid. Hot methyl alcohol converts it into 3-methylcarbonatogallic acid. In alcoholic solution it gives a faint coloration with ferric chloride, which increases in intensity on keeping. It is transformed by diazomethane into *methyl 4 : 5-carbonato-3-methoxybenzoate*, $OC{<}^{O}_{O}{>}C_6H_2(OMe){\cdot}CO_2Me$, long needles, m. p. 134° (corr.), which, when boiled with water, probably yields methyl 4 : 5-dihydroxy-3-methoxybenzoate. The latter is converted by the successive action of sodium hydroxide and hydro-

chloric acid into 4:5-dihydroxy-3-methoxybenzoic acid, which is apparently identical with the acid obtained by Vogl (A., 1899, i, 698). The latter gives m. p. 199—200° (uncorr.), whereas the authors find about 220° (corr. decomp.), but point out that the observed m. p. depends greatly on the mode of heating.

m-Digallic acid is prepared by the alternate addition of *N*-potassium hydroxide and of a solution of trimethylcarbonatogalloyl chloride in acetone to a cooled solution of carbonylogallic acid in acetone and *N*-potassium hydroxide. The product is treated with *N*-sodium hydroxide and subsequently with hydrochloric acid, when *m*-digallic acid, needles, m. p. about 280° (corr. decomp.) after softening at 260° (corr.), is obtained, the yield being 45% of the theoretical. The acid dissolves in water at 25° in the proportion 1:860, and gives a deep bluish-black coloration with ferric chloride. With aqueous potassium cyanide solution, it yields, after ten seconds, a pink coloration which disappears after a time, but returns on shaking the solution. When boiled during six hours with 1% hydrogen peroxide solution, it yields a dark brown coloration, but no precipitate. With 10% aqueous hydrogen peroxide under similar conditions, a clear solution is formed. In these particulars, the acid differs markedly from Nierenstein's *m*-digallic acid (*loc. cit.*). With diazomethane, it yields methyl 5(3′:4′:5′)-trimethoxybenzoyloxy-3:4-dimethoxybenzoate, which is identical with the product obtained previously (A., 1912, i, 888). Acetic anhydride converts it into *penta-acetyl-*m*-digallic* acid, needles, m. p. 193—194° (corr.), after softening at about 184° (Nierenstein's *m*-digallic acid gave a penta-acetyl derivative, m. p. 211—214°). An attempt to prepare the corresponding pentabenzoyl derivative was unsuccessful.

3:4:5-*Trimethoxybenzoic anhydride*, microscopic needles, m. p. 160—161° (corr.), is obtained by the action of 3:4:5-trimethoxybenzoyl chloride on 3:4:5-trimethoxybenzoic acid in chloroform solution in the presence of quinoline. Similarly, the mixed *anhydride* of 3:4:5-trimethoxybenzoic acid and pentamethyl-*m*-digallic acid, needles, m. p. 165—166° (corr.), is obtained from 3:4:5-trimethoxybenzoyl chloride and pentamethyl-*m*-digallic acid, and is identical with a product previously obtained during the synthesis of pentamethyl-*m*-digallic acid (A., 1912, i, 888).

*Pentamethyl-*p*-digallic acid* is formed in 75% yield from 3:4:5-trimethoxybenzoyl chloride and syringic acid according to the method employed in preparing the *m*-isomeride. It forms leaflets, m. p. 221—222° (corr.). The methyl ester, prepared by the action of diazomethane on the acid, has m. p. 172—173° (corr.), whereas Mauthner (A., 1911, i, 725) found m. p. 169—170°.

Tribenzoylgallyl chloride, $C_6H_2(OBz)_3\cdot COCl$, needles, m. p. 124—126° (corr.), is obtained by the action of phosphorus pentachloride on tribenzoylgallic acid in the presence of chloroform at the ordinary temperature. The corresponding ethyl *ester* has m. p. 126—128° (corr.), whilst the *anhydride*, $C_{56}H_{34}O_{15}$, needles, has m. p. 195—196°, and is more stable towards alcohol than simple substances of this class.

*Tetra-(tribenzoylgalloyl)-tribromophenol-*d*-glucoside*,

$$(C_{28}H_{17}O_7)_4C_6H_7O_6\cdot C_6H_2Br_3,$$

is prepared by the addition of tribromophenol-*d*-glucoside to a solution of tribenzoylgalloyl chloride and quinolin in chloroform. It is a white, amorphous powder, which softens at about 130°, and melts to a clear syrup at about 155°. In tetrachloroethane solution, it has $[\alpha]_D^{20} - 31{\cdot}01°$. *Hexa-(tribenzoylgalloyl)-mannitol*, obtained in a similar manner, has $[\alpha]_D^{20} + 19{\cdot}63°$ in tetrachloroethane solution. It soften at about 125°, and is completely molten at about 150°.

Tetrabenzoylphenylglucosazone, $C_6H_6O_4Bz_4(N_2HPh)_2$, softens at about 100°, is completely molten at about 130°, and begins to decompose at about 140°. When dissolved in acetylene tetrachloride, it has $[\alpha]^{20} - 12{\cdot}16°$ for the Auer light.

p-*Iodophenylmaltosazone*, $C_{12}H_{20}O_9(N_2H{\cdot}C_6H_4I)_2$, prepared by the action of *p*-iodophenylhydrazine on maltosone in aqueous-alcoholic solution, crystallises in yellow needles, m. p. 208° (corr.), after slight previous softening, the m. p., however, varying according to the mode of heating. The solution in pyridine exhibits mutarotation, constant values being probably obtained after three days. For one specimen, $[\alpha]_D^{20}$ was found to be $+83{\cdot}44°$ after eight minutes, $+66{\cdot}51°$ after thirty-two hours, $+66{\cdot}11°$ after forty-eight hours. When treated with tribenzoylgalloyl chloride at the ordinary temperature in the presence of quinoline and chloroform, *p*-iodophenylmaltosazone yields *hepta-(tribenzoylgalloyl)-*p*-iodophenylmaltosazone*,

$$(C_{28}H_{17}O_7)_7C_{12}H_{13}O_9(N_2H{\cdot}C_6H_4I)_2,$$

amorphous, pale yellow powder, which softens at about 145°, and is melted to a red liquid at 160°. In tetrachloroethane solution it has $[\alpha]^{20} - 8{\cdot}75°$.

The molecular weight of the above substances of high molecular weight was determined cryoscopically in bromoform solution, care being taken to obtain them free from any trace of adhering solvent. From experiments on the molecular weight of naphthalene dissolved in bromoform, the value 143 was adopted as constant for the solvent. The following mean results were obtained, the theoretical values being enclosed in brackets: tribenzoylgallic anhydride, 954 (946); tetra-(tribenzoylgalloyl)-tribromophenol-*d*-glucoside, 2036 (2349); hexa-(tribenzoylgalloyl)-mannitol, 2781 (2967); hepta-(tribenzoylgalloyl)-*p*-iodophenylmaltosazone, 3503 (4021). H. W.

Salicylaldehydephenylhydrazone. GEORG LOCKEMANN and FRANZ LUCIUS (*Ber.*, 1913, **46**, 1012—1021. Compare this vol., i, 296).—Salicylaldehyde phenylhydrazone (compare Biltz, A., 1894, 584) can appear in isomeric forms, which, however, do not differ in melting point, but in crystalline form, colour, and solubility. Their formation depends on the conditions of crystallisation and the illumination. The isomerism is therefore physical and not chemical, as supposed by Biltz.

The α-hydrazone is formed in rectangular prisms on slow crystallisation from dilute alcohol or benzene; these are pale or dark green when light is excluded, greyish or brownish-yellow in its presence. The green form occurs in presence of acetic acid; with ammonia the yellow modification is formed.

The β-hydrazone is deposited on quick crystallisation in colourless

needles, which become greenish-yellow on exposure to light. The γ-modification separates from light petroleum in bunches of green needles, which become yellow or orange on exposure. In all three modifications the coloration brought about by light slowly reverses in the dark. All three soften between 135° and 140°, m. p. 142—143°.

When benzoylated in pyridine solution, according to the proportion of benzoyl chloride, the *O*-monobenzoyl or the *O,N*-dibenzoyl derivatives are obtained. When sodium hydroxide is present, the dibenzoyl derivative is the main product, more or less hydrazone remaining unattacked.

On reduction of the dibenzoyl derivative with zinc dust and acetic acid, benzanilide and *o*-hydroxybenzylbenzamide,

$$OH\cdot C_6H_4\cdot CH_2\cdot NH\cdot CO\cdot C_6H_5,$$

are formed.

o-*Benzoylhydroxybenzylbenzamide*, prepared by benzoylating by the Schotten-Baumann process, forms colourless needles, m. p. 141—142°.

When hydrolysed either with cold alcoholic potassium hydroxide or warm alcoholic ammonia, *N*-benzoyl-*o*-hydroxybenzaldehydephenylhydrazone is obtained; it gives a dark bluish-green ferric chloride coloration. E. F. A.

Condensation Product of Piperonaldehyde with Ethyl Urethane. I. G. BIANCHI (*Gazzetta*, 1913, **43**, i, 237—243).—When these substances are heated for half an hour on the water-bath with a little hydrochloric acid, *piperonylidenebisurethane*, $C_{15}H_{18}O_6N_2$, m. p. 177—178°, is obtained; it crystallises in colourless needles. R. V. S.

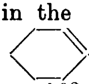
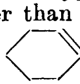
Preparation of Cyclic Ketones. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 256622).—When adipic acid, its homologues, or substitution products are heated they furnish satisfactory yields of the corresponding cyclic ketones; this reaction is conveniently carried out under reduced pressure, in the presence of an inert gas, and of a catalytic reagent, such as oxides, carbonates or other salts of the alkali metals, alkaline earths, or magnesium; of salts of the heavy metals, such as iron, nickel, cobalt, manganese, or uranium; or of phosphoric, boric, or other acids.

*cyclo*Pentanone, b. p. 49—50°/31 mm., is obtained in quantitative yield from adipic acid at 290—295° in the presence of barium hydroxide; with uranium nitrate the yield is 85%, and with ferrous sulphate 90%.

2-Methyl*cyclo*pentanone, b. p. 38°/11 mm. and 57—59°/29 mm., is similarly obtained at 300—305° from β-methyladipic acid, whilst suberic acid furnishes *suberone* (b. p. 179°) at 320—325° in the presence of iron. F. M. G. M.

Terpenes and Ethereal Oils. CXV. OTTO WALLACH (*Annalen*, 1913, **397**, 181—219).—A systematic examination has hitherto not been made of the problem how the position of the oxygen atom in a cyclic ketone influences the b. p. Recent examples in the literature

lead the author to the generalisation that in saturated, isomeric, cyclic ketones containing the same substituents the b. p. is lowest when the heaviest substituent is nearest to the oxygen atom and highest when this substituent is situated as far as possible from the oxygen atom. Since dihydro*iso*camphor has b. p. 211° and carvomenthone has b. p. 220—221°, the generalisation furnishes corroborative evidence that dihydro*iso*camphor is not 1-methyl-5-*iso*propyl*cyclo*hexan-2-one (compare A., 1912, i, 878).

Much more complicated and difficult is the problem of the relations between the constitutions and the b. p.'s of unsaturated cyclic ketones, since in such substances the position of the ethylenic linking must also be taken into account. By reference to the b. p.'s and the constitutions of many unsaturated cyclic ketones, the author shows that (i) ketones in which the ethylenic group and the carbonyl group form a conjugated system have a higher b. p. than isomeric ketones in which such a system does not obtain, and, moreover, that the b. p. is higher when the ethylenic linking in the conjugated system is part of the carbo-cyclic nucleus than when it is attached semicyclically or is present in a side-chain; for example, Δ^1-menthen-3-one, b. p. 235°, pulegone, b. p. 221—222°, and also carvenone, b. p. 232—233°, and dihydrocarvone, b. p. 221—223°; (ii) the replacement of the hydrogen atom in the system ·C:CH·CO· by an alkyl group R is accompanied by a fall in the b. p. which is the more pronounced the greater is the molecular weight of R; for example, 1-methyl-5-*iso*propyl-Δ^1-*cyclo*hexen-3-one, b. p. 244°, Δ^1-menthen-3-one, b. p. 235°, carvotanacetone, b. p. 228—229°, 1-methyl-2-*iso*propyl-Δ^1-*cyclo*hexen-3-one, b. p. 216—217°, and Δ^4-menthen-3-one, b. p. 211°, and (iii) the fall in the b. p. by the conversion of unsaturated ketones of the type –COMe into saturated ketones of the type C_6H_{11}·COMe is about 19°, and is therefore distinctly greater than the fall, about 3—4°, in the b. p. caused by the conversion of –CH_2·COMe into C_6H_{11}·CH_2·COMe.

1:4-*Dimethyl*-Δ^6-cyclo*hexen*-2-*oneoxime*, $NOH{:}C{<}\begin{matrix}CMe{=}CH\\CH_2{\cdot}CHMe\end{matrix}{>}CH_2$, m. p. 92—93°, and another *substance*, m. p. 169°, which is apparently an isomeride, are obtained by warming the nitrosochloride of 1:4-dimethyl-Δ^1-*cyclo*hexene with sodium acetate in glacial acetic acid. By hydrolysis, the former yields 1:4-*dimethyl*-Δ^6-cyclo*hexen*-2-*one* b. p. 189—190°, D^{22} 0·938, n_D^{22} 1·4753 (*semicarbazone*, m. p. 165°), which is oxidised to *p*-xylenol by ferric chloride and glacial acetic acid.

By reduction of Paal's method, 1:4-dimethyl-Δ^6-*cyclo*hexen-2-one yields 1:4-dimethyl*cyclo*hexan-2-one, b. p. 178°, D^{20} 0·9025, n_D^{20} 1·4446 (oxime, m. p. 108—109°, semicarbazone, m. p. 175—176°), which is also obtained by warming 1:4-dimethyl*cyclo*hexan-1:2-diol with dilute sulphuric acid. The saturated ketone and its oxime and semicarbazone have been described, frequently but erroneously, in the literature. By oxidation with chromic and dilute sulphuric acids, it is converted into δ-acetyl-β-methylvaleric acid (semicarbazone, m. p. 146—147°), which in turn is oxidised to β-methyladipic acid by sodium hypobromite.

By reactions similar to the preceding, tetrahydro-*m*-xylene nitrosochloride is converted successively into 1 : 3-*dimethyl*-Δ^2-cyclo*hexen*-4-*oneoxime*, 1 : 3-*dimethyl*-Δ^2-cyclo*hexen*-4-*one* (*semicarbazone*, m. p. 194—195°), and 1 : 3-dimethyl*cyclo*hexan-4-one (this vol., i, 278).

1- imethyl*cyclo*hexan-5-one, b. p. 181·5—182°, D^{19} 0·895, n_D 1·4425 (semicarbazone, m. p. 201°), and 1 : 3-dimethyl*cyclo*hexan-2-one, b. p. 174·5°, D^{20} 0·9140, n_D 1·4476 (oxime, m. p. 114—115°, semicarbazone, m. p. 176—177°), have been prepared and their physical constants and those of the oximes and semicarbazones compared with the values recorded by other investigators.

[With Louis Augspurger.]—By reactions similar to the preceding, 1-methyl-4-ethyl-Δ^3-*cyclo*hexene nitrosochloride has been converted successively into 1-*methyl*-4-*ethyl*-Δ^3-cyclo*hexen*-5-*oneoxime*, m. p. 59—60°, 1-*methyl*-4-*ethyl*-Δ^3-cyclo*hexen*-5-*one*, b. p. 203—204°, D^{19} 0·9310, n_D 1·4759 (*semicarbazone*, m. p. 152—153°), and 1-methyl-4-ethyl*cyclo*hexan-5-one, b. p. 197°, D^{20} 0·9000, n_D 1·4485 (semicarbazone, m. p. 178—181°, oxime, m. p. 80°). By oxidation with chromic acid the last substance yields a ketonic *acid*, $CO_2H\cdot CH_2\cdot CHMe\cdot CH_2\cdot CH_2\cdot COEt$ (*semicarbazone*, m. p. 145°.

1-iso*Propyl*cyclo*hexan*-4-*one*, b. p. 214—214·5°, D^{19} 0·9175, n_D^{19} 1·4561, (*dibenzylidene* compound, m. p. 105°), is obtained by the reduction of 1-*iso*propyl-Δ^1-*cyclo*hexen-4-one (A., 1908, i, 424) by Paal's method. 1-Methyl-3-*iso*propyl-Δ^6-*cyclo*hexen-5-one, b. p. 244° (decomp.), D^{21} 0·9340, n_D^{21} 1·4865 (semicarbazone, m. p. 167°), is reduced by Paal's method to 1-methyl-3-*iso*propyl*cyclo*hexan-5-one, b. p. 221—223°, D^{20} 0·8965, n_D 1·4541.

[With Rud. Müller and Fr. Henjes.]—The low b. p., 212°, of Δ^4-menthen-3-one, in comparison with those of the isomerides, Δ^1-menthen-3-one, 235—237°, carvenone, 232—233°, and carvotanacetone, 228—229°, led the authors to the opinion that an error must have been made either in the b. p. or in the constitution (compare Auwers, A., 1909, i, 592). It is now shown that no error had been committed. *i*-Δ^4-Menthen-3-one, prepared from *i*-menthene, has b. p. 212—213°, D^{20} 0·9165, n_D 1·4726, whilst *l*-Δ^4-menthen-3-one, prepared from menthol, is a yellow liquid having b. p. 211—212°, D^{18} 0·919, n_D 1·4729, and $[\alpha]_D^{18}$ − 67·46° in methyl alcohol. The active substance forms a *semicarbazone*, m. p. 170—171°, and a *dibenzylidene* derivative, yellow needles, m. p. 140—141°, $[\alpha]_D^{20}$ − 58·41° in chloroform. The constitution of the active menthenone is proved by its reduction to *l*-menthone by Paal's method, and ultimately to *l*-menthol by sodium and alcohol. The constitution of the *i*-menthenone has been proved by the synthesis of the ketone from 1-methyl*cyclo*hexan-4-one and magnesium *iso*propyl iodide, the resulting alcohol being dehydrated by dilute sulphuric acid, and the 1-methyl-4-*iso*propyl-Δ^3-*cyclo*hexene being converted through the nitrosochloride into the menthenoneoxime. The low b. p. of Δ^4-menthen-3-one, therefore, must be due to the position of the *iso*propyl group between the carbonyl group and the ethylenic group (compare above).

[With Fr. Henjes.]—Since little is accurately known of the derivatives of *i*-menthone, a large quantity of this ketone has been prepared by reducing Δ^1-menthen-3-one by Paal's method. It has b. p. 210°,

D^{20} 0·8975, n_D 1·4521, and forms a semicarbazone, m. p. 212°, oxime, m. p. 79—80° (benzoyl derivative, m. p. 69—70°), *iso*oxime, m. p. 87—88°, hydrochlorobenzylidene derivative, m. p. 119—120°, and yields a mixture of menthols by reduction. The reduction of *i*-menthoneoxime yields *i*-menthylamine, b. p. 208°, which forms a hydrochloride, m. p. above 250°, carbamide, m. p. 151—152°, phenylmenthylcarbamide, m. p. 135—136°, phenylthiocarbamide, m. p. 136—137°, and benzylidene compound, m. p. 141—142°. C. S.

Pinacolin Transformation. II. Asymmetric Cyclic and Acyclic Pinacones and Their Transformation Products. HANS MEERWEIN (*Annalen*, 1913, **396**, 200—263. Compare A., 1910, i, 856).—A thorough examination of the reaction whereby 1-*iso*propyl-*cyclo*pentane-1-α-diol is converted into 1 : 1-dimethyl*cyclo*hexan-2-one and of analogous reactions has led to the following important generalisations in connexion with the pinacolin transformation: (i) the pinacolin transformation is a true, intramolecular, atomic rearrangement; intermediate products cannot be isolated; (2) the course of the transformation is conditioned by different factors depending on the structure of the pinacone. In symmetric pinacones of the type $CRR'(OH)\cdot CRR'\cdot OH$, the transformation depends only on the relative ease of mobility of the groups R and R′, whilst in asymmetric pinacones, $CR_2(OH)\cdot CR'_2\cdot OH$, the stability of the hydroxyl groups is the determining factor; (3) by a study of the pinacolin transformation, it is possible, not only experimentally to ascertain the different stabilities (that is, the strength of their attachment to the carbon atoms) of the hydroxyl groups in asymmetric pinacones, but also, since such stability is determined mainly by the stabilities of the radicles attached to the same carbon atom, the relative strengths of the attachment of these radicles.

[With HANS PROBST.]—The interaction of methyl *cyclo*pentan-1-ol-1-carboxylate and an excess (4—5 mols.) of magnesium ethyl bromide or magnesium phenyl bromide leads by the usual method to the formation of 1-*hydroxy*-1-α-*ethylpropyl*cyclo*pentan*-1-*ol*,

$$\begin{matrix}CH_2\cdot CH_2\\ |\\ CH_2\cdot CH_2\end{matrix}\!\!>C(OH)\cdot CEt_2\cdot OH,$$

m. p. 39·5°, b. p. 136°/25 mm., and 1-α-*hydroxybenzhydryl*cyclo*pentan*-1-*ol*, $\begin{matrix}CH_2\cdot CH_2\\ |\\ CH_2\cdot CH_2\end{matrix}\!\!>C(OH)\cdot CPh_2\cdot OH$, m. p. 125°, colourless prisms, respectively. The former is converted by concentrated sulphuric acid at −10° into a mixture of 1 : 1-*diethyl*cyclo*hexan*-2-*one*,

$$CH_2<\begin{matrix}CH_2-CO\\ CH_2-CH_2\end{matrix}>CEt_2,$$

b. p. 93·5°/15 mm., D^{20} 0·9236, n_D^{20} 1·4621 (the constitution of which is proved by its oxidation to αα-*diethyladipic acid*,

$$CO_2H\cdot CEt_2\cdot CH_2\cdot CH_2\cdot CO_2H,$$

m. p. 90—92°, by nearly boiling 30% nitric acid), and 1-*propionyl*-1-*ethyl*cyclo*pentane*, $\begin{matrix}CH_2\cdot CH_2\\ |\\ CH_2\cdot CH_2\end{matrix}\!\!>CEt\cdot COEt$, b. p. 86°/16 mm., D^{20} 0·9104, n_D^{20} 1 4525, which is oxidised to 1-*ethyl*cyclo*pentane*-1-*carboxylic acid*,

m. p. −8°, b. p. 132°/18 mm., by nearly boiling 40% nitric acid. The separation of the mixture is readily effected by means of the semicarbazones, the *semicarbazone*, m. p. 202—203°, rhombic leaflets, of the *cyclo*hexane derivative being sparingly soluble in alcohol or other solvents, whilst the *semicarbazone*, m. p. 148·5°, slender needles, of the *cyclo*pentane derivative is easily soluble.

The pinacolin transformation of 1-α-hydroxybenzhydryl*cyclo*pentan-1-ol by cold concentrated sulphuric acid yields only 1 : 1-*diphenyl*cyclo*hexan-2-one*, m. p. 99°, stout needles (*semicarbazone*, m. p. 240°), by the oxidation of which by chromic and acetic acids benzophenone is produced.

[With F. Kremers.]—The product of the pinacolin transformation of 1-*iso*propyl*cyclo*hexane-1-α-diol contains about 33% of 1:1-*dimethyl*cyclo*heptan-2-one* (*semicarbazone*, m. p. 169°) in addition to the 1-acetyl-1-methyl*cyclo*hexane described by Tarbouriech.

1-α-*Hydroxybenzhydryl*cyclo*hexan-1-ol*,

$$CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C(OH)\cdot CPh_2\cdot OH,$$

m. p. 130°, stout prisms, prepared from methyl*cyclo*hexan-1-ol-1-carboxylate and magnesium phenyl bromide, is transformed by concentrated sulphuric acid at 0° into the *ethylene oxide*,

$$CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}O\\ |\\ CPh_2\end{matrix},$$

m. p. 92—94°, rhombic prisms, which does not react with semicarbazide and is oxidised to benzophenone, glutaric and adipic acids by chromic and acetic acids.

[With F. Kremers and R. Splittegarb.]—Ethyl 9-hydroxyfluorene-9-carboxylate reacts in the usual manner with an excess, 7—8 mols., of magnesium methyl iodide, magnesium ethyl bromide, or magnesium phenyl bromide to form, ultimately, 9-*β-hydroxy*iso*propylfluorenol*, $\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}>C(OH)\cdot CMe_2\cdot OH$, m. p. 101°, large, colourless needles, 9-*hydroxydiethylmethylfluorenol*, $\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}>C(OH)\cdot CEt_2\cdot OH$, m. p. 106°, colourless needles, and 9-α-*hydroxybenzhydrylfluorenol*,

$$\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}>C(OH)\cdot CPh_2\cdot OH,$$

m. p. 160—162°, slender needles, respectively. By cold concentrated sulphuric acid the first is transformed into 9-*acetyl-9-methylfluorene*, $\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}>CMe\cdot COMe$, m. p. 89°, b. p. 181°/18 mm. (*semicarbazone*, m. p. 254—256°), the second into 9-*propionyl-9-ethylfluorene*, m. p. 58° (*semicarbazone*, m. p. 236°), and the last, which is readily decomposed into benzophenone and fluorenol by 10% alcoholic potassium hydroxide, into 9 : 9-*diphenylphenanthrone*, $\begin{matrix}C_6H_4\cdot CPh_2\\ |\qquad\ |\\ C_6H_4\cdot CO\end{matrix}$, m. p. 197°, rhombic prisms. The constitution of 9-acetyl-9-methylfluorene is proved by its decomposition into 9-methylfluorene and acetic acid by alcoholic potassium hydroxide, and by its oxidation to 9-*methylfluorene-9-carboxylic acid*,

m. p. 166°, glistening leaflets, by 10% sodium hypobromite. 9 : 9-Diphenylphenanthrone is identical with the substance described as *s*-diphenyldiphenylene-ethylene oxide by Werner and Grob, but that it has the constitution denoted by its name is proved by the fact that it yields the acid, $CHPh_2\cdot C_6H_4\cdot C_6H_4\cdot CO_2H$, by heating with alcoholic potassium hydroxide. Similarly, the pinacolins obtained by Zincke and Tropp from a series of pinacones prepared from phenanthraquinone and magnesium alkyl haloids, and regarded by them as α-pinacolins (*s*-dialkyldiphenylene-ethylene oxides), are probably 9 : 9-dialkylphenanthrones, since the methyl compound (9 : 9-dimethylphenanthrone), for example, is converted into 2-iso*propyldiphenyl*-2′-*carboxylic acid*, $CHMe_2\cdot C_6H_4\cdot C_6H_4\cdot CO_2H$, m. p. 104—106°, by potassium hydroxide at 220—240°.

[With R. SPLITTEGARB.]—Acyclic, asymmetric pinacones have been prepared as similar as possible in structure to the preceding cyclic pinacones. Methyl α-hydroxy*iso*butyrate reacts with magnesium ethyl or phenyl bromide to form, ultimately, *β-methyl-γ-ethylamylene βγ-glycol*, $OH\cdot CMe_2\cdot CEt_2\cdot OH$, b. p. 99—101°/19 mm., and *αα-diphenyl-β-methylpropylene glycol*, $OH\cdot CPh_2\cdot CMe_2\cdot OH$, m. p. 91°, respectively. *βγ-Dimethylamylene βγ-glycol*, $OH\cdot CMe_2\cdot CMeEt\cdot OH$, b. p. 94—95°/21 mm., is prepared from *methyl methylethylglycollate*, b. p. 151·6—152° (the *ethyl* ester has b. p. 162°, and the *acid* itself has b. p. 133—134°/16 mm.), and magnesium methyl iodide.

β-Methyl-γ-ethylamylene βγ-glycol is transformed by concentrated sulphuric acid into *ethyl* tert.-*amyl ketone*, $CMe_2Et\cdot COEt$, b. p. 150·5—152°, D^{20} 0·8298 (*semicarbazone*, m. p. 98°), the constitution of which is proved by its oxidation to αα-dimethylbutyric acid by aqueous sodium hypobromite. By the pinacolin transformation, βγ-dimethylamylene βγ-glycol yields *methyl* tert.-*amyl ketone*,

$$CMe_2Et\cdot COMe,$$

b. p. 130·6°, D^{20} 0·8243 (*semicarbazone*, m. p. 136—138°), which also yields αα-dimethylbutyric acid by oxidation. αα-Diphenyl-β-methylpropylene-αβ-glycol is transformed by cold concentrated sulphuric acid into methyl αα-diphenylethyl ketone, m. p. 41°, which is oxidised to αα-diphenylpropionic acid by sodium hypobromite.

[With F. KREMERS.]—*Bromodiphenylacetic acid*, $CPh_2Br\cdot CO_2H$, m. p. 133—134°, prepared from benzilic acid and hydrogen bromide in glacial acetic acid at 0°, is readily converted by methyl alcohol and sulphuric acid into methyl methoxydiphenylacetate, b. p. 191°/16 mm., m. p. 29°, which reacts with magnesium methyl iodide to form, ultimately, *γ-methoxy-γγ-diphenyl-β-methylpropane-β-ol*,

$$OMe\cdot CPh_2\cdot CMe_2\cdot OH,$$

m. p. 45—47°, b. p. 181—182°/16 mm.; the latter is converted by cold concentrated sulphuric acid into methyl αα-diphenylethyl ketone, not into ω-phenyl-ωω-dimethylacetophenone.

[By the AUTHOR.]—The various explanations of the pinacolin transformation are stated and criticised. The most widely accepted theory assumes the intermediate formation of ethylene oxides, but is not in agreement with observations of the author, Tiffeneau, Montagne, and others. The formation of tangible, intermediate products has not been observed, the transformation occurring by loss of water and the

migration of one group. The water must be eliminated before the migration occurs, because *s*- and *as*-diphenylmethylpropylene glycol yield the same pinacolin, $CPh_2Me\cdot COMe$, and *s*- and *as*-dimethyldiethylethylene glycol also produce the same pinacolin, $CMe_2Et\cdot COEt$. If these changes are explained by an interchange in position of a hydroxyl and an alkyl or aryl group and subsequent elimination of water, the author claims that sometimes one group, sometimes another, changes position with the hydroxyl group without any regularity or obvious reason.

The first step in the transformation, therefore, is

$$OH\cdot CR_2\cdot CR_2\cdot OH \longrightarrow \cdot CR_2\cdot CR_2\cdot O\cdot .$$

The complex then changes to a stable state, either $O<\begin{matrix}CR_2\\|\\CR_2\end{matrix}$, which is quite exceptional, or $CR_3\cdot COR$. Symmetric pinacones,

$$OH\cdot CRR'\cdot CRR'\cdot OH,$$

contain hydroxyl groups of like function, and therefore yield, by loss of water, the complex $\cdot CRR'\cdot CRR'\cdot O\cdot$. The final state of this complex depends on the relative mobilities of R and R'; in general, the methyl group migrates more readily than its homologues, aliphatic groups less readily than aromatic, and substituted aromatic groups more readily than the phenyl radicle. In asymmetric pinacones, $OH\cdot CR_2\cdot CR'_2\cdot OH$, the hydroxyl groups are not of similar function, and, therefore, the first step of the pinacolin transformation may be the formation of $\cdot CR_2\cdot CR'_2\cdot O\cdot$ or $\cdot CR'_2\cdot CR_2\cdot O\cdot$ or both, the actual course being determined by the relative stabilities of the two hydroxyl groups. When the stabilities are about equal, two products are obtained, as, for example, 1 : 1-diethyl*cyclo*hexan-2-one and 1-propionyl-1-ethyl*cyclo*pentane from 1-hydroxydiethylmethyl*cyclo*pentan-1-ol. Hitherto, nothing has been known of the influence of alkyl groups on the stability of hydroxyl groups; since *as*-dimethyldiethylethylene glycol is transformed into ethyl tert.-amyl ketone, it appears that the hydroxyl group in the neighbourhood of the heavier alkyl group has the greater stability. C. S.

Syntheses by means of Sodamide. ALBIN HALLER and ÉDOUARD BAUER (*Ann. Chim. Phys.*, 1913, [viii], **28**, 373—414).—A résumé of information on this subject, referring principally to the results recorded in the following Abstracts: 1909, i, 108, 654; 1911, i, 726, and 1912, i, 270. T. A. H.

A Fourth Modification of Benzophenone. WALTER A. WAHL (*Chem. Zentr.*, 1913, i, 813—814; from *Öfvers. Finska Vetens. Soc. Förhandl.*, 1911, **54**, *A*, 10. Compare A., 1912, ii, 1044).—When benzophenone is melted in a narrow, thin-walled glass tube at 50°, and then plunged into a carbon dioxide-ether mixture, a vitreous mass is obtained which develops spherulitic groups of fibrous crystals at $-60°$ to $-65°$ which melt at $-51°$. Tammann observed that the speed of crystallisation of stable benzophenone (I) below $-40°$ is so small that this form cannot be produced at such low temperatures at all. The new labile modification (IV) can therefore melt without

passing into the stable form. The other modifications are Tammann's (II) with m. p. 45—48° and Zincke's (III), m. p. 26°. J. C. W.

Anthracene. III. Derivatives of Anthrone. KURT H. MEYER and ALBERT SANDER (*Annalen*, 1913, **396**, 133—151).—The influence of substituents in position 9 on the desmotropy of anthrone has been further examined. Anthrone itself, even in solution, exists chiefly in the ketonic modification; anthraquinol and its methyl ether, however, are mainly enolic.

On account of its non-fluorescence, insolubility in cold alkalis, and indifference to alcoholic bromine, 9-phenylanthrone exists in the ketonic form. By solution in hot alkali and precipitation by acid in the cold, it is obtained in the form of *9-phenylanthranol*,

$$C_6H_4{<}{\genfrac{}{}{0pt}{}{C(OH)}{CPh}}{>}C_6H_4,$$

which is sulphur-yellow and yields intensely fluorescent solutions; by keeping or by crystallisation, the anthranol reverts to the anthrone.

The equilibrium of the two modifications of this substance (and also of the following substances) in solution has been determined as follows. An alcoholic solution, about 0·1%, at the ordinary temperature is intensely illuminated by an iron arc and is titrated with $N/10$-alcoholic bromine. Since only the enolic form reacts with bromine and is fluorescent, the disappearance of the fluorescence furnishes a sharp end-point. The same result is attained by starting with the anthrone or the anthranol, provided that the solution has been kept for a sufficiently long time. By this method it is shown that glacial acetic acid favours the formation of the ketonic modification, that all anthrone derivatives are immediately converted into anthranols by pyridine, that equilibrium is not attained in benzene or chloroform even after prolonged boiling, and that the velocity of transformation in alcohol is very much increased by the addition of concentrated hydrochloric acid and, still more, of sodium acetate.

9-Nitroanthrone, which is readily obtained by the nitration of anthrone in glacial acetic acid by nitric acid, D 1·5, at 60°, is converted into 9-nitroanthranol (Meisenheimer's *aci*-nitroanthrone) by solution in hot alkali and precipitation in the cold by acids. After equilibrium has been established in alcohol, the solution contains 97% of the ketonic form. The end-point is readily detected, since 9-nitroanthranol is yellow, and 9-nitroanthrone is colourless, in solution. 9-Nitroanthrone is converted into *9-nitroanthranyl acetate*,

$$C_6H_4{<}{\genfrac{}{}{0pt}{}{C(OAc)}{C(NO_2)}}{>}C_6H_4,$$

m. p. 182°, citron-yellow leaflets or needles, by acetyl chloride in cold pyridine, and into *9-nitroanthranyl benzoate*, m. p. 238° (decomp.), amber-yellow prisms, by benzoyl chloride and pyridine on the water-bath.

9-Anilinoanthrone, $C_6H_4{<}{\genfrac{}{}{0pt}{}{CO}{CH(NHPh)}}{>}C_6H_4$, m. p. 154—156°, reddening at 146°, faintly yellow needles, prepared from 9-bromoanthrone and aniline in boiling benzene, is converted by treatment

with alcoholic potassium hydroxide and subsequent acidification into 9-*anilinoanthranol*, $C_6H_4<\begin{smallmatrix}-C(OH)-\\C(NHPh)\end{smallmatrix}>C_6H_4$, m. p. 155°, reddish-brown crystals, which forms orange-red solutions with intense yellowish-green fluorescence. The alcoholic solution, after several days, contains about 80% of the anthranol. Both forms are converted into anthraquinol and aniline by boiling dilute acids and alcohol. 9-Anilino-anthrone is converted into 9-*aniloanthrone*, $C_6H_4<\begin{smallmatrix}-CO-\\C(:NPh)\end{smallmatrix}>C_6H_4$, m. p. 123—124°, red needles, by alcoholic potassium hydroxide and potassium ferricyanide, and into 9-*anilinoanthranyl benzoate*,

$$C_6H_4<\begin{smallmatrix}-C(OBz)-\\C(NHPh)\end{smallmatrix}>C_6H_4,$$

m. p. 226°, yellow crystals, by benzoyl chloride and cold pyridine.

9-*β-Naphthylaminoanthrone*, m. p. 179—180°, yellow needles, 9-*β-naphthylaminoanthranol*, m. p. 187—188°, bluish-black needles, and 9-*β-naphthyliminoanthrone*, m. p. 167—168°, dark red crystals, are prepared by methods similar to the preceding.

With the object of preparing 9-aminoanthrone, a cold solution of 9-bromoanthrone in dry benzene was saturated with ammonia. The product, however, is 9-*bromodianthrone*,

$$CO<\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}>CBr\cdot CH<\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}>CO,$$

amber crystals, which, above its m. p., 187°, or by boiling with xylene and copper powder, is converted into dianthrone. 9-Aminoanthrone in a very impure state is produced by reducing benzeneazoanthranol with zinc dust and alcoholic sodium hydroxide in an atmosphere of nitrogen. C. S.

Experiments on the Determination of the Constitution of Enolic Substances. JOHANNES SCHEIBER and PAUL HEROLD (*Ber.*, 1913, **46**, 1105—1110).—The authors have attempted to apply the use of ozone and subsequent decomposition of the ozonide formed for the determination of the constitution of enolic substances. The advantages claimed for the method are that operations can be carried out at low temperatures and that the addition of ozone, as far as is yet known, takes place without previous structural alteration of the substances investigated.

A solution of benzoylacetone in chloroform was treated with ozone and the ozonide subsequently decomposed by warm water. The cooled solution deposited an almost quantitative amount of benzoic acid, whilst the filtrate, when treated with phenylhydrazine, yielded methylglyoxalosazone, m. p. 146° (Harries and Türk, A., 1905, i, 413, give 145°). Neither acetic acid nor carbon dioxide could be detected. Benzoylacetone appears therefore to be enolised according to the formula OH·CPh:CH·COMe, which confirms the work of Smedley (T., 1910, **97**, 1486).

Oxalacetone, when similarly treated, gave a 93·5% yield of oxalic acid, from which it follows that enolisation must also have occurred to some extent towards the acetyl group. Although acetic acid could not

be detected, this is confirmed by the fact that phenylhydrazine did not yield pure methylglyoxalosazone.

The ozonide obtained in small quantity from ethyl acetoacetate, when decomposed by water, yielded with phenylhydrazine acetate a precipitate of pure ethyl phenylhydrazonoglyoxylate,

$$NHPh\cdot N\colon CH\cdot CO_2Et,$$

m. p. 128° (Reissert, A., 1895, i, 461, gives 129°; v. Pechmann, 1896, i, 678, finds 130—131°), from which the formula $OH\cdot CMe\colon CH\cdot CO_2Et$ is deduced for the enolised ester.

Ethyl benzoylacetoacetate under similar treatment gave rise to benzoic acid and to the somewhat impure osazone of ethyl diketobutyrate, $CMe(N_2HPh)\cdot C(N_2HPh)\cdot CO_2Et$. Although the benzoic acid formed has not yet been estimated, the enolised form of ethyl benzoylacetoacetate must possess mainly the configuration

$$OH\cdot CPh\colon C(COMe)\cdot CO_2Et.$$

Diacetylbenzoylmethane, m. p. 34°, similarly yielded benzoic acid mixed with small quantities of a substance which could not be identified with certainty, whilst, after removal of benzoic acid, the bisphenylhydrazone of triketopentane, m. p. 155° (Sachs and Barschall, A., 1901, i, 670, give 156°), was isolated by means of phenylhydrazine. The authors conclude that the enolised form of diacetylbenzoylmethane consists mainly of the α-form, $CPh(OH)=C<\begin{smallmatrix}COCH_3\\COCH_3\end{smallmatrix}$, probably mixed with small amounts of the β-variety, $CMe(OH)=C<\begin{smallmatrix}COCH_3\\CO\cdot C_6H_5\end{smallmatrix}$.

H. W.

Phthalylglycyl Derivatives of Acetylacetone, Benzoylacetone, and Ethyl Cyanoacetate. JOHANNES SCHEIBER [with K. KLOPPE and K. SCHNABEL] (*Ber.*, 1913, **46**, 1100—1105).—The author has extended his work on the condensation of ethyl sodioacetoacetate with phthalylglycyl chloride (A., 1909, i, 390).

The sodium derivative of acetylacetone reacts readily with phthalylglycyl chloride in the presence of ether or benzene. The main product of the reaction is *bisphthalylgylcylacetylacetone*, smaller quantities of C-*phthalylglycylacetylacetone* and o-*phthalylglycylacetylacetone* being also formed. The latter substance is, however, mainly formed when the silver derivative of acetylacetone is substituted for the sodium derivative. If the reaction is carried out in boiling benzene solution, *phthalylglycyl anhydride* is also obtained.

Bisphthalylglycylacetylacetone,

$$C_6H_4<\begin{smallmatrix}CO\\CO\end{smallmatrix}>N\cdot CH_2\cdot CO\cdot O\cdot CMe\colon C(COMe)\cdot CO\cdot CH_2\cdot N<\begin{smallmatrix}CO\\CO\end{smallmatrix}>C_6H_4,$$

has a variable m. p., probably due to partial enolisation. Thus, a product, m. p. 182° (highest observed m. p.), after recrystallisation from glacial acetic acid had m. p. 168°. Cold sodium ethoxide converts it into *C*-phthalylglycylacetylacetone. With aniline it yields *phthalylglycylacetylacetone anilide*, $C_6H_4\colon(CO)_2\colon N\cdot CH_2\cdot CO\cdot C(COMe)\colon CMe\cdot NHPh$, yellow needles, m. p. 172°. Phenylhydrazine converts it into *phthalylglycylacetylacetonepyrazolephenylhydrazone* (formula I or II), lemon-yellow leaflets, m. p. 192°, the same substance being obtained from the

above anilide or from *C*-phthalylglycylacetylacetone. It is not decomposed by sodium hydroxide, does not reduce Fehling's solution, and gives a blue coloration with ferric chloride when dissolved in concentrated sulphuric acid.

$$C_6H_4{:}(CO)_2{:}N\cdot CH_2\cdot C(N_2HPh)\cdot C{<}\begin{matrix}CMe{=}N\\ \vert \\ CMe{-}NPh\end{matrix}.$$

(I.)

$$NPh{<}\begin{matrix}CMe{:}C\cdot CMe{:}N_2HPh\\ \vert \\ N{=}C\cdot CH_2\cdot N{:}(CO)_2{:}C_6H_4\end{matrix}.$$

(II.)

C-Phthalylglycylacetylacetone, m. p. 124°, is soluble in aqueous sodium hydroxide without decomposition, and gives an immediate blood-red coloration with alcoholic ferric chloride.

O-Phthalylglycylacetylacetone, m. p. 107°, is insoluble in aqueous sodium hydroxide, and yields a red coloration with ferric chloride after some time. It is decomposed by a solution of phenylhydrazine in glacial acetic acid with formation of *phthalylglycylphenylhydrazide*, $C_6H_4{:}(CO)_2{:}N\cdot CH_2\cdot CO\cdot NH\cdot NHPh$, m. p. 192°, which was also prepared from phthalylglycyl chloride and phenylhydrazine. When, however, the free acid was heated with phenylhydrazine in dilute acetic acid solution, the main product was anilinophthalimide, $C_6H_4{:}(CO)_2{:}N\cdot NHPh$, m. p. 179°.

Phthalylglycyl anhydride, $C_{20}H_{12}O_7N_2$, white needles, m. p. 242°, is transformed by phenylhydrazine into phthalylglycylphenylhydrazide, and by aniline into phthalylglycylanilide, m. p. 231—232°. The latter substance was also obtained from phthalylglycyl chloride and aniline.

The action of phthalylglycyl chloride on the sodium derivative of benzoylacetone yields *bisphthalylglycylbenzoylacetone* and O-*phthalylglycylbenzoylacetone*. The former, m. p. 151°, gradually gives a red coloration with ferric chloride in alcoholic solution, and is converted by cold sodium alkoxide into C-*phthalylglycylbenzoylacetone*, m. p. 135°. The latter immediately gives an intense red coloration with ferric chloride.

O-Phthalylglycylbenzoylacetone, m. p. 147—148°, gives no coloration with ferric chloride, and is insoluble in sodium hydroxide. Phenylhydrazine eliminates the phthalylglycyl radicle.

With ethyl sodiocyanoacetate, phthalylglycyl chloride yields practically solely *ethyl phthalylglycylcyanoacetate*, long needles, m. p. 149°. The ester is immediately soluble in alkali and alkali carbonate solutions, and gives an immediate intense red coloration with ferric chloride. An alcoholic solution of phenylhydrazine converts it into phthalylglycylphenylhydrazide. In glacial acetic acid solution at the ordinary temperature, however, phenylhydrazine converts it into a *substance*, $C_{21}H_{20}O_5N_4$, m. p. 156°, which is probably an additive product. It is soluble in sodium hydroxide, does not give Bülow's reaction, and reduces Fehling's solution in the cold. Concentrated sulphuric acid regenerates the ester.
H. W.

Action of Hydrochloric Acid on *p*-Benzoquinonesulphonic Acid. ALPHONSE SEYEWETZ (*Compt. rend.*, 1913, **156**, 901—903).—Concentrated hydrochloric acid acting on sodium *p*-benzoquinone-

sulphonate at temperatures below 20° yields after twelve hours a crystalline mass of *sodium chloroquinolsulphonate*, $C_6H_2Cl(OH)_2\cdot SO_3Na$, white needles, soluble in water, instantly reducing silver nitrate. On oxidation it is converted into chloro-*p*-benzoquinonesulphonic acid.

If the reaction takes place at above 20°, the products are chloroquinol and 2 : 6-dichloroquinol. W. G.

Action of Nitrous Acid on Dianilino-*p*-benzoquinoneanil. CONSTANTIN I. ISTRATI and M. A. MIHAILESCU (*Bull. Acad. Sci. Roumaine*, 1912/3, **1**, 25—29. Compare Istrati, A., 1903, i, 82).—When an excess of sodium nitrite is added to a solution of dianilino-*p*-benzoquinoneanil in cold glacial acetic acid, a number of *products* are obtained, of which three, m. p. 209°, 248° and 286° respectively, have been isolated. The first of these separates from toluene in brilliant red leaflets. It is not attacked by boiling solutions of alkali hydroxides. It dissolves in concentrated sulphuric acid and in fuming nitric acid, but is precipitated unchanged when these solutions are diluted with water. It gives Liebermann's reaction, but the presence of a nitro-group could not be established. The formula,

$$NO\cdot NPh\cdot C{<}{\begin{matrix}CH\text{———}CO\\C(NPh)\cdot CH\end{matrix}}{>}C\cdot N{:}C{<}{\begin{matrix}CH{:}CH\\CH{:}CH\end{matrix}}{>}CO,$$

is assigned to it, the dinitrosoamine first formed undergoing partial rearrangement with the formation of the oxime of a substituted *p*-benzoquinoneimide, from which the *p*-benzoquinone is formed by elimination of hydroxylamine. H. W.

Metaquinonoids. RICHARD MEYER (*Ber.*, 1913, **46**, 1220).—Stark and Garben (this vol., i, 361) relying on the earlier work of Meyer and Desamari (A., 1908, i, 658) included Liebermann and Dittler's tribromoresoquinone as a substance of metaquinonoid type. Later experiments of these authors, however, had already shown that the compound was a bimolecular keto-bromide, $C_{12}H_2O_4Br_6$ (A., 1909, i, 241, 657). J. C. W.

Preparation of Anthraquinone from Anthracene. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 256623).—Anthraquinone is obtained in 94—96% yield when an intimate mixture of anthracene, glass wool, or asbestos powder, and a metal or metallic oxide (such as zinc dust or lead oxide) is carefully treated with nitric acid fumes at 75—100° for about nine hours; the temperature is then slowly raised to 280°, when the anthraquinone sublimes in long, yellow needles. F. M. G. M.

Preparation of Chlorinated Anthraquinones and Anthracenes. H. SCHILLING (*Ber.*, 1913, **46**, 1066—1069).—Starting from 1- and 2-chloroanthraquinone and from 1 : 5- and 1 : 8-dichloroanthraquinone, the author has prepared a number of the higher chlorinated anthraquinones by converting them into the corresponding chloroanthraquinonesulphonic acids and replacing the sulphonic acid with chlorine by treatment of the potassium salts of the sulphonic acids with chlorine in aqueous solution at 100°. The sulphonation

was carried out by heating the chloroanthraquinones with sulphuric acid containing 20% of anhydride for four hours at 150—160°, both alone and in the presence of mercurous sulphate. Although the position of the sulphonic acid groups has not been definitely established, it is assumed from the results of Schmidt (A., 1904, i, 256) and Iljinsky (A., 1904, i, 176) that in the presence of the mercurous salt the sulphonic acid group takes up the α-position, whilst if no catalyst is employed the group enters the β-position.

With sulphuric acid alone monosulphonic acids are obtained. In the presence of mercurous sulphate 1-chloro- and the two dichloroanthraquinones yield disulphonic acids, whilst 2-chloroanthraquinone forms a monosulphonic acid. In addition to the disulphonic acid the 1 : 5-dichloro-compound also yields a monosulphonic acid.

The potassium salts of the chloroanthraquinonesulphonic acids are colourless or pale yellow, and are sparingly soluble in water.

The chloroanthraquinones are converted by reduction with zinc dust and ammonia into the corresponding chloroanthracenes, of which the monochloro-compounds form colourless, strongly, fluorescent leaflets or needles, whereas the di-, tri-, and tetra-chloro-derivatives crystallise in yellow needles.

In the following, (*a*) denotes sulphonation in the absence, (*b*) in the presence, of mercurous sulphate.

1-Chloroanthraquinone yields (*a*) 1-*chloroanthraquinonesulphonic acid* and (*b*) 1-*chloroanthraquinone-αα-disulphonic acid*; *αβ-dichloro-* (m. p. 166—168°) and *ααα-trichloro-anthraquinones*, m. p. 165—168°, which are reduced to *αβ-dichloro-* (m. p. 130—135°) and *ααα-trichloro-anthracene* (m. p. 133—135°).

2-Chloroanthraquinone gives rise to (*a*) 2-*chloroanthraquinone-β-* and (*b*) *-α-sulphonic acids*; *ββ-* and *αβ-dichloroanthraquinones* have m. p. 284—285° and 278—280° respectively, and yield *ββ-* and *αβ-dichloro-anthracenes*, m. p. 216° and 155—160°.

1 : 5-Dichloroanthraquinone gives rise to (*a*) 1 : 5-*dichloroanthraquinone-β-sulphonic acid* and (*b*) 1 : 5-*dichloroanthraquinone-α-sulphonic* and *-αα-disulphonic acids*; 1 : 5-*β-* (m. p. 230—235°) and 1 : 5-*α-trichloroanthraquinone*, m. p. 256°, and 1 : 5 : 4 : 8-*tetrachloroanthraquinone*, m. p. 339°; 1 : 5-*β-trichloroanthracene* has m. p. 170—175°, the 1 : 5 : 4 : 8-*tetrachloro*-compound, m. p. 275° or 285—286°, and the 1 : 5 : *α-trichloro*-compound, m. p. 270—275°.

1 : 8-Dichloroanthracene yields (*a*) 1 : 8-*dichloroanthraquinone-β-sulphonic acid* and 1 : 8-*dichloroanthraquinone-αα-disulphonic acid*; 1 : 8 : *β-trichloroanthraquinone*, m. p. 295—300°, and 1 : 8 : *β-trichloro-anthracene*, m. p. 185—190°.

1-*Chloroanthracene* has m. p. 81—82°, 2-*chloroanthracene*, m. p. 215°, 1 : 5-*dichloroanthracene*, m. p. 185°, and 1 : 8-*dichloroanthracene*, m. p. 156°. F. B.

Preparation of Selenocyanates of the Anthraquinone Series. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co (D.R.-P. 256667).—When the anthraquinone diazoselenocyanates are carefully heated (preferably in the presence of copper or cuprous salts) nitrogen

is eliminated and the selenocyanate group enters the ring :

$$C_{14}H_7O_2\cdot N_2\cdot SeCN = N_2 + C_{14}H_7O_2\cdot SeCN.$$

1-*Selenocyanoanthraquinone*, yellowish-red needles, m. p. 249°, is obtained when aminoanthraquinone (2·2 parts) is diazotised in concentrated sulphuric acid with nitrosyl sulphate, ice added, and the precipitated diazonium sulphate collected, dissolved in water, and treated with an aqueous solution of potassium selenocyanate (1·5 parts); the precipitated red *diazoanthraquinone selenocyanate* when warmed is converted into 1-selenocyanoanthraquinone, which is purified by crystallisation from nitrobenzene. *Potassium* 1-*selenocyanoanthraquinone*-5-*sulphonate* is prepared in a similar manner from sodium 1-amino-anthraquinone-5-sulphonate. F. M. G. M.

Preparation of 2-Anthraquinone Sulphide. IRMA ULLMANN-GOLDBERG (D.R.-P. 255591).—2-*Dianthraquinonyl sulphide*, orange-yellow prisms, m. p. 275—276°, is obtained when 2-chloroanthraquinone is boiled for six hours with an equal weight of potassium xanthate and 10 parts of amyl alcohol. F. M. G. M.

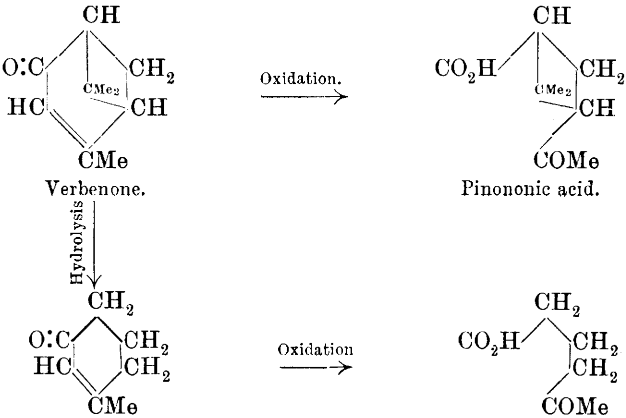
Action of Colloidal Metallic Hydroxides on Hydroxyanthraquinones. R. HALLER (*Farber-Zeit.*, 1912, **23**, 489—492, 523—528).—A description of the preparation of colloidal solutions of aluminium, chromium, and ferric hydroxides, and of the complex salts: $Al_2(SO_4)_2(OH)_2$, $Al_2(SO_4)_2(OAc)_2$, $Al_2(SO_4)(OAc)_4$, $Al_2(SO_4)(OH)_2(OAc)_2$, $Al_2(OAc)_6$, $Al_2(OAc)_4(OH)_2$, and $Al_2(OAc)_2(OH)_4$; these were combined with alizarin, purpurin, anthrapurpurin, flavopurpurin, and alizarin-orange, and the physical and chemical properties of the *compounds* so obtained are comparatively tabulated with the normal iron, aluminium, and chromium salts.

The following properties were studied, absorption spectra, together with their behaviour in the presence of hydrochloric acid, ammonium hydroxide, calcium chloride, sodium chloride, sodium hydrogen phosphate, and absolute alcohol. F. M. G. M.

Bupleurol or Dihydronerol. Constitution. II. LUIGI FRANCESCONI and E. SERNAGIOTTO (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 148—154. Compare this vol., i, 283).—Reasons are advanced showing that bupleurol probably has the structure: $CHMe_2\cdot[CH_2]_3\cdot C(:CH_2)\cdot CH_2\cdot CH_2\cdot OH$. R. V. S.

The Autoxidation of Turpentine. ARNOLD BLUMANN and OTTO ZEITSCHEL (*Ber.*, 1913, **46**, 1178—1198).—On distilling a resinified Grecian turpentine in steam, the less volatile portions were found to respond to tests for aldehydes (compare Schiff, A., 1883, 1141). An oil, $C_{10}H_{14}O$, was obtained on fractionation, but it was stable towards alkalis, did not readily yield an acid on oxidation, or a secondary alcohol with the Grignard reagent, neither would it undergo condensations. It was therefore considered to be a ketone with pseudo-aldehydic properties, like Wallach's *iso*propyl-Δ^2-hexenone (A., 1908, i, 425). Further investigations showed that it was unsaturated, and that it gave a saturated secondary alcohol with sodium

and moist ether, and a saturated ketone by Paal's reduction. It was completely identified with Kerschbaum's verbenone (A., 1900, i, 353), and its constitution was established, the chief evidence being that it gave pinononic acid on oxidation with permanganate (experiments by F. MEISTER), and that hydrolysis with dilute sulphuric acid resulted in the formation of acetone and a methyl*cyclo*hexenone, which gave γ-acetobutyric acid on oxidation.



Verbenone. Pinononic acid.

3-Methyl*cyclo*-Δ^2-hexene-1-one. γ-Acetobutyric acid.

Its rotation was stated by Kerschbaum to be $+66°$, but it is really more by 180°. The *l*-modification was also obtained from French turpentine. Besides verbenone, the crude product contained alcoholic substances, evidence of the existence of verbenol being obtained, although the substance could not be completely purified.

The fact that the unsaturated linking of pinene is preserved after autoxidation seems contradictory, but it is assumed that the addition of water at this point precedes oxidation, and that after the latter process has occurred at the neighbouring $-CH_2$-group, the water is again eliminated.

From 900 grams of the less volatile constituents of Grecian turpentine which had been exposed to air for six months, 146 grams were collected at 105—107°/5 mm. *d*-Verbenone, $C_{10}H_{14}O$, was separated from this by a neutral sulphite solution with sodium hydrogen carbonate (compare Tiemann, A., 1899, i, 247), or as the semicarbazone, in the form of a colourless oil, which soon became yellow in the light. It had b. p. 227—228°, or 100°/16 mm., m. p. 6·5°, D^{15} 0·981, D^{20} 0·9780 $[\alpha]_D$ $+249·62°$, $[\alpha]_D$ in alcohol $+229·60°$, $[\alpha]_D$ in benzene $+245·70°$, n_D^{18} 1·49928. It formed an *oxime*, $C_{10}H_{14}\cdot NOH$, m. p. 115°, was scarcely affected by hydrogen chloride in carbon disulphide or ether, or by acetic anhydride, but it absorbed hydrogen chloride with partial decomposition in glacial acetic acid. On reduction with sodium in moist ether, it yielded *dihydro*-d-*verbenol*, $C_{10}H_{18}O$, in silky needles with the celery-like smell of verbenone, m. p. 58°, b. p. 218°, α_D $+1°30'$ (10% alcoholic solution). The *acetate*, D^{15} 0·9926, α_D $-0·50°$ (25 mm.), and the *phthalate*, $C_{18}H_{22}O_4$, m. p. 127—129°, were prepared. On

oxidation it yielded *dihydro*-d-*verbenone*, $C_{10}H_{16}O$, which was also obtained by reduction of verbenone with colloidal palladium and hydrogen as an oil, b. p. 222°, D^{15} 0·9685, D^{18} 0·966, D^{20} 0·9642, $[\alpha]_D$ +52·19°, n_D 1·47535. The *semicarbazone*, m. p. 220—221°, the *oxime*, m. p. 77—78°, and the *benzylidene* compound, m. p. 152—153°, or 103—104° after three months, were obtained. Verbenone was also treated with magnesium methiodide, when the lowest fraction of the product was found to be an inactive hydrocarbon, *methylverbenene*, $C_{11}H_{16}$. The pure substance had b. p. 49°/8 mm., 175—176°/771 mm., D^{15} 0·876, D^{20} 0·872, n_D^{20} 1·4969.

One kilogram of French turpentine was also exposed to air for three months, and 370 grams of less volatile products were fractionated, yielding 41·5 grams at 90—100°/12 mm. By means of neutral sulphite, 18 grams of l-*verbenone* were obtained, having a lower rotation than the isomeride, $[\alpha]_D$ −126·84°, D^{15} 0·980, n_D 1·4994, and forming a *semicarbazone*, m. p. 185—190°. The semicarbazone from inactive verbenone had m. p. 180—181°.

The alcohol present in the residue which remained after shaking the high fraction with sulphite was isolated by means of benzoyl chloride in pyridine. The benzoate, D^{15} 1·048, gave an oil on hydrolysis, which solidified in a freezing mixture to a mass of large leaflets. After pressing out the impurities the purified d-*verbenol*, $C_{10}H_{16}O$, had the constants, b. p. 216—218°, with elimination of water, D^{15} 0·9742, D^{18} 0·9722, D^{20} 0·9702, $[\alpha]_D$ +132·30°, n_D^{20} 1·4890. No solid derivatives could be obtained, but the alcohol gave verbenone with chromic acid, and pinononic acid with permanganate. When the crude or pure substance was heated with acetic anhydride, water was easily removed and l-*verbenene*, $C_{10}H_{14}$, was obtained, b. p. 159—160°, D^{15} 0·8852, D^{20} 0·8822, α_D^{19} −74·90° (100 mm.), n_D^{20} 1·49855. On the other hand, phosphoric oxide or zinc chloride yielded a hydrocarbon which was proved to be *p*-cymene, since it gave *p*-hydroxy*iso*propylbenzoic acid on warming with permanganate. The residue from *l*-verbenone was treated as above, but, although *l*-verbenol was found, it was still more difficult to purify it. J. C. W.

Synthetic β-Glucosides of the Terpene Alcohols. JUHO HÄMÄLÄINEN (*Biochem. Zeitsch.*, 1913, **49**, 398—412).—The alcohols were shaken in ethereal solution with acetobromoglucose and silver carbonate, which were added in portions alternately. The glucosides were then obtained from the acetyl compounds thus produced by hydrolysis with barium hydroxide. The following substances were obtained: d-*Citronellol-tetra-acetyl*-d-*glucoside*, $C_{24}H_{38}O_{11}$, m. p. 30° (corr.), white needles from dilute alcohol. d-*Citronellol*-d-*glucoside*, $C_{16}H_{30}O_6$, a viscid syrup, with $[\alpha]_D^{20}$ −28·59°; it is hydrolysed by emulsin. cyclo*Hexanol-tetra-acetyl*-d-*glucoside*, $C_{20}H_{30}O_{10}$, m. p. 119—120° (corr.), and cyclo*hexanol*-d-*glucoside*, $C_{12}H_{22}O_6$, m. p. 133—135° (corr.) (without water of crystallisation), with $[\alpha]_D^{20}$ −42·52°. The substance with water of crystallation has m. p. 128·5—129·5° (corr.); it is not very readily hydrolysed with emulsin. *Terpineol*-32°-*tetra-acetyl*-d-*glucoside*, $C_{24}H_{36}O_{10}$, m. p. 114—116°. *Terpineol*-32°-d-*glucoside*, $C_{16}H_{28}O_6$, sinters at 50°, m. p. 90°, with $[\alpha]_D^{20}$ −10·94° when

anhydrous, and has a bitter taste. The form with $1H_2O$ has m. p. 80·5—82·5° (corr.). The glucoside is not readily hydrolysed by emulsin. *Terpineol*-35°-*tetra-acetyl*-d-*glucoside*, $C_{24}H_{36}O_{10}$, m. p. 130—132° (corr.). *Terpineol*-35°-d-*glucoside*, $C_{16}H_{28}O_6$, sinters at 100°, m. p. 110° (water free), with $[\alpha]_D^{20}$ $-5·88°$; it has a bitter taste; with water of crystallisation it melts at 106—108° (corr.); it is slowly hydrolysed by emulsin. d-*Dihydrocarveol-tetra-acetyl*-d-*glucoside*, $C_{24}H_{36}O_{10}$, m. p. 155—156° (corr.). d-*Dihydrocarveol*-d-*glucoside*, $C_{16}H_{28}O_6$, m. p. (with water of crystallisation) 164—165° (corr.), with $[\alpha]_D^{20}$ $+36·52°$. It is only sparingly soluble in water, and is hydrolysed readily by emulsin. cis-*Terpin-tetra-acetyl*-d-*monoglucoside*, $C_{24}H_{38}O_{11}$, m. p. 129—139° (corr.). cis-*Terpin*-d-*monoglucoside*, $C_{16}H_{30}O_7,H_2O$, m. p. 143—149° (corr.), with $[\alpha]_D^{20}$ $-11·09°$, is not readily hydrolysed by emulsin. S. B. S.

Synthesis of Alkyl Glucosides by means of Emulsin, β-Phenylethyl Glucoside, and β-Cinnamyl Glucoside. ÉMILE BOURQUELOT and MARC BRIDEL (*Compt. rend.*, 1913, **156**, 827—829; *J. Pharm. Chim.*, 1913, [vii], **7**, 335—340).—The authors have prepared two other glucosides by their usual method (compare A., 1912, i, 672).

β-Phenylethyl glucoside, $C_6H_{11}O_6·CH_2·CH_2Ph$, crystallises in colourless needles, having a bitter taste. It has $[\alpha]_D$ $-23·92°$, and reduces Fehling's solution.

β-Cinnamyl glucoside, $C_6H_{11}O_6·CH_2·CH:CHPh$, crystallises in colourless needles, $[\alpha]_D$ $-41·12°$, and having only a slight reducing action. Both of these glucosides are readily hydrolysed by emulsin in aqueous solution. W. G.

Synthesis of Alkyl Galactosides by means of Emulsin. β-Methyl Galactoside and β-Allyl Galactoside. ÉMILE BOURQUELOT and MARC BRIDEL (*Compt. rend.*, 1913, **156**, 1104—1106*).—The two galactosides were prepared in the usual way by the action of emulsin on solutions of galactose in the respective alcohols. After evaporating off the excess of alcohol under reduced pressure, the unaltered galactose was destroyed by fermentation with bottom yeast in the presence of dextrose.

β-Allyl galactoside crystallises in colorless needles, $[\alpha]_D$ $-12·5°$, and, like the methyl galactoside, it is readily hydrolysed by emulsin in aqueous solution. W. G.

Rhamnoxanthin from Rhamnus cathartica and Frangulin from Rhamnus frangula. N. KRASOVSKI (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 188—193. Compare A., 1909, ii, 174).—Examination of the two glucosides, rhamnoxanthin, and frangulin, and of their derivatives and products of hydrolysis indicates their identity. The name frangulin is suggested for retention. T. H. P.

Preparation of the Active Principle of Apocynum. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 255537. Compare T., 1909, **95**, 734).—The boiling carbon tetrachloride extract of the rhizome of *Apocynum cannabinum* furnished a *compound*, glistening prisms, m. p. 135—140°, with an extremely bitter taste, and contain-

* and *J. Pharm. Chim.*, 1913, [vii], **7**, 444—448.

ing C = 63·5% and H = 8·4% (compare Finnemore, T., 1908, **93**, 1513; P., 1909, **25**, 77). F. M. G. M.

The Blue Pigment from Crenilabrus pavo. RICHARD VON ZEYNEK (*Monatsh.*, 1913, **34**, 535—551. Compare A., 1902, i, 168). —A fuller account of the blue protein substance present in the fins, scales, and skin of *Crenilabrus pavo.* The fins, which are the best source of the substance, are extracted with acetone and ether successively, which remove a yellow *substance*, microscopic needles; this is easily soluble in chloroform, giving a solution which, on treatment with acetic anhydride and a drop of concentrated sulphuric acid, assumes a deep red colour, shortly changing to a bluish-green. After the above treatment, the fins are extracted with water, which dissolves out the coloured substance; this is purified by repeated precipitation by ammonium sulphate, and obtained as an amorphous solid. The optical properties of the substance have been re-investigated. The addition of magnesium sulphate, ammonium chloride, or sodium chloride causes the substance to separate slowly from its aqueous solution, and it is precipitated by the ordinary alkaloid reagents; its neutral solution coagulates at 75—77°, precipitating green flocks. The colour is only slowly bleached by hydrogen peroxide and hydrazine hydrate, but it is very sensitive towards acids, which evidently cause decomposition, as subsequent neutralisation fails to restore the original colour.

D. F. T.

Chlorophyll. XXI. Introduction of Magnesium into Chlorophyll Derivatives. RICHARD WILLSTÄTTER and LENNART FORSÉN (*Annalen*, 1913, **396**, 180—193).—It has previously been shown that metals, such as copper, iron, and zinc, can easily be introduced into derivatives of chlorophyll, such as the phæophorbides, phytochlorins, phytorhodins, and the various porphyrins, producing substances which are characterised by their stability in acid or alkaline media. Also derivatives of the phytochlorins and the phytorhodins have been prepared containing barium or potassium, and characterised by their instability towards acids. The magnesium derivatives are intermediate between these two extremes in their degree of stability. The present paper deals with the important problem of the methods whereby magnesium can be introduced into chlorophyll derivatives which do not contain a metallic constituent.

Two methods are described: heating the chlorophyll derivative with methyl-alcoholic potassium hydroxide and magnesium oxide under pressure, and secondly, treating it with an excess of ethereal magnesium methyl iodide.

Thus by heating phytochlorin-*e* (violet modification) with concentrated methyl-alcoholic potassium hydroxide and magnesium oxide in a silver autoclave at 180°, isolating the resulting potassium salt, and acidifying it with sodium dihydrogen phosphate, a new phyllin, called *cyanophyllin*, $C_{33}H_{34}O_4N_4Mg,Et_2O$, is obtained; it is a greenish-blue substance, characterised by the colour and fluorescence of its solutions and by its extraordinary instability, whereby the corresponding porphyrin is produced.

At 200° under similar conditions, phytochlorin-*e* is converted into a second phyllin, called *erythrophyllin*, $C_{33}H_{34}O_4N_4Mg$, which forms a red, fluorescent solution in ether. Still under the same conditions, phytochlorin-*e* at 220° is converted into phyllophyllin, $C_{32}H_{34}O_2N_4Mg$, which has previously been analysed only in the form of its salts on account of its instability. Phyllophyllin forms a bluish-red fluorescent ethereal solution, and readily loses its magnesium, yielding phylloporphyrin.

By treatment with magnesium methyl iodide (1 or 2 mols.) in ether, phæophytin-*a* yields precipitates containing magnesium and iodine, from which, however, the phæophytin is regenerated by treatment with water or other reagents. With an excess of magnesium methyl iodide (8 mols.), chlorophyll yields a substance from which unchanged chlorophyll is regenerated by treatment with sodium dihydrogen phosphate. In a similar manner the precipitate obtained from phæophytin-*a* and magnesium methyl iodide (8 mols.) yields, when rapidly treated with 10% sodium dihydrogen phosphate, pure chlorophyll-*a* identical with the substance prepared from natural sources.

In a similar manner, all porphyrins can be converted into the corresponding phyllins; thus phylloporphyrin methyl ester and magnesium methyl iodide in boiling ether yield a substance by the decomposition of which by sodium dihydrogen phosphate the methyl ester of phyllophyllin, $C_{33}H_{36}O_2N_4Mg$, is obtained in large, rhombic leaflets.

C. S.

[Action of Sodium Methoxide on Bilirubic Acid, Bilirubin, and Hemibilirubin.] OSKAR PILOTY (*Ber.*, 1913, **46**, 1000—1001).—Polemical (compare Fischer and Röse, A., 1912, i, 575; this vol., i, 382; also Piloty and Thannhauser, A., 1912, i, 736, 925). Bilic and bilirubic acids are the same substance; further, *iso*phonopyrrolecarboxylic acid is identical with the *iso*phonopyrrolecarboxylic acid of Fischer and Bartholomäus (A., 1912, i, 493), whilst dehydrobilic acid represents Fischer's xanthopyrrolecarboxylic acid or xanthobilirubic acid. The former name is to be preferred in each instance.

E. F. A.

The Action of Hydrogen Peroxide on Hippomelanin. JENNY ADLER-HERZMARK (*Biochem. Zeitsch.* 1913, **49**, 130—136).—Hippomelanin, obtained from melanotic lymph glands of a horse, dissolves in hydrogen peroxide when treated by the method of Rona and Riesser. About two-thirds of the nitrogen is thereby obtained in the form of ammonia. Part of the substance is converted into a product of the nature of melanic acid, which has been obtained from melanin by other methods. This product is slightly soluble in water, and is obtained in solution by the above-mentioned treatment in the form of an ammonium salt, from which the free acid can be precipitated by mineral acids, and from which an insoluble mercury salt can be obtained. No evidence could be obtained of the formation of guanidine or other basic organic substances.

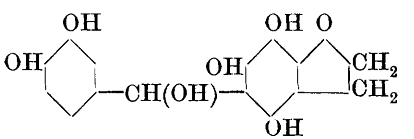
S. B. S.

Furoylformic Acid and Furylglycollic Acid. EMIL FISCHER and FRITZ BRAUNS (*Ber.*, 1913, **46**, 892—896).—The similarity of pyromucic acid to benzoic acid extends even to the conversion through the chloride and cyanide into the corresponding ketonic acid.

Pyromucyl chloride, obtained from pyromucic acid and thionyl chloride, was treated in cooled ethereal solution with hydrogen cyanide and pyridine; the resultant oil was separated by distillation into a distillate of *furoyl cyanide*, hexagonal tablets, m. p. 25°, b. p. 32°/0·15 mm., and a residue of pyromucic anhydride. Furoyl cyanide is converted by dilute sodium hydroxide, or slowly by moist ethereal solution, largely into pyromucic acid. When kept with hydrochloric acid (D 1·19) for twenty-four hours, *furoylformic acid*, $C_4H_3O\cdot CO\cdot CO_2H$, is formed, which separates in colourless, microscopic needles, m. p. 94—95°, when the ethereal extract is treated with light petroleum; *silver* salt, amorphous; *phenylhydrazone*, m. p. near 154° (decomp.). The reduction of furoylformic acid by shaking with sodium amalgam and water yields *furylglycollic acid*, $C_4H_3O\cdot CH(OH)\cdot CO_2H$, m. p. indefinite at 114° (decomp.); the *calcium*, *silver*, and *lead* salts were prepared. Furoylformic acid thus shows marked similarity to benzoylformic acid.

D. F. T.

Hydroxycatechin and Catechincarboxylic Acids. MAXIMILIAN NIERENSTEIN (*Annalen*, 1913, **396**, 194—200).—*Hydroxycatechin* (annexed formula), m. p. 284—285° (decomp.), prepared by the reductive acetylation of catechone by acetic anhydride and zinc dust and hydrolysis of the product, crystallises in yellow needles and forms a colourless *hexamethyl ether*, m. p. 102°, by treatment with diazomethane.



The yellow colour of hydroxycatechin, as also the red colour of 1 : 2 : 7 : 8-tetrahydroxydiphenylene oxide, is attributed to the influence of the hydroxyl group in the peri-position to the oxygen atom of the furan ring. Consequently, the presence of the more strongly acidic carboxyl group in the place of the peri-hydroxyl group should produce a still more intensely coloured catechincarboxylic acid. The interaction of catechin, carbon tetrachloride, and aqueous potassium hydroxide, however, leads to the formation of a colourless *catechincarboxylic acid*, m. p. 274—277° (decomp.), needles, which has the constitution $CO_2H\cdot C_6H_2(OH)_2\cdot CH(OH)\cdot C_6H(OH)_2{<}^{O}_{CH_2}{>}CH_2$, since the *methyl catechincarboxylate pentamethyl ether*, $C_{22}H_{26}O_8$, m. p. 92°, obtained from it by the action of diazomethane, yields hemipinic acid by oxidation with alkaline potassium permanganate.

The catechincarboxylic acid has been resolved by means of its strychnine salts into the optically active components. l-*Catechincarboxylic acid* crystallises in small needles and has m. p. 270—273° (decomp.), and $[\alpha]_D^{18}$ − 68·22° in alcohol; the d-*acid*, small needles, has m. p. 273° (decomp.) and $[\alpha]_D^{18}$ + 76·4° in alcohol.

C. S.

Adrenaline from the Whale. EDWARD R. WEIDLEIN (*J. Ind. Eng. Chem.*, 1912, **4**, 636—645).—The suprarenal glands of the whale are found to be about 500 times larger than those of sheep and fifty times larger than those obtained from cattle.

From the tabulated results of numerous experiments the conclusion is drawn that glands preserved in chloroform yield about 0·2% pure adrenaline (m. p. 212°, $[\alpha]_D^{25}$ $-52{\cdot}00°$) after preservation during six to nine months, the loss during purification amounting to 13·8%. Pure adrenaline gives a marked increase in blood pressure (as shown by curves) without a subsequent depressant action, this latter effect being considered to be due to impurities, proteins (such as lecithin and phosphates) present in the glands, and to decomposition products which are formed by oxidation on keeping for even a a short time in aqueous solution.

The commercial adrenaline used for comparison gave the secondary depressant action until purified, although declared to be the best on the market.

The extraction and purification of the active suparenal principle from the whale, cattle, sheep, and pigs is described, and it is demonstrated to be identical from each source. F. M. G. M.

Berberine. MARTIN FREUND (*Annalen*, 1913, **397**, 1—30).—A general discussion of the results of researches on dihydroberberine derivatives (compare following abstracts), one of the most important being the conversion of berberine into hydrastinine by a smooth and practicable method. C. S.

Derivatives of Benzyldihydroberberine. MARTIN FREUND and KARL FLEISCHER (*Annalen*, 1913, **397**, 30—52).—Benzyldihydroberberine (Freund and Beck, A., 1905, i, 151) yields the stannichloride of *benzyltetrahydroberberine*,

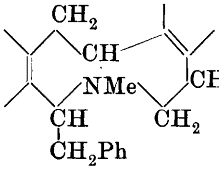
$$C_6H_2(OMe)_2{<}\begin{matrix}CH_2\text{———————}CH\text{———————}\\ CH(CH_2Ph)\cdot\overset{|}{N}\cdot CH_2\cdot CH_2\end{matrix}{>}C_6H_2{:}CH_2O_2,$$

m. p. 163—165°, pale yellow, rhombic plates (*hydrochloride*, white needles; *sulphate*, decomp. 227°; *nitrate*, decomp. 175°), by reduction with stannous chloride and boiling 96% alcohol and hydrochloric acid, D 1·19. A second base is not formed, but when benzyldihydroberberine, dissolved in alcohol and 30% sulphuric acid, is reduced at a lead cathode at 50—60° (current-density at the cathode 0·06 ampere per sq. cm.), benzyltetrahydroberberine is produced, together with an *isomeride*, $C_{27}H_{27}O_4N$, m. p. 126°, a grey, crystalline powder, which is called *ψ-benzyltetrahydroberberine*. With methyl iodide at 100° it forms a *methiodide*, decomp. 200°, yellow powder, whilst *benzyltetrahydroberberine methiodide*, colourless, rhombic plates, has decomp. 224°. Both methiodides, by treatment with silver oxide and 50% alcohol and then with boiling potassium hydroxide, yield the same tertiary base, *de-benzyl-*N*-methyltetrahydroberberine*, $C_{28}H_{29}O_4N$, m. p. 121—122·5°, colourless, quadratic plates (*sulphate*, m. p. 209—210°; *hydrochloride*, decomp. 238—240°; *hydriodide*, m. p. 193—194°). Since de-benzyl-*N*-methyltetrahydroberberine is converted into hydrastinine and 3 : 4-dimethoxy-2-styrylbenzaldehyde by oxidation with sodium dichromate in boiling acetic acid (this fissive oxidation is quite similar

to that of landanosine described by Pyman [T., 1909, 95, 1267]), it receives the formula :

$$CHPh:CH\cdot C_6H_2(OMe)_2\cdot CH_2\cdot CH<\begin{matrix}C_6H_2(:CH_2O_2)\\NMe\text{——}CH_2\end{matrix}>CH_2,$$

although, perhaps, a constitution containing the annexed skeleton is in better agreement with the facts that the de-base cannot be reduced and does not react with bromine.



3 : 4-*Dimethoxy-2-styrylbenzaldehyde*, $CHPh:CH\cdot C_6H_2(OMe)_2\cdot CHO$, m. p. 71—74°, long, colourless needles, does not react with bromine in chloroform (steric hindrance ?), and forms an *oxime*, m. p. 125—140°, *pheuylhydrazone*, m. p. 120—122°, yellow needles, *semicarbazone*, m. p. 190—192°, and *anil*, m. p. 107—109° ; by reduction with sodium and warm alcohol, it is converted into 3 : 4-*dimethoxy-2-β-phenylethylbenzyl alcohol*, $CH_2Ph\cdot CH_2\cdot C_6H_2(OMe)_2\cdot CH_2\cdot OH$, m. p. 96—98°, colourless needles.

De-benzyl-*N*-methyltetrahydroberberine forms with methyl iodide at 100° a *methiodide*, m. p. 210°, yellow plates, which is converted, by successive treatment with silver oxide and 50% alcohol and with boiling potassium hydroxide, into *de-benzyl*-NN-*dimethyltetrahydroberberine*, $C_{29}H_{31}O_4N$, m. p. 93—94·5° (*sulphate*, m. p. 197° ; *hydrochloride*, m. p. 238°), which cannot be reduced and is given the formula

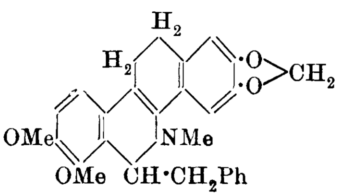
$$CHPh:CH\cdot C_6H_2(OMe)_2\cdot CH:CH\cdot C_6H_2(:CH_2O_2)\cdot CH_2\cdot CH_2\cdot NMe_2,$$

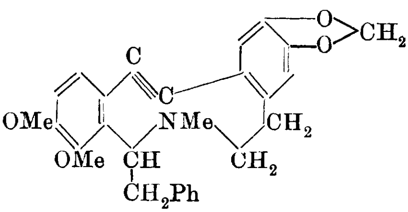
because it yields 3 : 4-dimethoxy-2-styrylbenzaldehyde by fissive oxidation. It forms a *methiodide*, m. p. 268°, which is decomposed and yields trimethylamine and 3 : 4-*dimethoxy*-3′ : 4′-*methylenedioxy-2-styryl-6′-vinylstilbene*,

$$CHPh:CH\cdot C_6H_2(OMe)_2\cdot CH:CH\cdot C_6H_2(CH:CH_2)<\begin{matrix}O\\O\end{matrix}>CH_2,$$

m. p. 120—122°, colourless needles, by the usual treatment.

Benzyldihydroberberine and methyl iodide at 100° yield a *substance*, decomp. 181°, which is not a methiodide, because it loses hydrogen iodide by treatment with alcoholic ammonia and yields a *substance*, $C_{28}H_{27}O_4N$, m. p. 187—188°, pale yellow, rhombic plates, which is called *de-benzyl*-N-*methyldihydroberberine* ; the hydriodide of the latter is identical with the original additive compound. The constitution of de-benzyl-*N*-methyldihydroberberine has not been definitely settled ; either of the annexed formulæ may be possible, and serves to explain many of the following transformations of the substance, but objections can be raised against both :



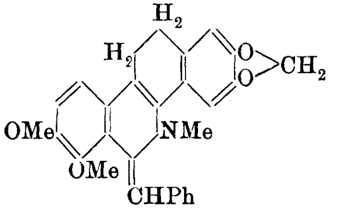


De-benzyl-*N*-methyldihydroberberine forms a *methiodide*,

$$C_{28}H_{27}O_4NMeI,H_2O,$$

decomp. 167°, reddish-yelllow prisms, and is reduced by stannous chloride and boiling alcohol and hydrochloric acid, D 1·19, to the stannichloride of a *substance*, $C_{28}H_{29(or\ 31)}O_4N$, m. p. 162·5—164°, colourless leaflets (*hydrochloride*, decomp. about 215°; *sulphate*, decomp. above 170°), which is called *α-hydro-de-benzyl-*N*-methyldihydroberberine*. It is unchanged by bromine, iodine, or methyl iodide, and has only faintly basic properties. By reduction at a lead cathode in alcohol and 30% sulphuric acid at 40—50°, and with a cathodic current density of 0·075 ampere per sq. cm. and at 24 volts, de-benzyl-*N*-methyldihydroberberine is converted into a mixture of α-hydro-de-benzyl-*N*-methyldihydroberberine and a *substance*, $C_{28}H_{29(or\ 31)}O_4N$, m. p. 134—136°, microscopic plates, which is called *β-hydro-de-benzyl-*N*-methyldihydroberberine*. The mixture is readily separated, since only the β-compound forms a *methiodide*. Analysis fails to determine whether the α- and β-compounds are isomeric or whether one contains more hydrogen than the other. The preceding methiodide is converted, by treatment with silver oxide and subsequent boiling with an alkali, into *β-hydro-de-benzyl-NN-dimethyldihydroberberine*, $C_{29}H_{31(or\ 33)}O_4N$, m. p. 126°, colourless needles, the *methiodide*, decomp. 239°, of which yields trimethylamine and a non-nitrogenous substance by the usual treatment.

The oxidation of de-benzyl-*N*-methyldihydroberberine by sodium dichromate and acetic acid at 90° produces, after dilution with water, a yellow (unexamined) solid and a green solution. Sodium carbonate precipitates from the latter *dehydro-de-benzyl-*N*-methyldihydroberberine* (annexed formula), m. p. 203—204°, yellow prisms, which forms a *hydrochloride* and *sulphate*, decomp. 229°, but not a methiodide. By reduction with stannous chloride, alcohol, and concentrated hydrochloric acid, or at a lead cathode in alcohol and 30% sulphuric acid at 40—50°, dehydro-de-benzyl-*N*-methyldihydroberberine is converted into a *substance*, $C_{28}H_{27(or\ 29)}O_4N$, m. p. 164—165°, pale yellow, hexagonal plates, which appears to be isomeric with α-hydro-de-benzyl-*N*-methyldihydroberberine.

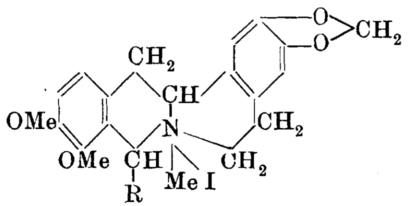


Benzyltetrahydroberberine methiodide in aqueous alcoholic suspension is converted by silver chloride into the *methochloride*, decomp. 228°, rhombic plates, an aqueous solution of which on the water-bath is converted by 5% sodium amalgam into de-benzyl-*N*-methyltetrahydroberberine and iso*hydro-de-benzyl-*N*-methyltetrahydroberberine*, $C_{28}H_{31}O_4N$, m. p. 96—98°, colourless plates (*hydriodide*, m. p. 229° [decomp.]). C. S.

Methyldihydroberberine and its Derivatives. MARTIN FREUND and HANNS COMMESSMANN (*Annalen*, 1913, **397**, 52—56).—Alkyl- or aryl-dihydroberberines react with methyl iodide to form the hydriodides of bases called de-alkyl-(or aryl-)-*N*-methyldihydroberberines; by the

electrolytic method; each of the de-bases yields two reduction products, α- and β-hydro-de-alkyl-(or aryl-)-*N*-methyldihydroberberines. Since these reduction products have similar properties, whether the alkyl or aryl group is methyl, ethyl, *iso*propyl, *iso*butyl, *iso*amyl, benzyl, or phenyl, the de-bases all have the same constitution, namely, that already given for the benzyl compound (Freund and Fleischer, preceding abstract).

By reduction, *R*-dihydroberberines each yield two stereoisomeric *R*-tetrahydroberberines, from which two stereoisomeric *R*-tetrahydroberberine methiodides (formula I) are obtained. (*R*-Tetrahydroberberines do not combine additively with iodides other than methyl iodide.) By treatment with silver oxide and subsequently with boiling alkali, the two methiodides yield one and the same de-base, which may have the constitution II, III, or IV. When *R* is CH_2Ph, the de-base has formula II (Freund and Fleischer, preceding abstract); when *R* is Pr^{β}, the de-base has constitution III (Freund and Lachmann, following abstract); when *R* is Me, Et, CH_2Pr^{β}, $CH_2{\cdot}CH_2Pr^{\beta}$, n-C_8H_{17}, or Ph, the de-base has formula IV.



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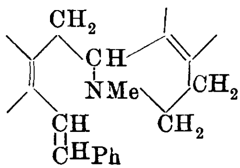

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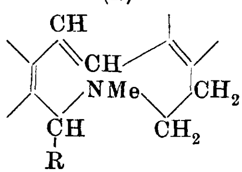

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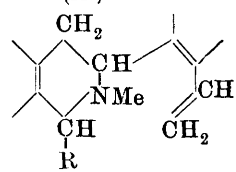


(IV.)

Methyltetrahydroberberine methiodide, $C_{22}H_{26}O_4NI$, m. p. 263—264°, colourless prisms, is converted by the usual method into *de-methyl-N-methyltetrahydroberberine*, $C_6H_2(OMe)_2{<}\begin{matrix}CH_2\text{—}CH\text{—}C_6H_2{:}CH_2O_2\\ CHMe{\cdot}NMe\quad CH{:}CH_2\end{matrix}$, m. p. 115—116°, colourless prisms (*hydrochloride*, m. p. 224—225° [decomp.]; *sulphate*, m. p. 211—212°; *nitrate*, m. p. 198—199° [decomp.]). The de-base does not yield hydrastinine by oxidation (de-benzyl-*N*-methyltetrahydroberberine is the only one that does), and forms a *methiodide*, m. p. 257° (decomp.), colourless needles.

Methyldihydroberberine and methyl iodide form the *hydriodide*, m. p. 218° (decomp.), yellowish-green needles, of *de-methyl-N-methyldihydroberberine*, $C_{22}H_{23}O_4N$, m. p. 155°, yellow, irregular prisms (*sulphate*, m. p. 116° [decomp.]; *hydrochloride*, m. p. 104°). By electrolytic reduction at a lead cathode in alcohol and 20% sulphuric acid, the de-base is converted into *α-hydro-de-methyl-N-methyldihydroberberine*,

$C_{22}H_{25}O_4N$, m. p. 146° (*sulphate*, m. p. 223° [decomp.]; *hydrochloride*, m. p. 155° [decomp.]; *nitrate*, decomp. 198°), and *β-hydro-de-methyl-N-methyldihydroberberine*, $C_{22}H_{25}O_4N$, m. p. 215° (*sulphate*, m. p. 135—138° [decomp.]; *hydrochloride*, decomp. 220°; *nitrate*, decomp. 234°). The constitutions of the de-base and its reduction products are analogous to those of de-benzyl-*N*-methyldihydroberberine and its reduction products (Freund and Fleischer, preceding abstract). C. S.

Ethyldihydroberberine and Its Derivatives. MARTIN FREUND and HANNS COMMESSMANN (*Annalen*, 1913, **397**, 57—69).—The reduction of ethyldihydroberberine at a lead cathode yields Freund and Mayer's ethyltetrahydroberberine, m. p. 151° (A., 1905, i, 657), and *ψ-ethyltetrahydroberberine*, $C_{22}H_{25}O_4N$, m. p. 117—119°, faintly yellowish-green, irregular plates, which forms a *sulphate*, m. p. 236° (decomp.), *hydrochloride*, decomp. 248°, and *nitrate*, decomp. 210°.

Ethyltetrahydroberberine and methyl iodide at 100° yield the *methiodide*, $C_{22}H_{25}O_4NMeI$, m. p. 228—229°, colourless needles, which is converted by the usual process into *de-N-methyl-α-ethyltetrahydroberberine*,
$C_6H_2(OMe)_2<\begin{matrix}CH_2-CH-C_6H_2{:}CH_2O_2\\ CHEt\cdot NMe\ \ CH{:}CH_2\end{matrix}$, m. p. 134° (*hydrochloride*, decomp. 220°; *sulphate*, decomp. 239°; *nitrate*, decomp. 152°). The de-base does not yield hydrastinine by oxidation, is also produced by the successive action of silver oxide and potassium hydroxide on *ψ-ethyltetrahydroberberine methiodide*, m. p. 211° (decomp), and is reduced at a lead cathode in alcohol and 20% sulphuric acid to *hydro-de-N-methylethyltetrahydroberberine*,

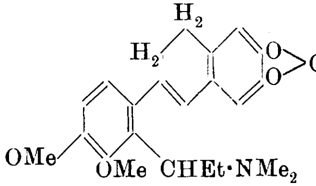
$$C_6H_2(OMe)_2<\begin{matrix}CH_2\text{———}\\ CHEt\cdot NMe\end{matrix}>CH\cdot C_6H_2Et{:}CH_2O_2,$$

m. p. 124—125° (*sulphate*, m. p. 230°; *hydrochloride*, m. p. 243°). De-*N*-methylethyltetrahydroberberine and methyl iodide at 100° form the *methiodide*, $C_{23}H_{27}O_4NMeI$, decomp. 230°, which is converted by silver oxide and potassium hydroxide in the usual manner into *de-NN-dimethylethyltetrahydroberberine*, $C_{24}H_{29}O_4N$, m. p. 85—86°. The *methiodide*, m. p. 208—209°, of the latter is decomposed into trimethylamine and *3 : 4-dimethoxy-3′ : 4′-methylenedioxy-2-propenyl-6′-vinylstilbene*, $CHMe{:}CH\cdot C_6H_2(OMe)_2\cdot CH{:}CH\cdot C_6H_2({:}CH_2O_2)\cdot CH{:}CH_2$, m. p. 82—83°, stout needles, by the usual treatment.

Ethyldihydroberberine and methyl iodide yield the *hydriodide*, m. p. 210° (decomp.), of *de-N-methylethyldihydroberberine*, $C_{23}H_{25}O_4N$, m. p. 142—143°, softening at 136—137°. The de-base forms a *methiodide*, $C_{23}H_{25}O_4NMeI$, m. p. 250° (decomp.), which yields by the usual method of decomposition *de-NN-dimethylethyldihydroberberine*, $C_{24}H_{27}O_4N$, m. p. 115—116° (*sulphate*, m. p. 191—192° [decomp.]; *nitrate*, decomp. 168°; *hydrochloride*, decomp. 163—164°).

The reduction of de-*N*-methylethyldihydroberberine at a lead cathode in alcohol and 20% sulphuric acid yields a mixture of *α-hydro-de-N-methylethyldihydroberberine*, $C_{23}H_{27}O_4N$, m. p. 137°, and *β-hydro-de-N-methylethyldihydroberberine*, $C_{23}H_{27}O_4N$, m. p. 168°. The α-base forms a *sulphate*, decomp. 188°, *hydrochloride*, decomp. 266°, and *nitrate*, decomp. 170°, does not form a methiodide, and is converted

into de-*N*-methylethyldihydroberberine by bromine in chloroform and basification of the product. The β-base is unattacked by bromine, and forms a *sulphate*, decomp. 107—108°, *hydrochloride*, decomp. 250°, *nitrate*, decomp. 185°, and *methiodide*, m. p. 245° (decomp.). The decomposition of the last in the usual manner by silver oxide and potassium hydroxide yields a *substance*, m. p. 104—120°, which is probably a mixture of two isomeric *β-hydro-de-*NN*-dimethylethyldihydroberberines* (formulæ I and II); the *methiodide* has decomp. 230°.



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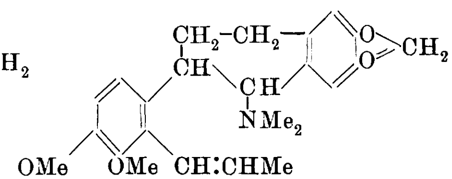
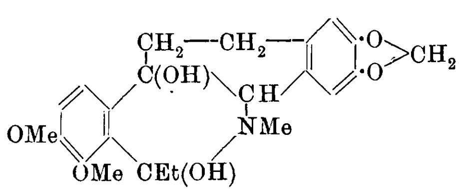


(II.)

By oxidation with sodium dichromate and acetic acid at 80°, de-*N*-methylethyldihydroberberine yields a *substance*, $C_{23}H_{27}O_6N$, m. p. 130° (decomp.) (*hydrochloride*, m. p. 225°, colourless needles), which is called *oxy-de-*N*-methylethyldihydroberberine hydrate*, and possibly has the annexed constitution. This substance is also produced by the oxidation of α- or β-hydro-de-*N*-methylethyldihydroberberine; in addition, a second *substance*, $C_{23}H_{25(\text{or } 23)}O_4N$, m. p. 178°, yellow crystals, is formed, which is provisionally named iso-*de-*N*-methylethyldihydroberberine*.



C. S.

isoPropyldihydroberberine and its Derivatives. MARTIN FREUND and ROBERT LACHMANN (*Annalen*, 1913, **397**, 70—84).—Berberine sulphate and ethereal magnesium *iso*propyl bromide react to form, after the usual treatment, iso*propyldihydroberberine*,

$$C_6H_2(OMe)_2<\begin{matrix} CH{=\!=}C\cdot C_6H_2(:CH_2O_2) \\ CHPr^{\beta}\cdot N\text{————}CH_2 \end{matrix}>CH_2,$$

m. p. 167—168°, citron-yellow needles. By electrolytic reduction in alcohol and 20% sulphuric acid at 50—60° and a current density 0·06 ampere per sq. cm. at the cathode, *iso*propyldihydroberberine yields the two stereoisomerides, iso*propyltetrahydroberberine*,

$$C_6H_2(OMe)_2<\begin{matrix} CH_2\text{—}CH\cdot C_6H_2(:CH_2O_2) \\ CHPr^{\beta}\cdot N\text{————}CH_2 \end{matrix}>CH_2$$

m. p. 157—158°, greenish-yellow, rhombic leaflets (*sulphate*, m. p. 197° [decomp.]; *nitrate*, decomp. 215°; *hydrochloride*, decomp. 226°; *platinichloride*, decomp. 205°; *perchlorate*, m. p. 226—227° [decomp.]), and ψ-iso*propyltetrahydroberberine*, m. p. 200—202°, colourless prisms (*nitrate*, decomp. 176°; *hydrochloride*, decomp. 254°). By treatment with alcoholic iodine at 100°, *iso*propyltetrahydroberberine is converted

into iso*propyldihydroberberine hydriodide*, $C_{23}H_{25}O_4N,HI,Et\cdot OH$, decomp. 110°, brown, rhombic plates, whilst the ψ-base is simply converted into its hydriodide.

iso*Propyltetrahydroberberine methiodide*, m. p. 210° (decomp.), colourless needles, and ψ-iso*propyltetrahydroberberine methiodide*, decomp. 247—248°, faintly yellow needles, each yield, by treatment with silver oxide and 50% alcohol, and subsequently with boiling potassium hydroxide, a mixture of a-*de*-N-*methyl*iso*propyltetrahydroberberine*, $C_{24}H_{29}O_4N$, m. p. 132·5° (*sulphate*, decomp. about 200°; *hydriodide*, decomp. 197°, yellow needles), and b-*de*-N-*methyl*iso*propyltetrahydroberberine*, $C_{24}H_{29}O_4N$, m. p. 102—103° (*hydrochloride*, decomp. 226°; *hydriodide*, decomp. 218°; *nitrate*, decomp. 197°). The *a*-de-base is converted into the *b*-de-base by boiling alcohol, and yields ψ-*iso*propyltetrahydroberberine methiodide by digestion with aqueous alcohol and subsequent treatment with acetic acid and potassium iodide; it is unchanged by boiling nitrobenzene, by boiling dilute sulphuric acid and alcohol, or by electrolytic reduction. The *b*-de-base is comparatively stable. By prolonged boiling with glacial acetic acid and subsequent treatment of the basified and filtered solution with potassium iodide, it yields a *methiodide*, m. p. 236°, from which the *b*-de-base is regenerated directly.

Of all the de-bases examined by the authors (preceding and following abstracts), *a*-de-*N*-methyl*iso*propyltetrahydroberberine is the only one which resembles Gadamer and Voss's ethyl anhydro-base of tetrahydroberberine (A., 1910, i, 415) in being readily re-converted into the ammonium base or its salts by digestion with water or acids. The *a*-de-base, therefore, is given the constitution

$$C_6H_2(OMe)_2{<}{\begin{matrix}CH{:}CH\cdot C_6H_2({:}CH_2O_2)\\ CHPr^{\beta}\cdot NMe\text{———}CH_2\end{matrix}}{>}CH_2,$$

analogous to that of the ethyl anhydro-base of tetrahydroberberine. The *b*-de-base and all other de-alkyl (or -aryl-)-*N*-methyltetrahydroberberines have the only remaining constitution:

$$C_6H_2(OMe)_2{<}{\begin{matrix}CH_2-CH-C_6H_2{:}CH_2O_2\\ CHR\cdot NMe\ \ CH{:}CH_2\end{matrix}}$$

(compare preceding abstract). Given these constitutions, the preceding transformations of *a*- and *b*-de-*N*-methyl*iso*propyltetrahydroberberine become readily explicable. By electrolytic reduction, the *b*-de-base yields *hydro*-b-*de*-N-*methyl*iso*propyltetrahydroberberine*,

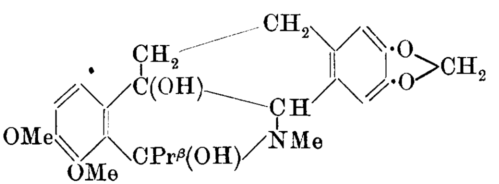
$$C_6H_2(OMe)_2{<}{\begin{matrix}CH_2\text{——}CH\cdot C_6H_2Et{:}CH_2O_2\\ CHPr^{\beta}\cdot NMe\end{matrix}}$$

colourless needles containing alcohol, m. p. 74—80° (*hydrochloride*, $C_{24}H_{31}O_4N,HCl$, decomp. 261°).

b-*De*-N-*methyl*iso*propyltetrahydroberberine methiodide*, $C_{24}H_{29}O_4NMeI$, colourless prisms (the *a*-de-base does not form a methiodide), is converted by the usual method into *de*-NN-*dimethyl*iso*propyltetrahydroberberine*, $C_{25}H_{31}O_4N$, m. p. 112—115°, colourless needles (*sulphate*, decomp. about 190°). *iso*Propyldihydroberberine and methyl iodide at 100° yield the *hydriodide*, decomp. 229°, yellow needles, of *de*-N-*methyl*iso*propyldihydroberberine*, $C_{24}H_{27}O_4N$ (for constitution, compare Freund and Fleischer, preceding abstract), m. p. 170—171°, pale

yellow crystals (*perchlorate*, decomp. 213°; *methiodide*, decomp. 232°, golden-yellow, rhombic prisms).

The electrolytic reduction of de-*N*-methyl*iso*propyldihydroberberine in alcohol and 20% sulphuric acid at 50—60° yields a mixture of *a-hydro-de-*N*-methyl*iso*propyldihydroberberine*, $C_{24}H_{29}O_4N$, m. p. 164·5—166°, greenish-yellow, rhombic plates (*nitrate*, decomp. 185°, rhombic plates; *sulphate*, m. p. 197°, prisms; *hydrochloride*, m. p. about 218°, needles; *hydriodide*, m. p. 234°; *perchlorate*, decomp. 236°), and *β-hydro-de-*N*-methyl*iso*propyldihydroberberine*, $C_{24}H_{29}O_4N$, m. p. 184—186°, almost colourless, rhombic prisms (*nitrate*, decomp. 188°; *hydriodide*, decomp. 226—227°). The *a*-compound does not form a methiodide, and yields de-*N*-methyl*iso*propyldihydroberberine by treatment with bromine in chloroform and basification of the product. The *β*-base forms a *methiodide*, $C_{24}H_{29}O_4N,MeI$, decomp. 253°, and is unchanged by bromine. By oxidation with sodium dichromate and acetic acid at 80—90°, de-*N*-methyl*iso*propyldihydroberberine and its *a*- and *β*-hydro-derivatives each yield the same product, *hydroxy-de-*N*-methyl*iso*propyldihydroberberine hydroxide* (annexed formula?), decomp. 129°, light brown crystals, which forms a *hydrochloride*, decomp. about 205°, and *hydriodide*, decomp. 238°. C. S



*iso***Butyldihydroberberine and Its Derivatives.** MARTIN FREUND and HAROLD HAMMEL (*Annalen*, 1913, **397**, 85—93).—*iso-Butyldihydroberberine*, $C_{24}H_{27}O_4N$, m. p. 112—113°, yellow needles, leaflets, or prisms, prepared in the usual manner from berberine hydrochloride and ethereal magnesium *iso*butyl bromide, forms a *nitrate*, m. p. 205° (decomp.), pale yellow leaflets, *hydriodide*, m. p. 223° (decomp.), yellow leaflets, and *platinichloride*, decomp. 220°, orange needles. It reacts with methyl iodide to form the *hydriodide*, m. p. 206° (decomp.), pale yellow needles, of *de-*N*-methyl*iso*butyldihydroberberine*, $C_{25}H_{29}O_4N$, m. p. 147—148° (*hydrochloride*, m. p. 148° [decomp.]; *platinichloride*, m. p. 217°; *hydrobromide*, m. p. 115—120° [decomp.]). The de-base is unchanged by bromine in chloroform, and forms a *methiodide*, $C_{25}H_{29}O_4NMeI$, m. p. 172° (decomp.), pale yellow leaflets, which is converted in the usual manner into *de-*NN*-dimethyl*iso*butyldihydroberberine*, $C_{26}H_{31}O_4N$, m. p. 130—131°, almost colourless plates. The *methiodide* of the last substance, $C_{26}H_{31}O_4NMeI$, m. p. 164° (decomp.), yellow needles, decomposes into methyl iodide and the original base when heated at about 95° or boiled with aqueous alcoholic potassium hydroxide; the base is also obtained when the methiodide is treated successively with silver oxide and boiling potassium hydroxide.

By reduction at a lead cathode in alcohol and 25% sulphuric acid, de-*N*-methyl*iso*butyldihydroberberine yields a mixture of *a-hydro-de-*N*-methyl*iso*butyldihydroberberine*, $C_{25}H_{31}O_4N$, m. p. 158—160°, almost

colourless, rhombic plates (*hydrobromide*, decomp. 223°; *hydriodide*, m. p. 189°), and *β-hydro-de-*N*-methyl*iso*butyldihydroberberine*, $C_{25}H_{31}O_4N$, m. p. 179° (*hydrochloride*, decomp. about 240°; *hydrobromide*, m. p. 239°; *hydriodide*, m. p. 239° [decomp.]). The α-compound does not form a methiodide, and is converted into de-*N*-methyl*iso*butyldihydroberberine by treatment with bromine in chloroform and basification of the product. The β-compound is unchanged by bromine, and forms a *methiodide*, $C_{25}H_{31}O_4N,MeI$, m. p. 246° (decomp.), which regenerates the β-compound by heating at 240°, and is converted by successive treatment with silver oxide and boiling potassium hydroxide into *β-hydro-de-*NN*-dimethyl*iso*butyldihydroberberine*, $C_{26}H_{33}O_4N$, m. p. 136—137°, colourless, rhombic leaflets. By electrolytic reduction at a lead cathode in sulphuric acid, *iso*butyldihydroberberine yields a mixture of iso*butyltetrahydroberberine*, $C_{24}H_{29}O_4N$, m. p. 127—129°, greenish-yellow, rhombic leaflets (*hydrochloride*, m. p. 237°; *hydriodide*, m. p. 256°; *sulphate*, m. p. 234°; *methiodide*, m. p. 193°), and *ψ-*iso*butyltetrahydroberberine*, $C_{24}H_{29}O_4N$, m. p. 197°, colourless plates (*hydrochloride*, m. p. 270—273° [decomp.]; *hydriodide*, m. p. 250° [decomp.]).

C. S.

n-Octyldihydroberberine and *iso*Amyldihydroberberine and their Derivatives. MARTIN FREUND and DANIEL STEINBERGER (*Annalen*, 1913, **397**, 94—106).—A suspension of berberine sulphate in ether, by treatment with ethereal magnesium n-octyl iodide and decomposition of the product by ice and hydrochloric acid, yields the *hydriodide*, $C_{28}H_{35}O_4N,HI,H_2O$, m. p. 122—124°, reddish-brown crystals, of *octyldihydroberberine*, $C_{28}H_{35}O_4N$, m. p. 88·5—89°, yellow needles. In a similar manner, berberine sulphate and magnesium *iso*amyl bromide, after the addition finally of concentrated potassium iodide, yield the *hydriodide*, decomp. 141°, yellow crystals, of iso*amyldihydroberberine*, $C_{25}H_{29}O_4N$, an amorphous, yellow substance.

By reduction with stannous chloride, hydrochloric acid, D 1·19, and alcohol, *iso*amyldihydroberberine yields only iso*amyltetrahydroberberine*, $C_{25}H_{31}O_4N$, m. p. 95—96° (*sulphate*, decomp. 237°; *hydriodide*, decomp. 255°; *nitrate*, decomp. 209—210), whilst by reduction at a lead cathode in alcohol and 20% sulphuric acid at 40—50°, it yields, in addition, *ψ-*iso*amyltetrahydroberberine*, $C_{25}H_{31}O_4N$, m. p. 172° (*hydrochloride*, decomp. 231—232°; *hydriodide*, decomp. 239—240°; *nitrate*, decomp. 210—211°).

iso*Amyltetrahydroberberine methiodide*, decomp. 191°, and *ψ-*iso*amyltetrahydroberberine methiodide*, decomp. 223—224°, each yield, by the usual method of decomposition, *de-*N*-methyl*iso*amyltetrahydroberberine*, which forms a *hydrochloride*, $C_{26}H_{33}O_4N,HCl$, decomp. 185°, *sulphate*, decomp. 190—191°, and *hydriodide*, decomp. 224—225°, and does not yield hydrastinine by oxidation.

*iso*Amyldihydroberberine and methyl iodide at 100° yield the *hydriodide* of *de-*N*-methyl*iso*amyldihydroberberine*, $C_{26}H_{31}O_4N$, m. p. 102°, pale yellow plates. By reduction with stannous chloride, hydrochloric acid, and alcohol, the de-base yields *α-hydro-de-*N*-methyl*iso*amyldihydroberberine*, $C_{26}H_{33}O_4N$, m. p. 128°, rhombic leaflets, which forms a *sulphate*, decomp. 187—188°, *nitrate*, decomp. 146°, *hydro-*

chloride, decomp. 232°, and *hydriodide,* decomp. 228°, does not form a methiodide, and is converted into de-*N*-methyl*iso*amyldihydroberberine by treatment with bromine in chloroform. By reduction at a lead cathode, de-*N*-methyl*iso*amyldihydroberberine yields, in addition to the preceding α-compound, *β-hydro-de-*N*-methyl*iso*amyldihydroberberine,* $C_{26}H_{33}O_4N$, m. p. 145°, rhombic prisms (*hydrochloride,* decomp. 220—221°; *hydriodide,* decomp. 226—227°; *methiodide,* m. p. 260°).

By prolonged heating with alcoholic ammonia in the presence of air, *iso*amyldihydroberberine hydriodide is converted into *dehydro*iso*amyldihydroberberine,*

$$C_6H_2(OMe)_2<\begin{matrix}C{=\!=\!=\!=}C\cdot C_6H_2(:CH_2O_2) \\ C(C_5H_{11})\cdot N{-\!-\!-\!-}CH_2\end{matrix}>CH_2(?),$$

m. p. 249° (decomp.), hexagonal, yellow plates, which rapidly darken in the air and light. The dehydro-compound yields *iso*amyl- and *ψ-iso*-amyl-tetrahydroberberines by electrolytic reduction, does not form salts with acids in the cold, and by boiling for eight to ten minutes with 96% alcohol and 20% hydrochloric acid or sulphuric acid, D 1·215, is converted into the *hydrochloride,* $C_{25}H_{29}O_5N,HCl$, decomp. 204°, yellow needles, or the *sulphate,* $C_{25}H_{29}O_5N,H_2SO_4$, decomp. 265°, yellow needles, of *hydroxy*iso*amyldihydroberberine,*

$$C_6H_2(OMe)_2<\begin{matrix}C(OH){=\!=\!=}C\cdot C_6H_2(:CH_2O_2) \\ CH(C_5H_{11})\cdot N{-\!-\!-\!-}CH_2\end{matrix}>CH_2,$$

m. p. 120—125°, sintering at 65°, dark yellow needles; a by-product of both reactions is a *substance,* decomp. 180—185°, reddish-brown, rhombic crystals. C. S.

Phenyldihydroberberine and its Derivatives. Martin Freund and Eugen Zorn (*Annalen,* 1913, **397**, 107—117).—Phenyldihydroberberine (Freund and Beck, A., 1905, i, 151) forms a *hydrochloride,* m. p. 160°, yellow prisms, *sulphate,* decomp. 170°; pale yellow needles, *nitrate,* decomp. 224°, and *hydriodide,* m. p. 215°. By reduction at a lead cathode in alcohol and 30% sulphuric acid, it yields Gadamer's phenyltetrahydroberberine (*sulphate,* decomp. 241°), and *ψ-phenyltetrahydroberberine,* $C_{26}H_{25}O_4N$, m. p. 204—205°, white needles (*hydriodide,* m. p. 235°); only the former can be isolated when the reduction is effected by stannous chloride and boiling alcohol and hydrochloric acid.

Phenyltetrahydroberberine methiodide, m. p. 243°, faintly yellow plates, and *ψ-phenyltetrahydroberberine methiodide,* m. p. 247°, white crystals, yield methyl iodide and the respective bases by heating. By treatment with silver oxide and boiling potassium hydroxide in the usual manner, each methiodide yields *de-phenyl-*N*-methyltetrahydroberberine,*

$$C_6H_2(OMe)_2<\begin{matrix}CH_2{-\!-}CH{-}C_6H_2:CH_2O_2 \\ CHPh\cdot NMe\quad CH:CH_2\end{matrix},$$

m. p. 153°, which forms a *hydrochloride,* m. p. 232°, *hydriodide,* decomp. 208°, and *methiodide,* m. p. 238° (decomp.). By reduction at a lead cathode, the de-base is converted into *hydro-de-phenyl-*N*-methyltetrahydroberberine,* $C_6H_2(OMe)_2<\begin{matrix}CH_2{-}CH{-} \\ CHPh\cdot NMe\end{matrix}>C_6H_2Et:CH_2O_2$, m. p. 142—143° (*hydrochloride,* m. p. 271—272°; *hydriodide,* m. p. 257°).

Phenyltetrahydroberberine methiodide is converted into the metho-

chloride in dilute alcohol, and the latter, after evaporation of the alcohol, is treated with 5% sodium amalgam on the water-bath. The product is 2-mp-*dimethoxy*-o-*benzylbenzylhydrastinine*,

$$CH_2Ph\cdot C_6H_2(OMe)_2\cdot CH_2\cdot CH{<}\begin{matrix}C_6H_2(:CH_2O_2)\\ NMe\text{——}CH_2\end{matrix}{>}CH_2,$$

m. p. 109·5—110·5°, colourless plates (*hydriodide*, m. p. 217—219°), from which hydrastinine is obtained by oxidation with sodium dichromate and acetic acid at 90°.

Phenyldihydroberberine and methyl iodide at 100° yield the *hydriodide*, m. p. 245°, yellow prisms, of *de-phenyl*-N-*methyldihydroberberine*, $C_{27}H_{25}O_4N$, m. p. 178—179°, yellow prisms (*sulphate*, m. p. 160°; *methiodide*, decomp. 220°). By reduction at a lead cathode in cold alcohol and 30% sulphuric acid, the de-base is converted into a mixture of *α-hydro-de-phenyl*-N-*methyldihydroberberine*, $C_{27}H_{27}O_4N$, m. p. 178—179°, yellow, rhombic prisms (*sulphate*, m. p. 206°, colourless prisms; no methiodide), and *β-hydro-de-phenyl*-N-*methyldihydroberberine*, $C_{27}H_{27}O_4N$, m. p. 211—212°, rhombic plates (*hydrochloride*, m. p. 257°; *methiodide*, m. p. 247—248°, pale yellow leaflets). C. S.

Preparation of Morphine Esters of Halogenated Fatty Acids. CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.-P. 256156. Compare this vol., i, 385).—*Dichloroacetylmorphine*, a yellow powder, decomp. 204°, is obtained when cooled anhydrous morphine (5 parts) is slowly treated with chloroacetyl chloride (10 parts) and subsequently heated at 90—100°.

Chloroacetylmorphine, colourless crystals, decomp. 227°, is obtained by the partial hydrolysis of the preceding compound or by employing 6 parts of chloroacetyl chloride in the foregoing preparation. *Di-α-bromoisovalerylmorphine*, sintering at 61° and decomposing at 133°, is formed by the action of α-bromo*iso*valeryl chloride on morphine in the presence of pyridine. F. M. G. M.

The Symmetry of Sparteine. LOUIS CORRIEZ (*Chem. Zentr.*, 1913, i, 29; from *Bull. Sci. Pharmacol.*, 1912, **19**, 602—610. Compare Moureu and Valeur, A., 1912, i, 296).—An attempt to prove the symmetry of the sparteine molecule was made by decomposing the hydrochloride of α-sparteine methochloride and the hydrobromide of α-sparteine methobromide in a vacuum at 250°, but the reaction was of a complicated nature, since the resulting sparteine haloids partly decomposed into sparteine. An attempt to obtain the same iodobromide by treating sparteine iodide with hydrogen bromide and sparteine bromide with hydrogen iodide was also without success. A homogeneous, faintly yellow *iodobromide*, $C_{15}H_{26}N_2,HI,HBr,H_2O$, was obtained in the former case, in cubes with $[\alpha]_D$ −16°21′, but the latter process led to a mixture, containing, in all probability, the dibromide, di-iodide, and iodobromide. J. C. W.

Hæmopyrrole. OSKAR PILOTY and JOSEF STOCK (*Ber.*, 1913, **46**, 1008—1013. Compare A., 1912, i, 923).—Crude hæmopyrrole has been separated into two fractions, the one, hæmopyrrole-I, consisting of a mixture of bases which give crystalline salts with picric acid in ethereal solution; the other, hæmopyrrole-II, comprising bases which

either do not form a picrate or of which the picrates are soluble in ether. The hæmopyrrole-II fraction comprises only 12—13% of the whole; it consists as to more than one-half of pyrroles with less than eight atoms of carbon, the remainder containing pyrroles with eight carbon atoms. It consists of at least three components differing from the five hæmopyrroles already known, and the lowest boiling fraction forms a very soluble, orange-coloured picrate, m. p. 108°, whilst a high boiling fraction closely resembles bis-dimethylpyrrole (Piloty and Wilke, A., 1912, i, 899). E. F. A.

Preparation of a Dichloroisatin [and of 5 : 7-Dichloroisatin]. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 255772 and 255774. Compare A., 1909, i, 966).—When an aqueous solution or suspension of isatin, or of 5-chloroisatin (m. p. 247°), is chlorinated at the ordinary temperature in the presence of potassium iodide, it gives rise to an unstable *dichloroisatin*, which crystallises from acetic acid in hard, red crystals, and has m. p. 155°; when this is dissolved in sodium hydrogen sulphite it loses chlorine, and the subsequent addition of acid precipitates 5-chloroisatin, whilst by the action of concentrated sulphuric acid at 80° in the presence of iodine the labile chlorine atom migrates into the ring, yielding 5 : 7-dichloroisatin (m. p. 221°). F. M. G. M.

Preparation of a Dichlorobromoisatin. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 255773 and 255775. Compare preceding abstract).—When an aqueous suspension of 5-bromoisatin is treated at about 15° with chlorine in the presence of potassium iodide, it furnishes a *chloro-5-bromoisatin* (red prisms, m. p. 145°), in which the chlorine atom is labile and eliminated by the action of sodium hydrogen sulphite, whilst with concentrated sulphuric acid at 80° in the presence of potassium iodide it yields 7-*chloro-5-bromoisatin*, yellow needles, m. p. 231°. F. M. G. M.

Lepidylamine. PAUL RABE (*Ber.*, 1913, **46**, 1024—1025).—4-Cyanoquinoline is reduced, either on treatment with nascent hydrogen or on shaking with molecular hydrogen and a palladium sol, to 4-*aminomethylquinoline* (*lepidylamine*), $C_6H_4<\begin{matrix}C(CH_2\cdot NH_2)\\N{=\!=\!=}CH\end{matrix}>CH$. This is a colourless oil, b. p. 172°/8 mm., but becomes violet on exposure to the air. The *monohydrochloride*, which is neutral to litmus, forms a colourless, crystalline powder, m. p. 206—208° (decomp.), which becomes blue on exposure to air. The *dihydrochloride* crystallises in well formed, colourless needles, decomp. above 250°. It is acid to litmus. E. F. A.

Quinolyl Ketones. I. PAUL RABE and RICHARD PASTERNACK (*Ber.*, 1913, **46**, 1026—1032).—By the interaction of magnesium phenyl bromide and ethyl cinchonate under special conditions, phenyl 4-quinolyl ketone, m. p. 60°, is obtained. This differs from the compound, m. p. 294°, described under the same name by Remfry and Decker (A., 1908, i, 364). In addition to ketones the esters of quinoline-4-

carboxylic acid give rise to carbinols when submitted to the Grignard synthesis. Similarly, 4-cyanoquinolines give rise to ketones and amines; thus 4-cyanoquinoline and magnesium ethyliodide yield 4-quinolyl ethyl ketone and 4-quinolyldiethylaminomethane. In addition some quantity of 4-ethylquinoline is formed.

4-*Benzylquinoline* is a viscid, strongly refractive, yellow oil, b. p. 222—223°/19 mm.; the *sulphate* forms colourless, rhombic crystals $+ 2H_2O$, m. p. 105—108°, or anhydrous, m. p. 132—133°. The *picrate* forms yellow prisms and plates, m. p. 178°; the *methiodide* crystallises in orange plates, m. p. 226°.

Phenyl 4-quinolyl ketone, m. p. 60°, yields the following salts: the picrate, crystallising in pale yellow, interlaced needles, m. p. 220°; a *picrolonate*, forming dark yellow, rhombic crystals, decomp. 174°; an orange *methiodide*, with metallic lustre, m. p. 218°; an *oxime hydrochloride*, separating in matted needles, m. p. 256° (decomp.).

4-*Quinolylethylketone* is a yellow oil, b. p. 163—166°/8—9 mm.; the *acetate* forms colourless needles, m. p. 87°. The *oximino*-derivative crystallises in short, colourless crystals, decomp. about 220°.

4-*Quinolyldiethylcarbinol* crystallises in lustrous, colourless plates, m. p. 135°, b. p. 192—198°/13 mm.

4-*Quinolyldiethylaminomethane* crystallises in colourless plates, m. p. 126°. E. F. A.

Quinolyl Ketones. II. PAUL RABE and RICHARD PASTERNACK (*Ber.*, 1913, **46**, 1032—1034).—Ethyl quinolinecarboxylates in presence of sodium ethoxide condense with esters of the general constitution $R_1 \cdot CH_2 \cdot CO_2R_2$; thus ethylcinchonate and ethylacetate combine to form *ethyl-γ-quinoloylacetate*, $\begin{matrix} N \cdot C_6H_4 \\ \| \\ CH \cdot CH \end{matrix} \!\!> C \cdot CO \cdot CH_2 \cdot CO_2$, a yellow oil, which could not be distilled unchanged, and is characterised by forming a sparingly soluble acid sulphate. When heated with 25% sulphuric acid, 4-quinolyl methyl ketone is obtained.

Similarly, ethyl quinate and ethyl propionate condense to form *ethyl β-[6-methoxy-4-quinoloyl]-propionate*. This is characterised by the *picrate* crystallising in slender, yellow needles, m. p. 137—138°, and the *picrolonate*, orange, matted needles, decomp. 136°.

β-6-Methoxyquinolyl ethyl ketone, obtained on hydrolysis, crystallises in pale yellow needles, m. p. 57—58°. E. F. A.

Nature of Picolide and Pyrindole. Action of Propionic Acid on α-Picoline. MAX SCHOLTZ and W. FRAUDE (*Ber.*, 1913, **46**, 1069—1082. Compare A., 1912, i, 385, 648).—Derivatives of pyrrocoline have previously been prepared by Angeli (A., 1890, 1156), who termed the compound pyrindole, and this name is now adopted by the authors.

From the absence of basic properties and the formation of condensation products with only one molecule of phenylhydrazine, hydroxylamine, and semicarbazide, the conclusion is drawn that picolide contains one of its carbonyl groups directly attached to the nitrogen atom. This view is confirmed by the fact that towards alkyl

magnesium haloids, picolide behaves as a monoketone; it reacts with nly one molecule of the organo-magnesium compound, yielding tertiary alcohols of the formula $C_{10}H_8ON\cdot CMeR\cdot OH$.

The reactions of picolide and its transformation into pyrindole are best represented by the formula I, its formation from α-picoline being shown in the following scheme:

$$C_5H_4NMe \xrightarrow{Ac_2O} \begin{array}{l} CH{:}CH\cdot C{:}CH\cdot COMe \\ CH{:}CH\cdot N\cdot COMe \end{array} \xrightarrow{Ac_2O} H_2O +$$

$$\text{(I.)} \begin{array}{l} CH{:}CH\cdot C{:}C(COMe) \\ CH{:}CH\cdot N\cdot CO{-}CH \end{array}\!\!>\!CMe.$$

On account of its relationship to quinoline, the parent ring system (II) is termed quinolizine. Picolide is thus acetylmethylketoquinolizine, whilst the mono-nitro-compound obtained by the action of nitric acid is nitromethylketoquinolizine (III):

$$\text{(II.)} \begin{array}{l} CH{:}CH\cdot CH\cdot CH{:}CH \\ CH{:}CH\cdot N{-}CH{:}CH \end{array} \qquad \text{(III.)} \begin{array}{l} CH{:}CH\cdot C{:}C(NO_2)\cdot CMe \\ CH{:}CH\cdot N{-}CO{-}CH \end{array}.$$

Pyrindole couples with diazonium salts in acid solution, yielding crystalline azo-compounds, and reacts with acetic anhydride and benzoyl chloride to form an acetyl and benzoyl derivative. The position of the azo- and acyl-groups has not been definitely established, but from the analogous reactions with pyrrole it is assumed that the groups enter the α-position to the pyrrole ring; benzeneazopyrindole thus receives the formula:

$$\text{(IV.)} \begin{array}{l} CH{:}CH\cdot C{:}CH \\ CH{:}CH\cdot N{-}C \end{array}\!\!\geqslant\! CH \; N{:}NPh.$$

A number of other reactions, illustrating the similarity in the behaviour of pyrindole on the one hand and pyrrole and indole derivatives on the other, are also described.

The ready formation of picolide from α-picoline and acetic anhydride has induced the authors to investigate the behaviour of α-picoline towards other anhydrides, but only in the case of propionic anhydride could a definite product be isolated. The reaction proceeds in a manner entirely different to that occurring when acetic anhydride is employed, the resulting compound being a 2-pyridyl-3-ethyl-Δ^3-*cyclo*pentenone:

$$\text{(V.)}\; CH\!\lessdot\!\begin{array}{l} CH{:}CH \\ CH{-}N \end{array}\!\!>\!C\cdot CH\!<\!\begin{array}{l} CO{-}CH_2 \\ CEt{:}CH \end{array}.$$

The following condensation products were obtained by condensing aromatic aldehydes with picolide by means of sodium hydroxide in alcoholic solution:

Di-o-*nitrobenzylidenepicolide*, yellowish-brown crystals, which begin to decompose at 200°, m. p. 220°; the isomeric *meta*- and *para*-compounds have m. p. 212° and 316° respectively; *mono*-p-*nitrobenzylidenepicolide*, orange needles, m. p. 242°; *tetramethyldi*-p-*aminobenzylidenepicolide*, from *p*-dimethylaminobenzaldehyde, forms orange needles, m. p. 227°; *dianisylidenepicolide*, m. p. 212°.

Picolide reacts with magnesium methyl iodide to form the *compound*, $C_{10}H_8NO\cdot CMe_2\cdot OH$, crystallising in long, yellow needles, m. p. 169°,

and with magnesium phenyl bromide, yielding the *compound*,

$$C_{10}H_8ON{\cdot}CMePh{\cdot}OH,$$

which forms colourless, felted needles, m. p. 178°.

Benzeneazopyrindole (formula IV) crystallises in red needles, m. p. 109°, and *pyrindoleazo*-p-*toluene* in reddish-brown needles, m. p. 98°.

a-Naphthaleneazopyrindole forms a brown, crystalline powder, which begins to melt at 120° and then decomposes.

Benzoylpyrindole, $C_8H_6N{\cdot}COPh$, prepared by the interaction of pyrindole and benzoyl chloride at the ordinary temperature, crystallises in yellow needles, m. p. 96°.

Pyrindole reacts with carbonyl chloride in toluene solution to form *pyrindolecarboxyl chloride*, $C_8H_6N{\cdot}COCl$, which crystallises in colourless needles, m. p. 81°, and is hydrolysed by aqueous sodium hydroxide to *pyrindolecarboxylic acid*, needles, m. p. 135° (decomp.).

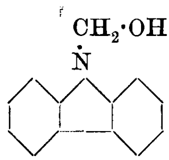
Diquinonylpyrindole, $\begin{array}{l} CH{:}CH{\cdot}C{=\!=\!=}C{\cdot}C_6H_4O_2 \\ CH{:}CH{\cdot}N{\cdot}CH{:}C{\cdot}C_6H_4O_2 \end{array}$, prepared from pyrindole and quinone in alcoholic solution, forms deep blue crystals, m. p. above 350°, and resembles the diquinonyldimethylpyrrole described by Möhlau and Redlich (A., 1912, i, 129°).

Pyrindole condenses with ethyl acetoacetate in alcoholic solution in the presence of hydrochloric acid, yielding *ethyl dipyrindoleacetoacetate*,

$\begin{array}{l} CH{:}CH{\cdot}C{=\!=\!=}C{\cdot}CMe(CH_2{\cdot}CO_2Et){\cdot}C{=\!=\!=}C{\cdot}CH{:}CH \\ CH{:}CH{\cdot}N{\cdot}CH{:}C{\cdot}CMe(CH_2{\cdot}CO_2Et){\cdot}C{:}CH{\cdot}N{\cdot}CH{:}CH \end{array}$, crystallising in microscopic, yellowish-green needles, m. p. 140°.

2-*Pyridyl*-3-*ethyl*-Δ^3-cyclo*pentenone* (V), prepared by heating a-picoline and propionic anhydride at 220°, forms colourless needles, m. p. 86°, and yields a *semicarbazone*, yellow needles, m. p. 201°. F. B.

Preparation of Methylolcarbazole. MARTIN LANGE (D.R.-P. 256757).—*Methylolcarbazole* (annexed formula) is obtained when a boiling alcoholic solution of carbazole (16·7 parts) is treated with anhydrous potassium carbonate (10 parts) and a 40% solution of formaldehyde (10 parts); on cooling, the product separates; it forms colourless needles, m. p. 127—128°, with an evolution of formaldehyde; mineral acids convert it into methylenecarbazole. F. M. G. M.



Preparation of *N*-Alkylcarbazolesulphonic Acids. LEOPOLD CASSELLA & Co. (D.R.-P. 256718. Compare A., 1910, i, 775).—Sulphonated *N*-alkylcarbazoles have not been prepared, although di- and tri-sulphonyl derivatives of carbazole itself are known. *Ethyl carbazolesulphonic acid* is obtained when fused *N*-ethylcarbazole (195 parts) is slowly treated with forty parts of concentrated sulphuric acid, heated at 120° and subsequently at 150—160°, and the mixture finally treated with sodium carbonate; the *barium*, *calcium*, *sodium*, and *potassium* salts are crystalline powders.

When fused with an alkali hydroxide, these compounds furnish hydroxy-*N*-alkylcarbazoles, which condense with *p*-nitrosophenols to yield indophenolsulphonic acids. F. M. G. M.

Ammonium-amides and the Action of Amines on Cyclammonium Salts and Analogous Compounds. HERMAN DECKER and PAUL BECKER (*Ber.*, 1913, **46**, 969—978).—It has already been shown that the action of ammonia or amines on the quaternary salts of phenylacridinecarboxylic acid yields not only the lactone, but also the lactam of aminophenylmethyldihydroacridinecarboxylic acid (Decker and Schenk, A., 1906, i, 304), and it was suggested that the change takes place with the intermediate formation of a compound corresponding to ammonium-amide, $NH_4\cdot NH_2$, the scheme:

$$NMeI{<}\substack{C_6H_4\\ C_6H_4}{>}C\cdot C_6H_4\cdot CO_2H \longrightarrow NH_2\cdot NMe{<}\substack{C_6H_4\\ C_6H_4}{>}C\cdot C_6H_4\cdot CO_2H$$

$$\downarrow$$

$$NMe{<}\substack{C_6H_4\\ C_6H_4}{>}C{<}\substack{NH-\\ C_6H_4}{>}CO \longleftarrow NMe{<}\substack{C_6H_4\\ C_6H_4}{>}C(NH_2)\cdot C_6H_4\cdot CO_2H$$

representing the probable series of changes. This view was confirmed by several considerations, and it is now greatly strengthened by the discovery that the parent substance, phenylacridine methiodide, is converted by concentrated ammonia into 5-amino-5-phenyl-10-methyldihydroacridine, $NMe{<}\substack{C_6H_4\\ C_6H_4}{>}CPh\cdot NH_2$. This finally disposes of any idea that the previous product may have been due to the action of ammonia on the previously formed lactone. The cause of the rearrangement is supposed to be the tendency of the positive amino-group to migrate from the positive nitrogen atom to a negative carbon atom. That such a substance as $NH_2\cdot NMe{<}\substack{C_6H_4\\ C_6H_4}{>}CPh$, which is assumed as the first product of the above reaction, should be capable of at least a fleeting existence is indicated by the formation of carbinylamines by the action of ammonia on the salts of the triphenylmethane dyes, in which the analogous steps:

$$(NH_2\cdot C_6H_4)_2\cdot C{:}C_6H_4{:}NH_2Cl \longrightarrow (NH_2\cdot C_6H_4)_2C{:}C_6H_4{:}NH_2\cdot NH_2 \longrightarrow (NH_2\cdot C_6H_4)_2C(NH_2)\cdot C_6H_4\cdot NH_2$$

probably occur (Noelting and Saas, this vol., i, 522; Villiger and Kopetschni, A., 1912, i, 1030). The structurally related xanthylium and thioxanthylium salts also yield carbinylamines with ammonia. The possibility that the acridinium salts may be of the carbonium structure which has been suggested for the triphenylmethane colours is very slight, as the former eliminate methyl iodide exceedingly readily, even, for example, when exposed in aqueous solution to daylight for several weeks.

5-Amino-5-phenyl-10-methyldihydroacridine, small, colourless rods, m. p. 121—122°, is obtained by the gradual addition of a concentrated solution of phenylacridine methiodide to a large excess of 20% ammonia solution; if a dilute solution of ammonia in slight excess is allowed to act on the methiodide, the product is hydroxyphenylmethyldihydroacridine, which is ver similar in appearance, and this accounts for the divergence of the results of Decker, Hock, and Djiwonsky (A., 1902,

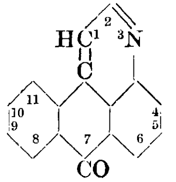
i, 830) and of Hantzsch (A., 1902, i, 113, 126). The above amino-compound dissolves in dilute acids, undergoing scission into phenylmethylacridinium and ammonium salts; when heated with alcohol, with or without the addition of a little sodium hydroxide, ammonia is again obtained, together with the 5-ethoxy-5-phenyl-10-methyldihydroacridine, colourless prisms, m. p. 112—113°, which is also obtained by similar treatment of the hydroxyphenylmethyldihydroacridine itself. When warmed with aniline, both the above amino-compound (a carbinylamine) and the corresponding hydroxy-compound are converted into the *carbinylanilide* with elimination of a molecule of ammonia and of water respectively.

If a solution of a phenylxanthylium salt is introduced into ammonia solution a mixture of the amino-compound and of the carbinol is obtained (compare Bünzly and Decker, A., 1904, i, 912); for the preparation of the pure amino-compound the phenylxanthylium ferrichloride, m. p. 169°, was introduced as a fine powder into 20% ammonia solution under benzene; the resultant carbinylamine (*9-amino-9-phenylxanthen*), $O<\substack{C_6H_4\\C_6H_4}>CPh\cdot NH_2$, leaflets, m. p. 112—113°, is extracted by the benzene; when boiled with alcohol it is converted into the ethyl ether of phenylxanthenol (Bünzly and Decker, *loc. cit.*). The formation of the carbinylamine is believed to follow the same course as with the corresponding acridine compound.

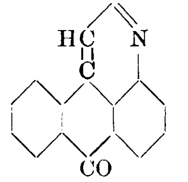
9-Amino-9-phenylthioxanthen, yellowish-red prisms, m. p. 118—120°, is obtained in a similar manner by the action of ammonia on phenylthioxanthylium ferrichloride, and undergoes similar conversion into the ethyl ether of thioxanthenol.

The recent discovery of Zincke and Weisspfennig (this vol., i, 389) of dinitrodiphenylamine amongst the reaction products of aniline and 2-dinitrophenyl*iso*quinolinium chloride is held to be a further confirmation of the existence of the ammonium-amides and of their decomposition according to the equation: $NA_4\cdot NR_2 = NA_3 + NR_2A$, where A represents an alkyl radicle. D. F. T.

Preparation of Anthracene Derivatives Containing Nitrogen. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 256297. Compare A., 1908, i, 456, 699; 1909, i, 263).—*a-Chloropyridanthrone*, yellowish-white needles, m. p. 260°, is prepared by the action of phosphorus pentachloride on the previously described 2-hydroxypyridanthrone (I); it reacts readily with primary aromatic amines to furnish compounds of the general formula (II).



(I.)



(II.)

2(1')-Anthraquinonylaminopyridanthrone is thus obtained by condensation with 1-aminoanthraquinone in nitrobenzene solution in the presence of copper iodide and sodium acetate; it does not melt below 300°. The analogous *compound* from aniline has m. p. 227—229°.

F. M. G. M.

Syntheses in the Group of the Indogenides. ANDRÉ WAHL and P. BAGARD (*Compt. rend.*, 1913, **156**, 898—901).—An endeavour to prepare, by the condensation of substituted isatins with oxindole, a new series of indogenides of the type $X<^{C_6H_3R}_{CO}>C:C<^{C_6H_3R'}_{CO}>Y$, where X and Y may be identical or different bivalent atoms or groups, and R and R' any substituents. These condensations did not, however, go so simply as in the case of isatin itself and oxindole (compare A., 1909, i, 330). Thioisatin and oxindole yields not thio-3 : 3'-bisindole, as expected, but "thioindigo scarlet," $NH<^{C_6H_4}_{CO}>C:C<^{CO}_{S}>C_6H_4$ (compare Kalle, D.R.-P. 241327). 1-Methylisatin on the other hand behaves like isatin itself, and gives 1-*methyl*iso*indigotin*,

$$NH<^{C_6H_4}_{CO}>C:C<^{C_6H_4}_{CO}>NMe,$$

brown needles.

2-Methylisatin when mixed with oxindole in acetic acid solution containing a little aqueous hydrochloric acid is hydrolysed and the product of condensation is simply 3 : 3'-bisindole. If the action takes place in an anhydrous medium in the cold, indirubin is formed. This thus furnishes an easy and rapid method of preparing indirubin, and gives a 90% yield.

W. G.

[Preparation of 1-Chloronitro-2 : 4-diacetylphenylenediamine.] AKTIEN-GESELLSCHAFT FÜR ANILINFABRIKATION (D.R.-P. 255858).—1-Chloro-2 : 4-phenylenediamine gives rise to a diacetyl derivative which on nitration furnishes 1-*chloronitro*-2 : 4-*diacetylphenylenediamine*, m. p. 234—235°, and on hydrolysis yields 1-*chloronitro*-2 : 4-*phenylenediamine*, m. p. 170°.

F. M. G. M.

Existence of Phenyldi-imide. WILHELM VAUBEL (*Ber.*, 1913, **46**, 1115—1116. Compare A., 1900, i, 522).—An acknowledgment of the criticism of Forster and Withers (T., 1913, **103**, 266) as to the nature of the compound described as phenyldi-imide.

H. W.

[Preparation of Anthraquinone Derivatives.] FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 256626).—3-*Bromo*-4-*aminoanthraquinoneacridone*, a blue powder, m. p. 260—270°, is obtained when 3-bromo-4-amino-1-anthraquinonylanthranilic acid is heated at 30° with chlorosulphonic acid.

F. M. G. M.

[Preparation of Indigoid Compounds.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 255691. Compare A., 1906, i, 696).—The *compound*, $C_6H_4<^{NH}_{CO}>C:C<^{-CH}_{C_6H_4}>N$, dark red needles, m. p. 212°

(decomp.), is obtained by the action of alkali hydroxides on indoxyl; if the action is allowed to proceed further, it gives rise to the *compound*, $C_6H_4<\substack{NH-\\CO_2H}>CH{:}C<\substack{-CH\\C_6H_4}>N$, and this, when boiled with an alkali carbonate, furnishes anthranilic acid and β-indolealdehyde (*loc. cit.*). F. M. G. M.

Action of Aliphatic Ketones on Indole and its Homologues: Polymeric Indoles. MAX SCHOLTZ (*Ber.*, 1913, **46**, 1082—1089).—Indole and its 2-methyl derivative condense with acetone, yielding compounds of the type: (I) $N\leqslant\substack{C_6H_4\\CH-}>C<\substack{CMe_2\\CMe_2}>C<\substack{C_6H_4\\-CH}\geqslant N$ and (II) $NH<\substack{C_6H_4\\-CH}\geqslant C\cdot CMe_2\cdot C\leqslant\substack{C_6H_4\\CH-}>NH$, accordingly as the condensation is effected by means of hydrochloric acid or acetic acid. Similar products are obtained from methyl ethyl ketone, but not from diethyl ketone.

Bisdimethyl-2-methylindolidenemethane,

$$C_8H_4NMe<\substack{CMe_2\\CMe_2}>C_8H_4NMe,$$

obtained in the form of its *hydrochloride* (colourless needles, m. p. 172°) by the addition of hydrochloric acid to an alcoholic solution of 2-methylindole and acetone, crystallises in colourless needles, m. p. 183°; the *hydrobromide*, prepared in a similar manner, has m. p. 172°.

Bis-2-methylindyldimethylmethane, $CMe_2(C_8H_5NMe)_2$, is obtained by boiling 2-methylindole with glacial acetic acid; it crystallises in colourless leaflets, m. p. 197°.

Bismethylethyl-2-methylindolidenemethane,

$$C_8H_4NMe<\substack{CMeEt\\CMeEt}>C_8H_4NMe,$$

prepared from methyl ethyl ketone, using hydrochloric acid as the condensing agent, forms colourless leaflets, m. p. 97°; the *hydrochloride* crystallises in colourless needles, m. p. 166°.

Ethyl acetoacetate and 2-methylindole yield *ethyl 2-methylindolideneacetoacetate*, $N\leqslant\substack{C_6H_4\\CMe}>C{:}CMe\cdot CH_2\cdot CO_2Et$, crystallising in long, colourless needles, m. p. 124°.

Bisdimethylindolidenemethane (formula I), prepared from indole and acetone, forms light yellow needles, m. p. 170°; the *hydrochloride* crystallises in orange-yellow needles, m. p. 169°.

Bisindyldimethylmethane (II) forms colourless prisms, m. p. 165°.

An alcoholic solution of indole, on treatment with hydrochloric acid at the ordinary temperature, yields the *hydrochloride* of tri-indole, crystallising in prisms, m. p. 183°; replacement of the hydrochloric acid by hydrobromic acid gives rise to the *hydrobromide* of di-indole, which forms slender, colourless needles (compare Keller, this vol., i, 403). F. B.

The Constitution of the Pyrazolinecarboxylic Acids. III. AUGUST DARAPSKY (*Ber.*, 1913, **46**, 863—867).—An experimental

investigation in favour of the view that the condensation products of the esters of the diazo-aliphatic acids with the esters of unsaturated carboxylic acids are in reality pyrazoline derivatives and not azine compounds with open-chain structure (compare Darapsky, this vol., i, 297; A., 1912, i, 391; Bülow, this vol., i, 101; A., 1912, i, 134, 316).

The reduction of 4-phenylpyrazole-3 : 5-dicarboxylic acid by sodium amalgam and water at 80—90° gave the same 4-phenylpyrazolidine-3 : 5-dicarboxylic acid (Buchner and Perkel, A., 1904, i, 101) as was obtained by a similar reduction of 4-phenylpyrazoline-3 : 5-dicarboxylic acid. The temperature of decomposition of the product ranges between 220° and 226° according to the rate of heating. D. F. T.

Constitution of Hypnal. DEMETRIUS E. TSAKALOTOS (*Bull. Soc. chim.*, 1913, [iv], **13**, 281—285).—Béhal and Choay (A., 1893, i, 301) have obtained two substances by the action of chloral on antipyrine, to which they assign the formulæ below, the first of which is used in

$$\begin{array}{ll} \text{CH—CO} & \text{CH—CO} \\ \| \quad\;\; >\text{NPh} & \| \qquad\quad >\text{NPh(OH)·CH(OH)·CCl}_3 \\ \text{CMe·NMe(OH)·CH(OH)·CCl}_3 & \text{CMe·NMe(OH)·CH(OH)·CCl}_3 \\ \text{(I.)} & \text{(II.)} \end{array}$$

pharmacy under the name hypnal. For the second, the author proposes the name bihypnal. The substances have m. p. 62·3° and 61·8° respectively, whereas Béhal aud Choay found 67—68° for either substance.

The author has examined the freezing-point curve of mixtures of chloral hydrate and antipyrine, and finds that it rises to a maximum at the two points at which chloral hydrate : antipyrine = 2 : 1 and = 1 : 1 respectively. From the general form of the curve, he is led to the conclusion that hypnal and bihypnal are molecular compounds, which, he considers, explains the practical identity of their m. p.'s H. W.

Some New Derivatives of Piperazine. MARIO GHIGLIENO (*Atti R. Accad. Sci. Torino*, 1912–13, **48**, 534—538).—When cyanacetic ester and anhydrous piperazine are heated together for one hour at 100—115°, *biscyanoacetylpiperazine*, $C_4H_8N_2(CO·CH_2·CN)_2$, is formed; it crystallises in colourless or slightly yellow needles, m. p. 248—250° (decomp.). When ordinary hydrated piperazine is used in the reaction, the corresponding *amide*, $C_4H_8N_2(CO·CH_2·CO·NH_2)_2$, is obtained; it crystallises in colourless needles or in prisms, which decompose about 174—175° when rapidly heated. The substance is acid in reaction, and gives metallic salts. It is converted into the dicarboxylic acid only with great difficulty. Anhydrous piperazine, m. p. 104°, is obtained by keeping ordinary piperazine over calcium chloride for a long time. R. V. S.

Pyrimidines. LX. Alkylation with Benzyl Chloride. TREAT B. JOHNSON and ZAI ZIANG ZEE (*Amer. Chem. J.*, 1913, **49**, 287—294).—Johnson and Derby (A., 1908, i, 1018) studied the action of benzyl chloride in presence of sodium ethoxide on certain derivatives

of 2-ethylthiol-6-pyrimidone, and found that in all cases the corresponding *N*-benzyl compounds were produced. It was shown that the substitution of a methyl group in the 4- or 5-position and a bromine atom or ethoxy-group in the 5-position of the ring does not favour the formation of 6-benzoxypyrimidines. The present work was undertaken with the object of investigating the action of benzyl chloride on a 2-thiol-6-pyrimidone in which both the 4- and 5-positions are substituted, and of determining whether a strongly negative group in the 4-position would favour the production of an *O*-benzyl derivative.

Ethyl 2-amino-5-methyl-6-pyrimidone-4-carboxylate,

$$NH<\begin{matrix}C(NH_2):N\\CO\text{---}CMe\end{matrix}>C\cdot CO_2Et,$$

obtained in small yield by the action of the sodium salt of ethyl oxalylpropionate on guanidine thiocyanate in presence of sodium hydroxide, forms prismatic needles, and does not show a definite m. p.

Ethyl 2-ethylthiol-1-benzyl-5-methyl-6-pyrimidone-4-carboxylate,

$$CH_2Ph\cdot N<\begin{matrix}C(SEt):N\\CO\text{--}CMe\end{matrix}>C\cdot CO_2Et,$$

m. p. 69—71°, prepared by heating ethyl 2-ethylthiol-5-methyl-6-pyrimidone-5-carboxylate with benzyl chloride in presence of sodium ethoxide, crystallises in colourless needles, and when hydrolysed with concentrated hydrochloric acid is converted into *1-benzyl-5-methyl-pyrimid-2 : 6-dione-4-carboxylic acid*, $CH_2Ph\cdot N<\begin{matrix}CO\text{--}NH\\CO\cdot CMe\end{matrix}>C\cdot CO_2H$, m. p. 277—279° (decomp.), which forms hexagonal tablets. When the latter compound is heated at 285—295° until effervescence ceases, *1-benzyl-5-methylpyrimid-2 : 6-dione* (*1-benzylthymine*),

$$CH_2Ph\cdot N<\begin{matrix}CO\text{--}NH\\CO\cdot CMe\end{matrix}>CH,$$

m. p. 203—205°, is obtained, which forms prismatic crystals.

An attempt was made to alkylate ethyl 5-methylpyrimid-2 : 6-dione-4-carboxylate with benzyl chloride in presence of sodium ethoxide, but without success. E. G.

[Phenazine] Correction. FRIEDRICH KEHRMANN (*Ber.*, 1913, **46**, 1220. Compare this vol., i, 298).—Fischer and Hepp (A., 1897, i, 257) had already observed that rosindones resulted by the action of alkalis on alkylnaphthaphenazonium salts. The author still holds that the green methylphenazonium iodide is a quinhydrone salt (compare Hantzsch, this vol., i, 393.) J. C. W.

The Triphenylmethane Colour Bases. EMILIO NOELTING and J. SAAS (*Ber.*, 1913, **46**, 952—967).—The authors have convinced themselves that the action of ammonia on triphenylmethane dyes is, as was believed by von Baeyer (A., 1910, i, 249), more complex than was at first supposed (Noelting & Philipp, A., 1908, i, 295). An independent investigation of the products of the action of ammonia has been recently published by Villiger and Kopetschni (A., 1912, i, 1030).

Commercial crystal-violet always contains some of the pentamethyl compound, which can be detected by acetylation, dissolving in water, and partly immersing in the liquid a piece of filter paper; the green colour of the acetyl derivative of the pentamethyl compound rises in the paper more rapidly than the violet. Even when Michler's ketone is condensed with pure dimethylaniline in the presence of phosphoryl chloride, the condensation product contains a quantity of pentamethyl compound. The product contains least pentamethyl compound if a large excess of the amine is taken for the condensation. The colourless substance obtained from the action of ammonia on crystal-violet is the carbinylamine, $NH_2\cdot C(C_6H_4\cdot NMe_2)_3$; it separates from a mixture of benzene and ligroin in prismatic tablets, m. p. 193—195°. The action of diethylamine on a solution of crystal-violet, on the other hand, precipitates the carbinol, m. p. 194—195°, which after recrystallisation has m. p. 207—209° (compare Villiger and Kopetschni, *loc. cit.*), whilst trimethylamine solution produces at first a violet solution of the ammonium base, $OH\cdot NMe_2{:}C_6H_4(C_6H_4\cdot NMe_2)_2$, which shortly begins to lose its colour and to deposit the carbinol in a pure state.

Ethyl-violet (hexaethyltriaminotriphenylcarbinol), obtained from tetraethyldiaminobenzophenone, diethylaniline and phosphoryl chloride alone, or mixed with benzene at 100°, on precipitation with potassium hydroxide yielded the free colourless carbinol, $OH\cdot C(C_6H_4\cdot NEt_2)_3$, m. p. 136—137°. When recrystallised from alcohol, the carbinol undergoes partial etherification, and the *ethyl ether*, $OEt\cdot C(C_6H_4\cdot NEt_2)_3$, m. p. 127—128°, can be readily obtained by the action of sodium ethoxide. The *carbinylamine*, $NH_2\cdot C(C_6H_4\cdot NEt_2)_3$, of ethyl-violet forms colourless needles, m. p. 141·5—142·5°.

Victoria-Blue *B*, obtained by purification of the commercial article and by condensation of pure Michler's ketone with phenyl-α-naphthylamine, forms deep blue tablets, m. p. 247—249°. No corresponding carbinol, carbinyl ether and amine were isolable, as the action of alkalis yielded only an *imine* base, $NPh{:}C_{10}H_6{:}C(C_6H_4\cdot NMe_2)_2$, deep violet, prismatic tablets, which is hydrolysed by dilute sulphuric acid to Michler's ketone and phenyl-α-naphthylamine (compare Nathanson and Müller, A., 1889, 1188).

Night-Blue, m. p. 219—220°, yields an analogous *imine* base,

$$C_6H_4Me\cdot N{:}C_{10}H_6{:}C(C_6H_4\cdot NMe_2)_2,$$

deep violet, prismatic tablets, which can also be hydrolysed to its components, Michler's ketone, and tolyl-α-naphthylamine.

α-Naphthol-Blue (tetramethyldiaminonaphthafuchsone), the condensation product of Michler's ketone, and α-naphthol, when pure, forms dark-coloured prisms, m. p. 266—270°; *hydrochloride*, green needles; *platinichloride*, dark coloured. No carbinol, carbinyl ether, or carbinylamine could be isolated; it gives a green *acetyl* derivative, and on reduction in acetic acid by zinc dust a *leuco-base*,

$$CH(C_6H_4\cdot NMe_2)_2\cdot C_{10}H_6\cdot OH,$$

prisms, m. p. 187—188°.

Naphtho-Blue (Noelting and Philipp, *loc. cit.*), the condensation product of Michler's ketone and dimethyl-α-naphthylamine, can be separated into a coloured and a colourless constituent; the latter is, as

earlier suggested, the carbinol, $OH\cdot C(C_6H_4\cdot NMe_2)_2\cdot C_{10}H_6\cdot NMe_2$, but the former is actually identical with α-Naphthol-Blue, and must be produced by a partial elimination of dimethylamine during the neutralisation of the reaction product; the product also always contains some pentamethyl compound, $C(C_6H_4\cdot NMe_2)_2{:}C_6H_4{:}NMe,HCe$, due to a loss of a methyl group similar to that observed in the preparation of crystal-violet. For the preparation of the pure colourless carbinol of Naphtho-Blue it is advisable to use in the condensation an excess of dimethyl-α-naphthylamine, and then to render the solution of the product alkaline at as low a temperature as possible. Treatment of the aqueous solution of the chloride with ammonia yields the colourless carbinylamine, m. p. 173—175°. D. F. T.

5-Aminopyrazole and Iminopyrines. III. 5-Imino-1-phenyl-3-methylpyrazolone. AUGUST MICHAELIS and ARTHUR SCHÄFER (*Annalen.*, 1913, **397**, 119—148. Compare A., 1911, i, 1037; 1905, i, 476).—1-*Phenyl*-3-*methyl*-4 : 5-*azipyrazole*, $N{<}\begin{matrix}NPh\cdot C{=}\\ CMe\cdot CH\end{matrix}{>}N$, m. p. 109°, yellowish-brown leaflets, prepared by warming 5-amino-1-phenyl-3-methylpyrazole (5-imino-1-phenyl-3-methylpyrazolone) in 50% acetic acid with concentrated hydrogen peroxide, is converted into 5-amino-1-phenyl-3-methylpyrazole by reducing agents and into 4-halogeno-5-amino-1-phenyl-3-methylpyrazoles by warming with concentrated halogen acids. 4-*Chloro*-1-*phenyl*-3-*methyl*-4 : 5-*azipyrazole*, m. p. 103°, red leaflets, is obtained by treating 4-chloro-5-amino-1-phenyl-3-methylpyrazole with hydrogen peroxide as above, or, in hydrochloric acid, with concentrated sodium nitrite. It is also obtained by leading chlorine into a hydrochloric acid solution of 5-amino-1-phenyl-3-methylpyrazole. The last method has enabled the authors to explain the constitution of the trichloro-compound obtained by Michaelis and Brust (*loc. cit.*); this is not 4-chloro-5-amino-1-dichlorophenyl-3-methylpyrazole as stated previously, but 4-*chloro*-5-*dichloroamino*-1-*phenyl*-3-*methylpyrazole*, m. p. 60°, since it yields 4-chloro-1-phenyl-3-methyl-4 : 5-azipyrazole by warming with water. Unlike the non-halogenated compound, 4-chloro-1-phenyl-3-methyl-4 : 5-azipyrazole is unchanged by halogen acids; it is reduced to 4-chloro-5-amino-1-phenyl-3-methylpyrazole by boiling concentrated sodium hyposulphite. 4-*Bromo*-1-*phenyl*-3-*methyl*-4 : 5-*azipyrazole*, $C_{10}H_8N_3Br$, m. p. 101°, reddish-brown leaflets, prepared by similar methods to the chloro-compound, yields 4-bromo-5-amino-1-phenyl-3-methylpyrazole by reduction, and is converted into 4 : 4-*dibromo*-5-*imino*-1-*phenyl*-3-*methylpyrazolone*,

$$NPh{<}\begin{matrix}N{=\!=\!=}CMe\\ C({:}NH)\cdot CBr_2\end{matrix},$$

m. p. 126°, colourless needles, and 4-*chloro*-4-*bromo*-5-*imino*-1-*phenyl*-3-*methylpyrazolone*, m. p. 124°, colourless needles, by warming with hydrobromic acid or hydrochloric acid, and subsequently basifying with ammonia. 4-*Iodo*-1-*phenyl*-3-*methyl*-4 : 5-*azipyrazole*, $C_{10}H_8N_3I$, m. p. 194°, yellowish-red needles, prepared by the oxidation of 4-iodo-5-amino-1-phenyl-3-methylpyrazole or by heating 5-amino-1-phenyl-3-methylpyrazole with alcoholic iodine and sodium hydroxide at 150°, is

unchanged by halogen acids, and is converted into 4-iodo-5-amino-1-phenyl-3-methylpyrazole by reduction. 1-*Phenyl*-3 : 4-*dimethyl*-4 : 5-*azipyrazole*, $C_{11}H_{11}N_3$, m. p. 105°, red leaflets, is prepared by oxidising 5-amino-1-phenyl-3 : 4-dimethylpyrazole in hydrochloric acid by hydrogen peroxide; it is soluble in concentrated halogen acids and is precipitated unchanged by alkalis. 4 : 5-*Anilo*-1-*phenyl*-3-*methylpyrazole*, $N\lessdot\genfrac{}{}{0pt}{}{NPh\cdot C}{CMe\cdot C}\!\!>\!NPh$, m. p. 169°, red leaflets or brownish-red needles, is prepared by treating a glacial acetic acid solution of 4-benzeneazo-5-amino-1-phenyl-3-methylpyrazole with concentrated sodium nitrite, whereby nitrogen and nitric oxide are evolved. By reduction with tin and alcoholic hydrochloric acid, it yields benzene and 4-amino-1-phenyl-3-methyl-5-pyrazolone hydrochloride, by the oxidation of which in the air rubazonic acid is produced. 4-β-*Naphthaleneazo*-5-*amino*-1-*phenyl*-3-*methylpyrazole*, $C_{20}H_{17}N_5$, m. p. 117°, yellow leaflets, prepared from β-naphthalenediazonium chloride and 5-amino-1-phenyl-3-methylpyrazole in aqueous sodium carbonate, is converted in a similar manner into 4 : 5-β-*naphthylimino*-1-*phenyl*-3-*methylpyrazole*, $C_{20}H_{15}N_3$, m. p. 178°, reddish-brown needles, by the reduction of which naphthalene and 4-amino-1-phenyl-3-methylpyrazole are formed.

5-*Formylamino*-1-*phenyl*-3-*methylpyrazole*, $C_{11}H_{11}ON_3$, m. p. 135°, colourless needles, prepared from the aminopyrazole and formic acid on the water-bath, and the corresponding *benzoylamino*-derivative, $C_{17}H_{15}ON_3$, m. p. 113°, long needles, have been prepared; the latter is converted into 4-*bromo*-5-*benzoylamino*-1-*phenyl*-3-*methylpyrazole*, m. p. 172°, by bromine in dilute acetic acid. 5-*Benzenesulphonylamino*-1-*phenyl*-3-*methylpyrazole* has m. p. 170°. 5-Acetylamino-1-phenyl-3-methylpyrazole and benzenediazonium chloride yield a *substance*,

$$C_{36}H_{41}O_4N_7,$$

m. p. 107°, yellow needles, which is being investigated.

Hot aqueous potassium cyanate and 5-amino-1-phenyl-3-methylpyrazole hydrochloride yield 5-*carbamido*-1-*phenyl*-3-*methylpyrazole*, $NH_2\cdot CO\cdot NH\cdot C\lessdot\genfrac{}{}{0pt}{}{NPh\cdot N}{CH{-}CMe}$, m. p. 215°, colourless needles.

5-Amino-1-phenyl-3-methylpyrazole and phenylcarbimide yield, by heating, 5-*phenylcarbamido*-1-*phenyl*-3-*methylpyrazole*, m. p. 205°; the *phenylthiocarbamido*-derivative, m. p. 150°, is prepared in a similar manner. The 5-aminopyrazole and carbon disulphide at 150° yield the s-*thiocarbamide*, $CS(NH\cdot C_{10}H_9N_2)_2$, m. p. 184°.

5-Amino-1-phenyl-3-methylpyrazole can be almost completely diazotised in nearly concentrated hydrochloric acid (compare Mohr, A., 1909, i, 190); the solution does not contain 4-oximino-5-imino-1-phenyl-3-methylpyrazolone, and yields coloured precipitates with alkaline β-naphthol and resorcinol. 1-*Phenyl*-3-*methylpyrazole*-5-*azoresorcinol*, $C_{16}H_{14}O_2N_4$, yellow needles, has m. p. 250°. 1-Phenyl-3-methylpyrazole-5-diazonium chloride and 1-phenyl-3-methyl-5-pyrazolone in acetic acid slowly form 1-*phenyl*-3-*methylpyrazole*-5(4′)-*azo*-1′-*phenyl*-3′-*methyl*-5′-*pyrazolone*, $\genfrac{}{}{0pt}{}{N{-}NPh}{CMe\cdot CH}\!\!>\!C\cdot N_2\cdot CH\lessdot\genfrac{}{}{0pt}{}{CO{-}NPh}{CMe{:}N}$, m. p. 175°, yellowish-red needles, which is soluble in alkalis. 5-*Diazoamino*-

1-*phenyl-3-methylpyrazole*, $C_{10}N_2H_9\cdot N_2\cdot NH\cdot C_{10}N_2H_9$, m. p. 182°, yellow leaflets, is obtained by treating 5-amino-1-phenyl-3-methylpyrazole in hydrochloric acid with less than 1 mol. of sodium nitrite, or by carefully treating the completely diazotised solution with aqueous sodium hydroxide.

5-Amino-1-phenyl-3-methylpyrazole and benzaldehyde at 135° yield 4-*benzylidenebis*-5-*amino*-1-*phenyl*-3-*methylpyrazole*, $CHPh(C_{10}N_3H_{10})_2$, m. p. 66°, faintly yellow powder, which forms a *hydrochloride*,

$$C_{27}H_{26}N_6,2HCl,$$

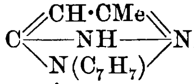
m. p. 218° (*platinichloride*, yellowish-red crystals), in the cold, but is converted into its generators by hot acids. The corresponding o-*nitrobenzylidene*, *salicylidene*, and *anisylidene* compounds, m. p. 89°, 120°, and 219° respectively, are described. C. S.

5-Amino-1-*o*- and *p*-tolyl-3-methylpyrazoles. AUGUST MICHAELIS and LUDWIG KLAPPERT (*Annalen*, 1913, **397**, 149—159).—*Aceto-acetonitrile*-o-*tolylhydrazone*, $CN\cdot CH_2\cdot CMe\colon N\cdot NH\cdot C_7H_7$, m. p. 115°, colourless needles, prepared from acetoacetonitrile and *o*-tolylhydrazine in 30% acetic acid, is converted, by heating with alcoholic hydrochloric acid at 120° for three hours and basifying, into 5-*amino*-1-o-*tolyl*-3-*methylpyrazole* (5-*imino*-1-o-*tolyl*-3-*methylpyrazolone*),

$$\begin{matrix}CH_2\cdot C(\colon NH)\\ |\\ CMe\colon N\text{———}\end{matrix}\!\!>N\cdot C_7H_7 \text{ or } \begin{matrix}CH\colon C(NH_2)\\ |\\ CMe\colon N\text{———}\end{matrix}\!\!>N\cdot C_7H_7,$$

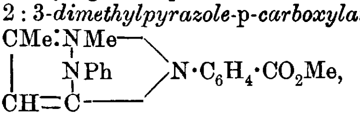
m. p. 93°, b. p. 314°, colourless crystals (*hydrochloride*, m. p. 113°), which reacts in hydrochloric acid with chlorine, in glacial acetic acid with bromine, and in alcohol with iodine, to form, after basifying, 4-*chloro*-5-*amino*-1-o-*tolyl*-3-*methylpyrazole*, m. p. 114°, and the 4-*bromo*-compound, m. p. 134°, and the 4-*iodo*-compound, m. p. 141°, respectively. By prolonged treatment with chlorine, a hydrochloric acid solution of 5-amino-1-*o*-tolyl-3-methylpyrazole yields 4-*chloro*-1-o-*tolyl*-3-*methyl*-4 : 5-*azipyrazole*, $N\!\!<\!\!\begin{matrix}CMe\text{——}CCl\\ |\\ N(C_7H_7)C\text{===}\end{matrix}\!\!>\!N$, m. p. 107°, red leaflets. 4-*Bromo*-1-o-*tolyl*-3-*methyl*-4 : 5-*azipyrazole*, m. p. 115°, red needles, and the 4-*iodo*-compound, m. p. 133°, reddish-brown leaflets, are prepared in a similar manner by means of bromine in acetic acid, and by alcoholic iodine at 140—150°.

5-Amino-1-*o*-tolyl-3-methylpyrazole is converted into 5-*acetylamino*-1-o-*tolyl*-3-*methylpyrazole*, m. p. 157°, colourless needles, by boiling acetic anhydride, into 4-*benzeneazo*-5-*amino*-1-o-*tolyl*-3-*methylpyrazole*, m. p. 118°, yellow leaflets, by benzenediazonium chloride in hydrochloric acid and subsequent addition of sodium carbonate, into 4-*oximino*-5-*imino*-1-o-*tolyl*-3-*methylpyrazolone*, m. p. 195°, red crystals, by sodium nitrite and 30% acetic acid, and into 5-*amino*-1-o-*tolyl*-3-*methylpyrazole methiodide*, $CH\!\!<\!\!\begin{matrix}C(NH_2)\cdot N\cdot C_7H_7\\ |\\ CMe\text{===}NMeI\end{matrix}$, m. p. 245°, colourless crystals, by boiling methyl alcoholic methyl iodide. The methiodide is changed by silver chloride to the *methochloride*, m. p. 241°, an aqueous solution of which yields, by treatment with concentrated sodium hydroxide, 2 : 5-*imino*-1-o-*tolyl*-2 : 3-*dimethylpyrazole* (1-o-*tolyl*-

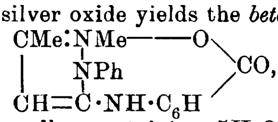
iminopyrine),  m. p. 35—36°, yellow crystals, from which have been prepared the *carbonate*, m. p. 98° (decomp.), *picrate*, m. p. 165°, yellow needles, *benzenesulphonyl* derivative, $C_{18}H_{19}O_2N_3S$, m. p. 179°, *benzoyl* derivative, m. p. 186°, and 4-*benzeneazo*-1-o-*tolyl-iminopyrine*, $C_{18}H_{19}N_5$, m. p. 188°, yellowish-brown leaflets.

The following compounds of the para-series are prepared by methods similar to the preceding: *Acetoacetonitrile*-p-*tolylhydrazone*, m. p. 123°, yellow leaflets; 5-*amino*-1-p-*tolyl*-3-*methylpyrazole*, m. p. 120°, colourless needles; 4-*bromo*-5-*amino*-1-p-*tolyl*-3-*methylpyrazole*, m. p. 128°, colourless needles; 4-*bromo*-1-p-*tolyl*-3-*methyl*-4 : 5-*azipyrazole*, m. p. 103°, orange-red leaflets; 4-*oximino*-5-*imino*-1-p-*tolyl*-3-*methylpyrazolone*, m. p. 198°, bordeaux-red crystals; 5-*amino*-1-p-*tolyl*-3-*methylpyrazole methiodide*, m. p. 135°, and *methochloride*; 1-p-*tolyliminopyrine* (*picrate*, m. p. 177°, yellow needles; *benzenesulphonyl* derivative, m. p. 203°; *carbonate*, decomp. 126°; and 4-*benzeneazo*-derivative, m. p. 191°, yellowish-brown leaflets). C. S.

5-*p*-Carboxylic Acids of Anilopyrine and their Esters. AUGUST MICHAELIS and WILHELM TITIUS (*Annalen*, 1913, **397**, 159—180).—The main object of the research is the production of further evidence in support of Michaelis's constitution for the iminopyrines. Antipyrine chloride and methyl *p*-aminobenzoate (3 mols.), heated at 130°, yield, by basifying the aqueous solution of the product, *methyl* 2 : 5-*anilo*-1-*phenyl*-2 : 3-*dimethylpyrazole*-p-*carboxylate* (*methyl anilopyrine*-p-*carboxylate*),

 m. p. 155°, greenish-yellow prisms,

which forms a *hydrochloride*, m. p. 142°, *platinichloride*, m. p. 200°, red crystals, *hydriodide*, m. p. 212° (decomp.), colourless needles, and *methiodide*, $C_{20}H_{22}O_2N_3I,3H_2O$, m. p. 102° (anhydrous, 202° [decomp.]), and is converted into the 4-bromo-compound, $C_{19}H_{18}O_2N_3Br$, m. p. 170°, yellow leaflets, by bromine in acetic acid. By hydrolysing the ester with concentrated alcoholic potassium hydroxide and treating the product with hydrochloric acid and finally with aqueous potassium iodide, the *hydriodide*, m. p. 236°, colourless needles, of anilopyrine-*p*-carboxylic acid is obtained. According to the authors, it has the constitution $CO_2H\cdot C_6H_4\cdot NH\cdot C\Big\langle\begin{matrix}NPh\cdot NMeI\\ CH-CMe\end{matrix}$, and by treating its aqueous solution with silver oxide yields the *betaine*,



which crystallises in needles containing $5H_2O$, m. p. 99—100° (the anhydrous substance is yellow and has m. p. about 150°), has a neutral reaction in dilute aqueous or alcoholic solution and a distinctly alkaline reaction in concentrated solution, does not form salts

with bases, but does so readily with acids (*hydrochloride*, $C_{18}H_{17}O_2N_3,HCl$; *platinichloride*, $2C_{18}H_{17}O_2N_3,H_2PtCl_6$, m. p. 217°, golden-yellow crystals), and, although soluble in aqueous alkalis, is precipitated therefrom by carbon dioxide. If iminopyrine has the constitution, $NPh<\begin{matrix}C(:NH)\cdot CH \\ NMe—CMe\end{matrix}$, ascribed to it by Roser and Stolz (A., 1904, i, 113), the preceding betaine must have the constitution

$$CO_2H\cdot C_6H_4\cdot N:C<\begin{matrix}NPh\cdot NMe \\ CH{=}CMe\end{matrix},$$

and therefore should exhibit acid properties. The betaine and methyl-alcoholic methyl iodide yield the hydriodide, m. p. 212°, of methyl anilopyrine-*p*-carboxylate, $CO_2Me\cdot C_6H_4\cdot NH\cdot C<\begin{matrix}NPh\cdot NMeI \\ CH—CMe\end{matrix}$.

By evaporating a hydrochloric acid solution of methyl anilopyrine-*p*-carboxylate and heating the residue under reduced pressure, methyl chloride is evolved, and the product, after treatment with sodium hydroxide, yields 5-anilo-1-phenyl-3-methylpyrazolone. This substance is produced by the decomposition of the initially-formed 5-*anilo*-1-*phenyl*-3-*methylpyrazolone*-p-*carboxylic acid*, $CO_2H\cdot C_6H_4\cdot N:C<\begin{matrix}NPh\cdot N \\ CH_2-CMe\end{matrix}$, colourless needles containing H_2O, m. p. 114° (the anhydrous substance, m. p. 140—150° [decomp.], is yellow).

Methyl 5-*methylanilino*-1-*phenyl*-3-*methylpyrazole*-p-*carboxylate* (*methyl* ψ-*anilopyrine*-p-*carboxylate*), $CO_2Me\cdot C_6H_4\cdot NMe\cdot C<\begin{matrix}NPh\cdot N \\ CH—CMe\end{matrix}$, m. p. 132°, colourless needles, is obtained by heating the methiodide of methyl anilopyrine-*p*-carboxylate at 200° under reduced pressure. It is converted into the 4-*nitroso*-compound, $C_{19}H_{18}O_3N_4$, m. p. 151°, pale green leaflets, by sodium nitrite and glacial acetic acid containing a few drops of hydrochloric acid, into the 4-*nitro*-compound, $C_{19}H_{18}O_4N_4$, m. p. 170°, pale yellow needles, by nitric acid, into a *dibromo*-derivative, $C_{19}H_{17}O_2N_3Br_2$, m. p. 115°, by bromine on the water-bath, and into the corresponding *acid*, $C_{18}H_{17}O_2N_3$, m. p. 193°, by hydrolysis. This acid is isomeric with the betaine mentioned previously, but exhibits pronounced acid reaction and properties, being soluble in dilute alkali hydroxides and carbonates and in ammonia; the crystalline *barium* salt, $Ba(C_{18}H_{16}O_2N_3)$, is described.

Ethyl 2 : 5-*anilo*-1-*phenyl*-2 : 3-*dimethylpyrazole*-p-*carboxylate* (*ethyl anilopyrine*-p-*carboxylate*), $C_{20}H_{21}O_2N_3$, m. p. 76°, greenish-yellow, fluorescent crystals, is prepared in the same manner as the methyl ester. It forms a *hydriodide*, $CO_2Et\cdot C_6H_4\cdot NH\cdot C<\begin{matrix}NPh\cdot NMeI \\ CH—CMe\end{matrix}$, yellow crystals containing H_2O, m. p. 110—111°, *methiodide*,

$$CO_2Et\cdot C_6H_4\cdot NMe\cdot C<\begin{matrix}NPh\cdot NMeI \\ CH—CMe\end{matrix},$$

colourless crystals containing $3H_2O$, m. p. 80° (anhydrous, 183°), and *ethiodide*, $C_{22}H_{26}O_2N_3I$, m. p. 176°, colourless needles, and by hydrolysis yields the same betaine as the methyl ester.

By heating the methiodide of the ethyl ester at 160—180° under re-

duced pressure, *ethyl 5-methylanilino-1-phenyl-3-methylpyrazole-*p*-carboxylate* (*ethyl ψ-anilopyrine-*p*-carboxylate*), $CO_2Et\cdot C_6H_4\cdot NMe\cdot C\begin{matrix} \diagup NPh\cdot N \\ \diagdown CH-CMe \end{matrix}$, m. p. 105°, colourless needles, is obtained, by the hydrolysis of which ψ-anilopyrine-*p*-carboxylic acid, m. p. 193°, is obtained.

In a similar manner the ethiodide of the ethyl ester yields *ethyl 5-ethylanilino-1-phenyl-3-methylpyrazole-*p*-carboxylate*, m. p. 95°, colourless needles. C. S.

Synthesis of Herzynine. R. ENGELAND and FRIEDRICH KUTSCHER (*Chem. Zentr.*, 1913, i, 28—29; from *Zentr. Physiol.*, 1912, **26**, 569—570. Compare A., 1911, ii, 528).—The substance, $C_9H_{15}O_2N_3$, which was isolated from mushrooms in the form of the aurichloride, has been identified with trimethylhistidine. This base is prepared by treating histidine hydrochloride in concentrated hydrochloric acid with silver nitrite and warming the syrup obtained by evaporating the filtrate with an alcoholic solution of trimethylamine, when the base is precipitated by phosphotungstic acid, converted into the chloride, then into the platinichloride, and finally into the *aurichloride*,

$$C_9H_{17}O_2N_3Au_2Cl_8,$$

m. p. 183° (decomp.). The direct methylation of histidine affects the glyoxaline ring, and, under certain conditions, a good yield of *pentamethylhistidine* may be obtained as an unstable base which forms a stable chloride and a sparingly soluble *aurichloride*, $C_{11}H_{21}O_2N_3Au_2Cl_8$, m. p. 220°, but does not respond to the diazo-reaction. J. C. W.

The Identity of Trimethylhistidine (Histidine-betaine) from Various Sources. GEORGE BARGER and ARTHUR J. EWINS (*Biochem. J.*, 1913, **7**, 204—206).—Proof is given of the identity of the histidine-betaine described by the author (T., 1911, **99**, 2336) with the compounds obtained by Reuter and Kutscher. The difference in the m. p. given for the dipicrate is due to this substance melting at 123—124° when hydrated ($2H_2O$) and at 205—206° when anhydrous. The dipicrate has m. p. 213°; the monopicrate, m. p. 201—202°. The aurichloride of betaine has m. p. 184°, not at 171° as previously stated. Histidine-betaine has $[\alpha]_D + 46.5°$. W. D. H.

Synthetical Alkaloids from Tyrosine, Tryptophan and Histidine. JULIUS WELLISCH (*Biochem. Zeitsch.*, 1913, **49**, 173—194).—The author discusses the mechanism of the various processes by means of which physiologically active bases can be synthesised in plants, especially from amino-acids which can be derived from the hydrolysis of proteins. Amongst these may be reckoned in the first instances, bases such as 3-β-aminoethylglyoxaline, 3-β-aminoethylindole, and phenylethylamine, which are derived from histidine, tryptophan, and phenylalanine by the simple scission of carbon dioxide. Another important series derivable from these amino-acids are the quinoline and pyridine derivatives, which can be obtained from the acids or the corresponding amines by condensation with aldehydes, such as formaldehyde, and subsequent ring formation. Attempts have been

made to prepare a series of alkaloids by the latter method. By the condensation of histidine with formaldehyde, which was carried out by heating the base with methylal and hydrochloric acid, *tetrahydro-1 : 3 : 5-benzotriazole-6-carboxylic acid*, $C_7H_9N_3O_2,2HCl$, in the form of its *hydrochloride*, m. p. 278° (corr.), was obtained. The *picrate* decomposes about 215°. The hydrochloride is lævorotatory ($[\alpha]_D^{25} = -84.24°$ by the micropolarisation method). On heating in a vacuum to 290°, carbon dioxide is evolved, and the corresponding *iminazole-*iso*piperidine* [*tetrahydro-1 : 3 : 5-benzotriazole*] *hydrochloride*,

$$C_6H_9ON_3,2HCl,$$

which decomposes at 258°, was obtained, and which separates from alcohol in a microcrystalline form. The carboxylic acid cannot be esterified by alcohol and hydrochloric acid, and only with very great difficulty by the action of ethyl iodide on the silver salt. Attempts were made ty obtain a corresponding product by the action of methylal on tryptophan, but a pure substance was not isolated. *l*-Tyrosine under similar conditions gives 7-hydroxytetrahydro*iso*quinoline-3-carboxylic acid (Pictet and Spengler, A., 1911, i, 750), which has $[\alpha]_D^{25} = -45.62°$ in hydrochloric acid. This on heating in a vacuum appears to be converted into an anhydride. The *ethyl* ester and its *picrate* were also prepared. Attempts to condense histidine with acetaldehyde and pyruvic acid did not lead to the isolation of pure products.

S. B. S.

Derivatives of *iso*Cinchomeronic Acid and 2 : 5-Diaminopyridine. HANS MEYER and FRIEDRICH STAFFEN (*Monatsh.*, 1913, **34**, 517—533).—Very few derivatives of *iso*cinchomeronic acid (pyridine-2 : 5-dicarboxylic acid) have been described (compare Weidel and Herzig, A., 1886, 477; Meyer, A., 1903, i, 364).

*iso*Cinchomeronic acid was obtained for this investigation by the condensation of aldehyde ammonia with twice its weight of paraldehyde in an autoclave at 220—230°, and oxidation of the resultant 2 : 5-methylethylpyridine with the theoretical amount of potassium permanganate. The m. p. of the acid can be raised from 237° to 254° (decomp.) by conversion into the methyl ester and regeneration; ammonium salt, m. p. 153°. If the acid is heated with excess of thionyl chloride, it is converted into iso*cinchomeronyl chloride*,

$$C_5NH_3(COCl)_2,$$

needles, m. p. 59°, which reacts with methyl alcohol in the cold, producing *methyl* iso*cinchomeronate*, needles, m. p. 164°, which is also obtainable by heating a mixture of the acid and alcohol with sulphuric acid at 100°. The acid chloride in the cold and the methyl ester at 100° react with ammonia solution, forming iso*cinchomeronamide*, $C_5NH_3(CO\cdot NH_2)_2$, colourless crystals, m. p. 310° (decomp.). When boiled in alcoholic solution with an equal weight of hydrazine hydrate, methyl *iso*cinchomeronate is converted into a crystalline solid, from which chloroform extracts the *methyl* ester of iso*cinchomeronic acid hydrazide*, $C_5NH_3(CO_2Me)\cdot CO\cdot NH\cdot NH_2$, yellow scales, m. p. 173° (decomp.), whilst the undissolved residue consists of iso*cinchomeronohydrazide*, $C_5NH_3(CO\cdot NH\cdot NH_2)_2$, prismatic needles, m. p. 268—269°

(decomp.), with rapid heating, which is obtained in almost theoretical yield if twice the above proportion of hydrazine hydrate be used in the preparation. The dihydrazide condenses with various aldehydes when heated with them, or when shaken in aqueous solution with them; iso*cinchomeronodibenzylidenehydrazide*, colourless needles, m. p. 290°; iso*cinchomeronodi*-o-*chlorobenzylidenehydrazide*, colourless leaflets, m. p. 308° (decomp.); iso*cinchomeronodi*-4-*hydroxy*-3-*methoxybenzylidenehydrazide*, a yellow, crystalline substance, m. p. 264—266°, which is turned red on the addition of mineral acids. An aqueous solution of the dihydrazide containing the theoretical quantity of hydrochloric acid reacts with sodium nitrite, giving a precipitate of iso*cinchomeronodiazoimide*, $C_5NH_3(CO{\cdot}N_3)_2$, colourless prisms, m. p. 114° (decomp. with explosion), together with a small amount of an acid *substance*, a colourless, crystalline powder, m. p. 307° (decomp.), which from its reaction with ferrous sulphate is a 2-substituted pyridine derivative. The carefully-dried hydrazide when boiled with alcohol first dissolves and then gives a deposit of *ethylurethylpyridylazoimide*,

$$N_3{\cdot}CO{\cdot}C_5NH_3{\cdot}NH{\cdot}CO_2Et,$$

colourless needles, m. p. 153° (with explosion), which by prolonged treatment with boiling alcohol is further converted into 2 : 5-*diethylurethylpyridine*, $C_5NH_3(NH{\cdot}CO_2Et)_2$, colourless needles, m. p. 198—199°, the ethoxyl groups of which, unlike those of the corresponding derivative of dipicolinic acid, are easily removed by hydriodic acid. The corresponding *methylurethylpyridylazoimide*,

$$N_3{\cdot}CO{\cdot}C_5NH_3{\cdot}NH{\cdot}CO_2Me,$$

and 2 : 5-*dimethylurethylpyridine* form colourless needles (which explode at 80—100° if rapidly heated, and melt at above 270° with decomp. if heated slowly) and colourless needles, m. p. 206—207° (decomp.) respectively.

If the above diethylurethylpyridine is boiled for three hours with hydriodic acid (D 1·8—1·9), yellow needles and leaflets of the *hydriodide* of 2 : 5-*diaminopyridine* separate on cooling; the free base, colourless needles, m. p. 107—110°, which is rapidly affected by air and light, can be isolated by triturating the hydriodide with crushed potassium carbonate and carefully extracting with hot benzene in an atmosphere of carbon dioxide. By the action of silver chloride the hydriodide is converted into the *hydrochloride*, colourless needles, which, like the free base, gives solutions in water and alcohol with a blue fluorescence; the unstable *platinichloride* crystallises in golden-yellow scales; *benzoyl* derivative, colourless needles, m. p. 229—230°. The base does not possess the usual properties of an aromatic para-diamine; it gives an intense reddish-yellow coloration with ferric chloride, and the hydrochloride reduces gold solutions and ammoniacal silver solutions. D. F. T.

Preparation of Acylacetic Esters. ANDRÉ WAHL and M. DOLL (*Bull. Soc. chim.*, 1913, [iv], **13**, 265—281. Compare A., 1911, i, 108).—The authors have continued their previous work on the condensation of ethyl acetate with its higher homologues by means of sodium, and have improved the yields by suitable modification of the

procedure, which is fully described. They have also extended the method to the cases of ethyl valerate and ethyl heptoate, and find that the yield of ketonic ester increases with increasing length of the carbon chain of the ester provided the latter is normal. With esters having side-chains, condensation is effected with greater difficulty.

Ethyl propionylacetate has now been obtained in 13% yield. It forms a green *copper* salt, m. p. 144°.

Ethyl butyrylacetate is readily converted into *ethyl* iso*nitrosobutyrylacetate*, which did not solidify even after several months and could not be distilled without decomposition. Phenylhydrazine converts it into 4-*oximino*-1-*phenyl*-3-*propyl*-5-*pyrazolone*, yellow needles, m. p. 128°. When acted on by benzenediazonium chloride, ethyl butyrylacetate is converted into a yellow *oil*, which is identified as ethyl phenylazobutyrylacetate, since it is converted by phenylhydrazine into 4-*phenylhydrazino*-1-*phenyl*-3-*propyl*-5-*pyrazolone*, $NPh<\begin{matrix}CO-C:N\cdot NHPh \\ N{=\!=}CPr\end{matrix}$, orange needles, m. p. 133—134°, and by *p*-nitrophenylhydrazine into 4-*phenylhydrazino*-1-p-*nitrophenyl*-3-*propyl*-5-*pyrazolone*, golden-yellow needles, m. p. about 209—210°. *Ethyl* p-*nitrophenylazobutyrylacetate* crystallises in fine yellow needles, m. p. 101°, whilst the corresponding *acid*, prepared by saponification of the ester with cold alcoholic sodium hydroxide and subsequent addition of acid, forms yellow crystals, m. p. 164°. 4-p-*Nitrophenylhydrazino*-1-*phenyl*-3-*propyl*-5-*pyrazolone*, $NPh<\begin{matrix}CO-C:N\cdot NH\cdot C_6H_4NO_2 \\ N{=\!=}CPr\end{matrix}$, red needles, m. p. 194°, 4-p-*nitrophenylhydrazino*-1-p-*nitrophenyl*-3-*propyl*-5-*pyrazolone*, orange needles, m. p. 243—244°, and 4-p-*nitrophenylhydrazino*-1-*tolyl*-3-*propyl*-5-*pyrazolone*, orange needles, m. p. 152°, were also prepared.

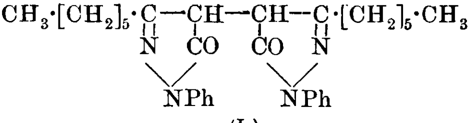
Ethyl valerylacetate, $CH_2Pr\cdot CO\cdot CH_2\cdot CO_2Et$, b. p. 110—112°/16 mm. (compare Blaise and Luttringer, *Bull. Soc. chim.*, 1905, [iii], **33**, 1103), is obtained in 28% yield. It gives a *copper* salt, green needles, m. p. 91°, which, when boiled with methyl alcohol, is converted into a blue basic *salt*, $C_9H_{15}O_3\cdot CuOMe$, m. p. 80°. It is transformed by hydrazine hydrate into 3-n-*butylpyrazolone*, white leaflets, m. p. 197°.

Ethyl *iso*valerate reacts slowly with ethyl acetate with the formation of poor yields of *ethyl* iso*valerylacetate*, b. p. 96—99°/14 mm. The latter gives a green normal *copper* salt, m. p. 122°, which when boiled with methyl alcohol forms indigo-blue crystals of the basic *salt*,

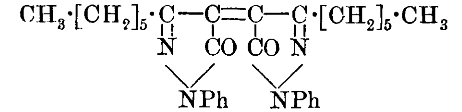
$$C_9H_5O_3\cdot CuOMe,$$

m. p. 106—107°.

Ethyl heptoylacetate, b. p. 123—126°/11 mm. (compare Moureu and Delange, A., 1903, i, 676), is obtained in 40% yield by the condensation of ethyl heptoate with ethyl acetate. The following new compounds have been prepared from it: 4-*phenylhydrazino*-1-*phenyl*-3-*hexyl*-5-*pyrazolone*, orange-yellow needles, m. p. 100—101°; 4-p-*nitrophenylhydrazino*-1-p-*nitrophenyl*-3-*hexyl*-5-*pyrazolone*, orange needles, m. p. 192°; 1-*phenyl*-3-*hexyl*-5-*pyrazolone*, nearly white leaflets, m. p. 83—84°, formed by heating at its b. p. for a few moments an acetic acid solution of molecular quantities of the ketonic ester and phenylhydrazine. If



(I.)



(II.)

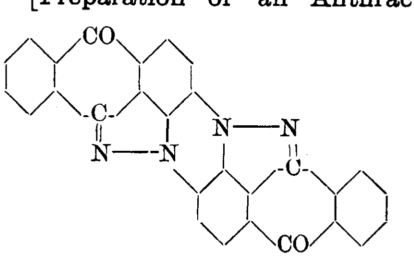
in the latter case 2 to 3 molecules of phenylhydrazine are employed for each molecule of ketonic ester, 1-*phenyl*-3-*hexylbispyrazolone* (formula I), crystalline powder, m. p. 276—278° (decomp.), is obtained, which, when heated in alkaline solution with sodium nitrite and subsequently acidified, yields the compound (formula II) crystallising in blue needles, m. p. 145°.

The method has also been successfully applied to certain cyclic esters. Ethyl benzoate and ethyl acetate gave ethyl benzoylacetate in 80% yield (compare Wahl, A., 1908, i, 647; Wahl and Silberzweig, A., 1912, i, 114), whilst the corresponding methyl ester gave an 85% yield of methyl benzoylacetate. *Propyl benzoylacetate*, prepared by boiling methyl benzoylacetate with propyl alcohol in a fractionating apparatus so arranged that the displaced methyl alcohol slowly distils, forms an amber liquid, b. p. 154—156°/12 mm., D^0 1·114. The normal *copper* salt forms green leaflets, m. p. 145—146°, whilst the basic *salt*, $C_{12}H_{13}O_3\cdot CuOMe$, consists of blue crystals, m. p. 195°.

The normal green *copper* salt, m. p. 133°, of *iso*butyl benzoylacetate is decomposed by boiling methyl alcohol with formation of the bluish-grey basic *salt*, $C_{13}H_{15}O_3\cdot CuOMe$, m. p. 191°, and by boiling ethyl alcohol into the blue basic *salt*, $C_{13}H_{15}O_3\cdot CuOEt$, m. p. 188°.

Under the conditions used in the preparation of the benzoylacetates, a 60% yield of methyl *o*-methoxybenzoylacetate and a 62% yield of methyl anisoylacetate were obtained. The yield of ethyl furoylacetate was 76% of the theoretical (compare Torrey and Zanetti, A., 1907, i, 146; 1908, i, 840; 1910, i, 892). H. W.

[Preparation of an Anthracene Derivative.] CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 255641).—The *compound* (annexed formula) is obtained when pyrazoleanthrone (A., 1906, i, 904) is boiled with potassium hydroxide (5 parts) and alcohol (10 parts) until the so-obtained blue colour ceases to gain intensity.



F. M. G. M.

New Derivatives of Azoxybenzene. ANGELO ANGELI and BRUNO VALORI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 132—140. Compare A., 1912, i, 321).—*p*-Azobenzenecarboxylic acid (which has m. p. 241°)

is conveniently prepared from *p*-aminobenzoic acid and nitrosobenzene When it is treated in acetic acid solution with hydrogen peroxide, *β-azoxybenzenecarboxylic acid*, $NPh\colon NO\cdot C_6H_4\cdot CO_2H$, is obtained; it crystallises in yellow needles, m. p. 241°. Its *ethyl* ester, $C_{15}H_{14}O_3N_2$, has m. p. 68°. The acid yields *p*-azobenzenecarboxylic acid on reduction. When it is treated with bromine in the presenee of iron filings, p-*bromo-β-azoxybenzenecarboxylic acid*, $C_{13}H_9O_3N_2Br$, is produced; it is a yellowish-white, crystalline powder, m. p. 280°. The *ethyl* ester of this acid, $C_{15}H_{13}O_3N_2Br$, has m. p. 114°. When *β*-azoxybenzenecarboxylic acid is nitrated in glacial acetic acid solution, p-*nitro-β-azoxybenzenecarboxylic acid*, $C_{13}H_9O_5N_3$, is obtained as a yellow, crystalline powder, m. p. about 260° with evolution of gas. If kept for an hour on the water-bath with excess of concentrated sulphuric acid, *β*-azoxybenzenecarboxylic acid undergoes rearrangement, yielding 4-*hydroxyazobenzene*-4′-*carboxylic acid*, $HO\cdot C_6H_4\cdot N\colon N\cdot C_6H_4\cdot CO_2H$, which forms red crystals, m. p. 266° (decomp.).

a-Azoxybenzenecarboxylic acid, $O\colon NPh\colon N\cdot C_6H_4\cdot CO_2H$, is formed in the preparation of the *β*-acid, and can be separated from it by reason of its greater solubility in acetic acid. It is also obtained by the action of chromic acid on the *β*-compound It forms pale yellow scales, m. p. 231°. Its *ethyl* ester, $C_{15}H_{14}O_3N_2$, has m. p. 77·5°. The *a*-acid is not acted on by bromine. On reduction with aluminium amalgam, it yields *p*-azobenzenecarboxylic acid.

β-p-*Azoxybenzenesulphonic acid*, $C_{12}H_{10}O_4N_2S$, prepared by the action of hydrogen peroxide on *p*-azobenzenesulphonic acid, forms pale yellow needles, m. p. 144°. The *silver* salt, $C_{12}H_9O_4N_2SAg$, crystallises in lustrous laminæ. The acid described under the name of *p*-azoxybenzenesulphonic acid by Limpricht (A., 1885, 984) cannot have this structure. *β*-*p*-Azoxybenzenesulphonic acid yields a bromo-derivative, p-*bromo-β-azoxybenzenesulphonic acid*, $C_{12}H_9O_4N_2SBr$, which does not melt at 280°. *β*-*p*-Azoxybenzenesulphonic acid suffers the Wallach rearrangement, yielding a red, crystalline powder, $C_{12}H_{10}O_4N_2S$, which blackens about 200°, but does not melt.

a-2 : 4 : 6:*Trinitroazoxybenzene*, $O\colon NPh\colon N\cdot C_6H_2(NO_2)_3$, is obtained in long, pale yellow needles, m. p. 170°, by the action of hydrogen peroxide on trinitroazobenzene. This substance dissolves unaltered in nitric acid (D 1·45) and in bromine, but when it is dissolved in nitric acid of D 1·52, and the solution kept for twelve hours, it yields a *tetranitro*-derivative, $C_{12}H_6O_9N_6$, which forms yellow prisms, m. p. 192°. R. V. S.

Diazo-compounds derived by the Action of Alkali on Nitrosophthalimidine. Simplified Preparation of Nitrosophthalimidine. ALFRED OPPE (*Ber.*, 1913, **46**, 1095—1099).—Aqueous alkali transforms nitrosophthalimidine into *o*-hydroxymethylbenzoic acid or its lactone (Graebe, A., 1889, 140), diazo-compounds being probably formed as intermediate products. The isolation of the latter has been accomplished by substituting absolute methyl-alcoholic sodium methoxide for aqueous alkali hydroxide in opening the lactam ring.

When a solution of sodium methoxide in absolute methyl alcohol

is added to a well-cooled suspension of nitrosophthalimidine in dry ether, a micro-crystalline salt separates, analysis of which gives results intermediate between those required for the *salt diazoxide*,

$$CO_2Na\cdot C_6H_4\cdot CH_2\cdot N_2\cdot ONa,$$

and the *ester diazoxide*, $CO_2Me\cdot C_6H_4\cdot CH_2\cdot N_2\cdot ONa$. The former could be obtained in the pure state by pouring the freshly-prepared reaction mixture into a large quantity of cooled ether, but the latter could not be obtained pure. When the above reaction mixture is treated with dry carbon dioxide before the separation of crystals occurs, *methyl* o-*diazomethylbenzoate*, $CO_2Me\cdot C_6H_4\cdot CH\colon N_2$, needles, m. p. 34°, is obtained, which is readily decomposed by phenol with quantitative evolution of nitrogen and formation of *methyl* o-*phenoxymethylbenzoate*, $CO_2Me\cdot C_6H_4\cdot CH_2\cdot OPh$, needles, m. p. 52·5°, b. p. 204°/13 mm. The corresponding free *acid* crystallises in needles, m. p. 126°, and is decomposed by fuming hydrochloric acid at 170—180° into phenol and *o*-hydroxymethylbenzoic acid. The latter is converted by heat into phthalide, leaflets, m. p. 73°.

The following process is recommended for the preparation of nitrosophthalimidine. Nearly boiling 25% hydrochloric acid is gradually added to a paste made by grinding phthalimide and zinc dust with a small quantity of water. The mixture is maintained at its boiling point until there is no further action on the zinc, filtered, cooled, and treated with a concentrated aqueous solution of sodium nitrite. In this manner, 100 grams of phthalimide yield 75 grams of nitrosophthalimidine. H. W.

Etherification of *o*-Hydroxyazo-compounds. II. G. CHARRIER and G. FERRERI (*Atti R. Accad. Sci. Torino*, 1913–13, **48**, 539—556. Compare A., 1912, i, 812).—1-*Benzeneazo*-2-*naphthyl ethyl ether*, $OEt\cdot C_{10}H_6\cdot N\colon NPh$, forms garnet-red tablets, m. p. 79°; in its preparation 50% potassium hydroxide is used instead of 30% sodium hydroxide. When the substance is reduced with zinc and acetic acid, aniline and 1-amino-2-naphthyl ethyl ether are produced. The *hydrochloride*, $C_{18}H_{16}ON_2,2HCl$, crystallises in heavy, green leaflets, which have a metallic lustre. The *hydrobromide* is a coffee-coloured, crystalline powder. The hydriodide is a heavy, dark coffee-coloured, crystalline powder.

1-o-*Tolueneazo*-2-*naphthyl ethyl ether*, $OEt\cdot C_{10}H_6\cdot N\colon N\cdot C_6H_4Me$, crystallises in garnet-red, flattened needles, m. p. 36°. It dissolves in concentrated sulphuric acid, giving a red coloration, and dissolves also in dilute acids, forming red solutions. The *hydrochloride*,

$$C_{19}H_{18}ON_2,2HCl,$$

crystallises in needles with a green, metallic lustre.

1-m-*Tolueneazo*-2-*naphthyl methyl ether*, $OMe\cdot C_{10}H_6\cdot N\colon N\cdot C_6H_4Me$, forms garnet-red, tabular crystals, m. p. 81°. The *hydrochloride* forms minute, red crystals with a golden lustre.

1-m-*Tolueneazo*-2-*naphthyl ethyl ether*, $OEt\cdot C_{10}H_6\cdot N\colon N\cdot C_6H_4Me$, crystallises in red leaflets, m. p. 84°. The *hydrochloride* is a heavy, coffee-coloured substance.

1-p-*Tolueneazo*-2-*naphthyl ethyl ether*, $OEt\cdot C_{10}H_6\cdot N\colon N\cdot C_6H_4Me$, crys-

tallises in red, prismatic needles, m. p. 48°. The *hydrochloride*, $C_{19}H_{18}ON_2,2HCl$, forms reddish-brown needles with a golden lustre.

1-m-*Chlorobenzeneazo-2-naphthyl methyl ether*,

$$OMe\cdot C_{10}H_6\cdot N{:}N\cdot C_6H_4Cl,$$

crystallises in bright red prisms or needles, m. p. 77°. The *hydrochloride* forms red needles.

1-m-*Chlorobenzeneazo-2-naphthyl ethyl ether*, $OEt\cdot C_{10}H_6\cdot N{:}N\cdot C_6H_4Cl$, forms red needles, m. p. 35°. The *hydrochloride* forms dark garnet-red crystals with a golden lustre.

1-p-*Chlorobenzeneazo-2-naphthyl methyl ether*,

$$OMe\cdot C_{10}H_6\cdot N{:}N\cdot C_6H_4Cl,$$

crystallises in shining red needles, m. p. 65°. The *hydrochloride*, $C_{17}H_{13}ON_2Cl,2HCl$, is a red, crystalline substance.

1-p-*Chlorobenzeneazo-2-naphthyl ethyl ether*, $OEt\cdot C_{10}H_6\cdot N{:}N\cdot C_6H_4Cl$, crystallises in red needles with a golden lustre, m. p. 53°. The *hydrochloride* is a reddish-brown, crystalline powder.

1-op-*Dichlorobenzeneazo-2-naphthyl methyl ether*,

$$OMe\cdot C_{10}H_6\cdot N{:}N\cdot C_6H_3Cl_2,$$

forms garnet-red leaflets, m. p. 98°. The *hydrochloride* is a red, crystalline powder having a metallic lustre.

1-op-*Dichlorobenzeneazo-2-naphthyl ethyl ether*,

$$OEt\cdot C_{10}H_6\cdot N{:}N\cdot C_6H_3Cl_2,$$

separates in garnet-red needles, m. p. 102°. The *hydrochloride* forms minute, reddish-brown crystals with a metallic lustre.

1-m-*Bromobenzeneazo-2-naphthyl methyl ether*,

$$OMe\cdot C_{10}H_6\cdot N{:}N\cdot C_6H_4\cdot Br,$$

crystallises in ruby-red needles, m. p. 92°. The *hydrochloride* is a red, crystalline substance having a metallic lustre.

1-m-*Bromobenzeneazo-2-naphthyl ethyl ether*, $OEt\cdot C_{10}H_6\cdot N{:}N\cdot C_6H_3\cdot Br$, forms crusts of golden-yellow needles, m. p. 52°. The *hydrochloride* crystallises in metallic-looking, green leaflets.

The m. p. of 1-*p*-methoxybenzeneazo-2-naphthylethylether is 55—56°, not 52—53°, as stated in the former paper. The *hydrochloride* of the ether is a reddish-brown, crystalline powder having a green metallic lustre.

1-m-*Nitrobenzeneazo-2-naphthyl methyl ether*,

$$OMe\cdot C_{10}H_6\cdot N{:}N\cdot C_6H_4\cdot NO_2,$$

crystallises in small, red needles, m. p. 94—95°. The *hydrochloride* is a red, crystalline substance, as also is the *hydrobromide*.

1-m-*Nitrobenzeneazo-2-naphthyl ethyl ether*, $OEt\cdot C_{10}H_6\cdot N{:}N\cdot C_6H_4\cdot NO_2$, forms garnet-red needles, m. p. 106—107°. The *hydrochloride* is a red, crystalline powder.

The salts of these ethers are to be assigned the constitutions indicated by the following formula:

$$\begin{matrix} R \\ Cl \\ H \end{matrix}\!>\!O\cdot C_{10}H_6\cdot N{:}N\!<\!\begin{matrix} Ar \\ Cl \\ H \end{matrix}.$$

R. V. S.

Hydroxyazo-compounds and Quinonephenylhydrazones of the Anthracene Series. KURT H. MEYER and KARL ZAHN (*Annalen*, 1913, **396**, 152—166).—Benzeneazoanthranol, identical with the substance obtained by Kaufler and Suchanek by the con-

densation of benzenediazonium chloride and anthranol, is prepared by treating 9 : 9-dibromoanthrone with alcoholic phenylhydrazine; only the one substance is produced at $-10°$ or at the b. p., or by working in other solvents. The same substance also is immediately recovered when the deep blue solution of benzeneazoanthranol in alcoholic potassium hydroxide is added to sulphuric acid at 0°. No evidence of the existence of the parent substance as anthraquinonephenylhydrazone has been obtained. Benzeneazoanthranol yields differently coloured solutions in different solvents, develops a deep brown coloration with concentrated sulphuric acid, forms coloured additive compounds with stannic chloride and aluminium chloride, reacts instantly with alcoholic bromine, and is stable to boiling acetic acid; it is hydrolysed by 5% alcoholic sulphuric or hydrochloric acid after boiling for seven hours. All these properties, except variability of colour in solution, are also characteristic of *benzeneazoanthranyl benzoate*,

$$NPh\colon N\cdot C{<}{}^{C_6H_4}_{C_6H_4}{>}C\cdot OBz,$$

m. p. 230—231°, dark red crystals with a metallic lustre, which is prepared by treating benzeneazoanthranol in acetone with aqueous sodium hydroxide and benzoyl chloride in the cold; by prolonged boiling with alcoholic hydrochloric acid, it yields benzoic acid, anthraquinone, and phenylhydrazine. On the contrary, *anthraquinonebenzoylphenylhydrazone*, $NPhBz\cdot N\colon C{<}{}^{C_6H_4}_{C_6H_4}{>}CO$, m. p. 172—173°, orange-yellow prisms, prepared by heating 9 : 9-dibromoanthrone, alcoholic benzoylphenylhydrazine and sodium carbonate, develops a yellow coloration with concentrated sulphuric acid, does not form additive compounds with metallic chlorides, is only slowly attacked by alcoholic bromine, and is rapidly hydrolysed by boiling dilute acetic acid. It cannot be transformed into benzeneazoanthranyl benzoate by ether and powdered potassium hydroxide.

Anthraquinonephenylmethylhydrazone, $NPhMe\cdot N\colon C{<}{}^{C_6H_4}_{C_6H_4}{>}CO$, m. p. 147—148°, red prisms with metallic lustre, is obtained by heating 9 : 9-dibromoanthrone with alcoholic *as*-phenylmethylhydrazine or by treating benzeneazoanthranol in aqueous acetone with sodium hydroxide and methyl sulphate. It is not affected by alcoholic potassium hydroxide, but is hydrolysed to anthraquinone and *as*-phenylmethylhydrazine by boiling dilute acetic acid or alcoholic hydrochloric acid. It is thus seen that the acylation of benzeneazoanthranol in alkaline solution is a process of direct substitution (an *O*-ester being formed), whilst the alkylation is a case of addition followed by elimination (an *N*-ether being formed).

At the present time aliphatic hydroxyazo-compounds, such as phenylazoacetylacetone, are generally regarded as hydrazones, for example, $NHPh\cdot N\colon C(COMe)_2$, because they yield *N*-esters $[NBzPh\cdot N\colon C(COMe)_2]$ by acylation. The evidence is by no means conclusive, however, because the hydroxyazo-compound can yield the *N*-ester as follows:

$$ONa\cdot CMe\colon C(N\colon NPh)\cdot COMe \longrightarrow {}^{NaO}_{Cl}{>}CMe\cdot C(\colon N\cdot NBzPh)\cdot COMe$$
$$\longrightarrow NBzPh\cdot N\colon C(COMe)_2.$$ The colour, solubility in aqueous alkalis,

and reactivity with alcoholic bromine are all in harmony with the formulation of aliphatic hydroxyazo-compounds as hydroxyazo-compounds.

Anthraquinoneoxime is obtained by treating 9:9-dibromoanthrone with alcoholic hydroxylamine and dry sodium carbonate. The same substance is at once precipitated when its alkaline solution is acidified with sulphuric acid at 0°; nitrosoanthranol is not isolated. C. S.

Action of Acids on Proteins. D. CĂLUGĂREANU (*Bull. Acad. Sci. Roumaine*, 1912/13, **1**, 40—42).—With the object of deciding whether the products of the action of acids on proteins are chemical compounds which are hydrolytically dissociated in aqueous solution, or are simply adsorption products, the author has studied the electrical conductivity of a number of acids (hydrochloric, sulphuric, chromic, acetic, citric, lactic, trichloroacetic, and picric) at different dilutions in aqueous solution, on the one hand, and in aqueous solution in the presence of various proteins (serum-albumen, serum-globulin, and gelatin) on the other, the experimental conditions being so chosen that the concentration of the protein remains constant, the concentration of acid alone varying.

Since the curves obtained are closely similar to that given by a solution of glycine under similar conditions, the author is led to the conclusion that the form of the curve is largely due to the hydrolytic dissociation of the product of the action of acids on the protein. He does not consider, however, that the phenomenon of adsorption is completely excluded. H. W.

The Relations of the Phenols and their Derivatives to Proteins. Mechanism of Disinfection. II. Effects of Various Factors on the Germicidal and Protein-precipitating Powers of the Phenols. EVELYN A. COOPER (*Biochem. J.*, 1913, **7**, 175—185. Compare A., 1912, ii, 1199).—The introduction of hydroxyl groups decreases, and of nitro- or methyl groups, increases, the bactericidal and protein-precipitating powers of phenol. The monohydric phenols are superior to the alcohols in both directions. Sodium chloride increases both properties through increasing the solubility of phenols in proteins; alcohol behaves in the opposite way. Solutions of phenol in fat possess no such activities. Small amounts of alkali inhibit the power to precipitate proteins, without affecting the germicidal power; the explanation of this is not apparent. The precipitating action of phenol is increased by the addition of acids. The absorption of phenols by bacteria is the initial stage in disinfection; the germicidal action is not due to a union of the phenols with the bacterial protoplasm (as with formaldehyde), but to a de-emulsifying action upon the colloidal suspension of some constituent protein or proteins essential for the vitality of the organisms.

W. D. H.

The Relations of the Phenols and their Derivatives to Proteins. Mechanism of Disinfection. III. The Chemical Action of *p*-Benzoquinone on Proteins. EVELYN A. COOPER (*Biochem. J.*, 1913, **7**, 186—196).—*p*-Benzoquinone gives a red colour

with various proteins and amino-acids (confirmatory of Würster and Raciborski); the proteins can be isolated in a coloured state from the solutions, but could not be decolorised. Their solubilities and other properties are changed, hence they had been chemically altered. *p*-Benzoquinone in absolute alcohol does not produce the colour; and treatment of the proteins with formaldehyde inhibits the reaction, except in the case of gelatin, aniline, and ammonia. The effect of formaldehyde indicates that proteins, proteoses, and amino-acids react with *p*-benzoquinone through their amino- or imino-groups. No colour reaction was obtained with *p*-benzoquinonedioxime, which shows probably that the reacting groups of the proteins condense with the ketonic groups of the quinone. The effect of the latter therefore resembles that of formaldehyde. Acetone differs from *p*-benzoquinone by acting as a protein precipitant. The germicidal power of *p*-benzoquinone is due to its chemical action on some constituent protein or proteins of the bacteria. W. D. H.

Nitro-derivatives of the Proteins. ALBRECHT KOSSEL and FRANZ WEISS (*Zeitsch. physiol. Chem.*, 1913, **84**, 1—10).—The arginine group in the molecule of the higher proteins is as accessible to nitration by means of a mixture of concentrated nitric and sulphuric acids as that in the protamines.

Nitroclupeine, like nitroarginine, when digested at 38° with normal sodium hydroxide solution loses carbon dioxide, ammonia, and nitrous oxide, a derivative of ornithine being formed. The amount of gas formed confirms this interpretation of the change, and the method is applicable to the determination of the nitro-group in nitroguanidine and of the nitroamino-groups in nitrated proteins.

In the case of edestin it is shown that in addition to the guanidine complex of the arginine constituent a further guanidine complex is present in the molecule, which forms a nitroamine. This is in agreement with Otori's (A., 1904, i, 1067) suggestion of such a second guanidine complex in ψ-mucin, casein, and gelatin. E. F. A.

Action of Arsenious Acid, Arsenic Acid, and Phosphoric Acid on Albumin. CORRADO BONGIOVANNI (*Gazzetta*, 1913, **43**, i, 161—163).—From measurements of the conductivity of solutions of albumin and of the above acids separately, and of the binary mixtures of the acids with albumin, the author finds no evidence that combination with the albumin occurs. The diminution of conductivity which takes place on mixing is to be ascribed to a lessening of the mobility of the ions by the colloidal substance. R. V. S.

Acid Decomposition Products of Hæmin. OSKAR PILOTY and EDMUND DORMANN (*Ber.*, 1913, **46**, 1002—1008).—The acid decomposition products of hæmin obtained on reduction with hydrogen iodide and acetic acid contain four components: phonopyrrolecarboxylic acid, xanthopyrrolecarboxylic acid, *iso*phonopyrrolecarboxylic acid, and an acid so far only obtained as a syrup.

In view of the possibility that xanthopyrrolecarboxylic acid, $C_{10}H_{15}O_2N$, might be *iso*phonopyrrolecarboxylic acid, $C_9H_{13}O_2N$,

contaminated with the product of the action of ethyl alcohol on its picrate, it has been further investigated and its individuality established.

The picrate of phonopyrrolecarboxylic acid when heated in ethyl or methyl alcoholic solution in presence of free picric acid is rapidly and completely esterified at the carboxyl group. The free methyl ester crystallises in long, flat, colourless needles, m. p. 59°; its picrate has m. p. 122°. The corresponding *ethyl* ester forms six-sided, colourless plates, m. p. 134°; its *picrate* crystallises in pale yellow, flat, prismatic needles of rhombic habit, m. p. 93°.

The acid mixture yields a fourth crystalline acid, $C_{10}H_{15}O_2N$, *phonopyrrolecarboxylic acid*-d, which crystallises in colourless needles pointed at either end. The *picrate* separates in characteristic yellow crystals, m. p. 132°. The new acid is perhaps identical with compounds described by H. Fischer (A., 1912, i, 384, 901), and obtained by the action of sodium methoxide on pyrrole derivatives. E. F. A.

Sulphuric Acid Hæmatoporphyrin. ANT. HAMSIK (*Zeitsch. physiol. Chem.*, 1913, **84**, 60—66).—Hæmatoporphyrin, prepared from hæmin by means of concentrated sulphuric acid, was obtained as an amorphous, dark blue powder. By solution in acetic acid containing 10% of water, the addition of concentrated hydrochloric acid, and enough dilute acid to make the amount of water 40%, the pigment was obtained partly crystalline in dark green needles or long rods, usually aggregated in stellate or bunched clusters, and partly crystalline in red aggregates of varying size, or in indefinite green masses.

Crystals were also obtained by dissolving the original product in acetone and hydrochloric acid. E. F. A.

The Kinetics of Invertin Action. LEONOR MICHAELIS and (Miss) MAUD L. MENTEN (*Biochem. Zeitsch.*, 1913, **49**, 333—369).—The authors, whilst accepting generally Victor Henri's generalisations as to the method of the ferment action, call attention to two defects in his experimental method. They show that the hydrogen-ion concentration of the solutions has not been taken into account, and that the multirotation of sugar has been neglected. They remedy the first defect by working in an acetate mixture, prepared according to Sörensen, which gives the optimal conditions of action, and they remedy the second defect by reading the polarisations after the sugar mixture has been allowed to remain with sodium hydroxide solution, which inhibits the action of the ferment. Like Henri, therefore, they use the polarimetric method for investigating the change. They assume that the invertin enters into combination with sucrose to form a labile compound, which decomposes according to the scheme: 1 mol. sucrose–invertin compound $\longrightarrow$ 1 mol. dextrose + 1 mol. lævulose + 1 mol. invertin. It is only through the intermediation of the sucrose–invertin compound that inversion takes place. The invertin can also combine with the scission products to form compounds, but as these are not labile, the only effect of their formation is to diminish the amount of ferment available for combination with the sucrose, and thus to inhibit the inversion. The present communication deals chiefly with the

methods for the determination of the dissociation constants of the various invertin–sugar compounds. For sucrose, the following equation is evolved: $v = C\Phi.[S]/([S]+k)$, where v is the initial reaction velocity, C is a constant depending on the arbitrarily chosen units employed for measuring change (in this case the rotation changes), S is the concentration of the sugar, k the dissociation constant, and Φ the concentration of the ferment. If Φ is kept constant and S is altered, $v/C\Phi$ can be replaced by V, and the equation becomes $V=[S]/([S]+k)$, which is identical in form with the residuary dissociation curve of an acid. The methods are given (graphic and others) for determining k, which for the sucrose–invertin compound was found to be 0·0167. By measuring the inhibition of inversion produced by various carbohydrates, the dissociation constant of the compounds of invertin with other sugars was ascertained. For this purpose the equation: $k^1 = Fk/\{(S+k)(v_0/v_1 - 1)\}$, was evolved, where k^1 is the constant in question, F is the amount of inhibitory sugar, v_0 and v_1 the initial rates of inversion in the presence and absence of inhibitory sugars (such as lævulose), and the other symbols have the meanings already described. It was found that mannitol and glycerol, as well as carbohydrates, had a power of combining with invertin, but that the affinity for these of the ferment, as determined by the dissociation constants, was less than that for sucrose. Lactose had practically no combining power, and therefore does not appreciably inhibit sugar inversion. The decomposition of the sucrose–invertin compound was found to be a unimolecular reaction. S. B. S.

The Dialysis of Maltase. LADISLAS KOPACZEWSKI (*Compt. rend.*, 1913, **156**, 918—921).—A sample of maltase (taka-diastase) was submitted, first to ordinary dialysis, and then to Dhéré's process of electrical dialysis (compare A., 1910, ii, 515). Ordinary dialysis causes the hydrolysing power of the maltase to increase very considerably to a maximum (200% of original power), after which it diminishes slightly to 180%. Prolonged dialysis produces no further change. Electrical dialysis at this stage removes more of the electrolytes present, and produces a slight further diminution in the diastatic power. The maltase travels in the electrical field towards the negative pole; thus purified, the maltase has a feebly acid reaction to helianthin, and conductivity measurements give $K = 3{\cdot}8 \times 10^{-6}$.

W. G.

Action of Ammonia Gas on Diastase. III. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1913, **84**, 161—188. Compare A., 1912, i, 113).—When dry ammonia gas is passed over diastase preparations a small quantity is absorbed. In addition to ammonium salt formation and physical adsorption, ammonia is taken up and an equivalent of water liberated in two ways. In one instance an atomic group is formed, which combines both with acids and with formaldehyde; in another, the new group has neither of these properties. Such changes are assumed to indicate the replacement of an alcoholic hydroxyl by an amino-group and the interaction of an aldehyde group with ammonia.

The enzymic activity of the diastase is increased rather than hindered by the action of the ammonia. It is assumed that diastatic activity is not connected with the presence of a free aldehyde group or of an alcoholic hydroxyl. E. F. A.

The Reversibility of Ferment Actions: Emulsin and β-Methyl Glucoside. EMILE BOURQUELOT and ÉMILE VERDON (*Compt. rend.*, 1913, **156**, 957—959).—Experiments on β-methyl glucoside and emulsin confirm in every respect the results previously obtained with β-ethyl glucoside (compare Bourquelot and Bridel, A., 1912, i, 928; this vol., i, 212; Bourquelot and Coirre, this vol., i, 410). W. G.

Action of High Temperatures on the Dried Nucleases of Vegetable Origin. E. C. TEODORESCO (*Compt. rend.*, 1913, **156**, 1081—1084. Compare A., 1912, i, 1042).—A study of the effect of heat on the enzymatic properties of dried nucleases from four different sources of vegetable origin. The dried nucleases of the plants studied only lose their activity towards sodium nucleate after heating for thirty minutes at the following moderately high temperatures. The nuclease from *Evernia prunastri* becomes inactive at 145°, that from *Lycoperdon gemmatum* between 141° and 156°, that from brewer's yeast at 153°, and that from *Sticta pulmonacea* at 162°. W. G.

Preparation of a Nitro-3-aminophenyl-1-arsinic Acid. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 256343).—Two isomeric nitroaminophenylarsinic acids are known, and the third isomeride has now been prepared as follows:

*Carboethoxy-*m*-arsanilic acid*, m. p. 180° (decomp.), is obtained by treating an aqueous solution of 3-aminophenylarsinic acid with ethyl chloro-formate; this, when dissolved in fuming sulphuric acid at 0° and treated with nitric acid (26%), furnishes the corresponding *nitro*-compound (a yellow, crystalline powder), which, on hydrolysis at 70—80° with concentrated sulphuric acid, gives rise to *2-nitro-3-aminophenylarsinic acid*, orange-yellow needles.

2 : 3-*Diaminophenylarsinic acid*, obtained by reducing the preceding compound with sodium hyposulphite at the ordinary temperature, forms glistening leaflets, m. p. 205—208°; it furnishes an *azoimide* on treatment with nitrous acid.

2-Nitro-3-hydroxyphenylarsinic acid is obtained by the action of concentrated potassium hydroxide on 2-nitro-3-aminophenylarsinic acid, and this on reduction with sodium hyposulphite gives rise to 2 : 2'-*diamino*-3 : 3'-*dihydroxyarsenobenzene*. F. M. G. M.

Physiological Chemistry.

Oxidising and Reducing Enzymes and their Rôle in the Process of Respiration. ALEXIS BACH (*Arch. Sci. phys. nat.*, 1913, **35**, 240—262).—A summary of the present knowledge of the subject. Emphasis is laid on the following conclusions: (1) In order to utilise the oxygen of the air to effect oxidation, the cell produces an enzyme (an oxygenase), a substance which is readily oxidised, fixing molecular oxygen to form a peroxide. (2) A second enzyme (the peroxydase) accelerates the oxidising action of the peroxides, acting on them in the same way as ferrous sulphate does towards hydrogen peroxide. (3) The peroxides are readily transformed by hydrolysis into hydrogen peroxide, which is also formed as a primary product during hydrolytic oxidation. Owing to its rapid rate of diffusion, this accumulation of hydrogen peroxide might damage the cell protoplasm. To guard against this, the cell produces an enzyme-catalase, which rapidly decomposes hydrogen peroxide into water and inert oxygen. Catalase thus acts as a regulator of the respiratory process. (4) To effect hydrolytic oxidation, an enzyme, perhydridase, is present, which accelerates both oxidation and reduction just as do the metals of the platinum group. The reductase consists of the enzyme, water, and an oxidisable substance which fixes the oxygen derived from the water, leaving the hydrogen free to effect reduction. E. F. A.

Mechanism of Stimulation by Lack of Oxygen. H. S. GASSER and ARTHUR S. LOEVENHART (*Proc. Amer. Soc. Biol. Chem.*, 1912–13, xxx—xxxi; *J. Biol. Chem.*, **14**).—Lack of oxygen decreases the oxidation, and so stimulates the cells of the respiratory, cardio-inhibitory, and vaso-motor centres. Decrease in oxidation stimulates per se, and not by the accumulation of katabolic products.

W. D. H.

The Relationship between the Sugar Content of Erythrocytes and Glycolysis. ADAM LOEB (*Biochem. Zeitsch.*, 1913, **49**, 413—425).—Observations of previous observers are confirmed, according to which the red blood corpuscles of different species possess different contents of sugar, which are characteristic of each species. In the case of man, the corpuscles contain about the same percentage of sugar as the serum; in the dog they contain less, and in the case of sheep and pig, the corpuscles only contain very small amounts of sugar. The corpuscles of ox occupy an intermediary place as regards the sugar content. The larger the sugar content of corpuscles, the greater the amount of glycolysis they produce on incubation. The conclusion is drawn that those corpuscles produce glycolysis most readily which are the most readily permeable by sugar. Glycolysis of added sugar is therefore not wholly dependent on the presence of white corpuscles. S. B. S.

Oxycholesterol. E. SCHREIBER and LÉNÁRD (*Biochem. Zeitsch.*, 1913, **49**, 458—465).—This substance pre-exists as such in the blood. It is also found in the brain, lungs, heart, intestine, spleen, kidneys, muscles, sometimes in the pancreas. It is, however, not present in the liver. The failure to find the substance in this organ is shown not to be due to imperfect technique. Oxycholesterol is absent from the blood in diabetic coma. Preliminary experiments are described which are directed towards ascertaining the action of the liver towards oxycholesterol. S. B. S.

The Nature of the Destruction of Hæmoglobin during the Autolysis of Organs. SOICHIRO MIURA (*Biochem. Zeitsch.*, 1913, **49**, 137—143).—The disappearance of the blood pigment from autolysing mixtures, as observed by Hess and Saxl, is confirmed. This is not due to an enzyme in the mixture, but is a coagulative process, which takes place rapidly in the presence of chloroform, which is used as an antiseptic; the blood colour disappears from solution, in fact, when a solution is incubated with chloroform without the presence of any organ. The hæmatin component remains unchanged in quantity during the process of incubation. When organs are present, the coagulum is carried down with the solids. S. B. S.

The Action of Leucocytes on Some Hexoses and Pentoses. III. Mechanism of Lactic Acid Formation from Carbohydrates. PHŒBUS A. LEVENE and GUSTAV M. MEYER (*J. Biol. Chem.*, 1913, **14**, 149—154).—Leucocytes transform dextrose into *d*-lactic acid, but cleavage does not proceed further. There must be many intermediate stages in this change. Embden's view that glyceraldehyde is one is not confirmed. Moreover, regardless of the nature of the hexose (mannose, lævulose, galactose, dextrose), the lactic acid is invariably of the *d*-form. Whether pyruvaldehyde is the phase immediately preceding the formation of lactic acid remains to be established. Tissues preserved under aseptic conditions act similarly. Dissociation of pentoses by leucocytes does not occur. W. D. H.

The Behaviour of Calcium in the Serum. PETER RONA and DENGO TAKAHASHI (*Biochem. Zeitsch.*, 1913, **49**, 370—380).—The dependence of the solubility of calcium on the hydrogen and hydrogen carbonate concentration was investigated. The values, according to the laws of mass action of $k_1=[Ca^{\cdot\cdot}][HCO_3]_2/[H_2CO_3]$ and $k_2=[Ca^{\cdot\cdot}][HCO'_3]/[H]$, were determined. The experimental method of determining these constants is given in detail, and the values $k_1=116\cdot10^{-6}$ and $k_2=350$ were found. Serum was submitted to dialysis against an outer fluid of definite volume of known hydrogen carbonate concentration, and the composition of the inner and outer fluids was ascertained when equilibrium had been established. From the data thus obtained, the conclusion is drawn that the calcium hydrogen carbonate is in free diffusible form, but forms metastable supersaturated solutions. By the method of com-

pensation dialysis, against known phosphate mixtures, results were obtained indicating that the phosphate is also freely diffusible. The non-diffusible calcium appears therefore to exist in the form of calcium protein compounds. S. B. S.

Mode of Action of the Anti-coagulating Substance of the Plasma of Propeptone. HENRI STASSANO (*Compt. rend.*, 1913, **156**, 912—915).—A continuation of previous work (compare this vol., i, 418) on the coagulation of the plasma of propeptone. On diluting samples of the plasma with equal volumes of solutions of different chlorides of equivalent strength, the period of time, prior to coagulation, increases with rise in molecular weight of the chloride. Diminution of the saline concentration by dialysis, or marked increase of it by addition of sodium chloride, produces coagulation. Addition of a strongly negative colloid hastens coagulation. The following conclusions are drawn: (1) In the plasma of propeptone the coagulation, in vitro, takes place in two stages: activation of the fibrin-ferment, followed by its action on the fibrinogen. There is also a third stage, commencing when the colloidal stability of the fibrinogen is brought about, which consists in the appearance of granules in the uniform gel, this phenomenon being very fugitive and only visible under the ultramicroscope in the case of blood. (2) The anti-coagulating substance of the propeptone plasma forms a complex with the fibrinogen, hindering its precipitation and giving rise to a coagulum, without the intervention of one of the above-mentioned methods. W. G.

Digestion in the Chick. T. P. SHAW (*Amer. J. Physiol.*, 1913, **31**, 439—446).—Extracts of the glandular structures of the floor of the mouth in the chick contain an amylolytic enzyme active in an alkaline medium. This was found in extracts made an hour after hatching. The crop secretes no enzymes, but simply retains the food whilst salivary digestion goes on. By the second day, the gastric juice secreted contains proteolytic and milk-curdling enzymes which are active in an acid medium. The functions of the pancreas are imperfectly developed before the seventh day after hatching; the pancreatic juice then contains the usual three enzymes. The liver contains glycogen on the twentieth day of incubation; it becomes glycogen-free twenty-four hours after hatching if no food is given. It is found in the liver on the second day after the administration of starchy food. Lactose is not a glycogen-former in chicks, but acts as an irritant to the gastric and intestinal mucous membrane. W. D. H.

The Dependence of Lipase Action on the Concentration of the Hydrogen Ion. HEINRICH DAVIDSOHN (*Biochem. Zeitsch.*, 1913, **49**, 249—277).—The lipoclastic action was investigated by the stalagmometric method with the employment of tributyrin as substrate. The optimal action of the duodenal lipase of sucklings (withdrawn by means of a tube) was at $[H^{\cdot}] = 3\cdot2 \times 10^{-9}$ or $p_H = 8\cdot5$. A series of experiments was carried out with the same amount of

ferment in solutions of different hydrogen ion concentrations, and the course of lipolysis investigated. It was assumed that, except under optimal conditions, a fraction only of the ferment was active, and a method is given of calculating this fraction. If this amount is plotted graphically as a function of the hydrogen ion concentration, a curve is obtained which is identical with the dissociation curve of a weak acid, and is of the same order of magnitude as a curve deduced in a similar manner for trypsin. The conclusion is drawn that the lipase, like trypsin, is an amphoteric electrolyte with the acid dissociation constant $k_a = 1 \cdot 0 \times 10^{-7}$. The lipolytic activity is proportional to the amount of ferment ion present. The lipase of the stomach has a broad optimal zone with $[H^{\cdot}]$ between 10^{-5} and 10^{-4}. The curve obtained for this ferment is similar to the invertin curve, and is that of the residuary dissociation curve of an ampholyte with the constant $k_a = 4 \cdot 5 \times 10^{-7}$. The active principle of the stomach lipase is bound to the dissociation residue, and the optimal activity corresponds with the isoelectric point of the ampholyte, the basic dissocation constant of which is about 10^{-12}. There is therefore a difference between the gastric and duodenal lipases, which can be distinguished from one another by ascertaining the optimal $[H^{\cdot}]$ concentration for their action. There is no evidence in the case of sucklings of regurgitation from duodenum. The lipase of human milk is apparently a pancreatic lipase.

S. B. S.

Method of Investigating Metabolism in Rabbits, Milk being the Only Food. Ernst Laqueur (*Zeitsch. physiol. Chem.*, 1913, **84**, 109—116).—A specially constructed cage for metabolism experiments on rabbits is described. For prolonged periods milk was the only nutriment given. The advantages of milk are that its nitrogen is easily estimated, the urine does not readily decompose, and its secretion is regular. The absorption of milk is rapid, and 95% of it is utilised as compared with 65—70% of oats and cabbage.

W. D. H.

Amino-acids and Sugar for Rectal Feeding. Hubert W. Bywaters and A. Rendle Short (*Arch. expt. Path. Pharm.*, 1913, **71**, 426—445).—The older observations on the nutritive value of enemata are untrustworthy. Not a trace of milk or egg (peptonised for twenty to thirty minutes) is absorbed. Amino-acids, however, are absorbed, and lead to an increase in urinary nitrogen; the ammonia is low in the urine, hence the absorption of putrefaction products is absent. Dextrose is better absorbed than lactose; fat is badly absorbed. The best enema for rectal feeding is milk which has been subjected to pancreatic digestion for twenty-four hours plus 5% of dextrose.

W. D. H.

The Functions of the Liver in the Metabolism of Fats. I. Henry S. Raper (*J. Biol. Chem.*, 1913, **14**, 117—134).—Cocoanut oil given to cats or dogs by the mouth can be detected in the liver in five to six hours. The amount present does not exceed 6% of

that absorbed. If cocoanut oil soap plus glycerol and bile are injected into the intestine of anæsthetised cats, about 30% of the absorbed fatty acid is found in the liver. If an emulsion of the oil is given intravenously, 25—60% is found in the liver. During absorption the fat in the chyle contains fatty acids with an average higher molecular weight than in the oil. The lower acids are therefore partly absorbed as sodium salts. The volatile acids from the liver absorb more iodine than those from normal livers. The increase is not great, but it probably indicates that saturated fatty acids containing 10, 12, or 14 carbon atoms may become unsaturated in the liver. W. D. H.

The Influence of Urea Administered by the Mouth on the Nitrogenous Metabolism of Pigs. EMIL ABDERHALDEN and ARNO ED. LAMPÉ (*Zeitsch. physiol. Chem.*, 1913, **84**, 218—222).—No evidence was found to support the view that urea in the food acts as a protein sparer. In reference to gelatin, attention is drawn to the fact that various commercial specimens yield as much as 1% of tyrosine, and may even yield tryptophan. It is evident that no certain conclusions as to the nutritive value of gelatin can be drawn from experiments with such variable material. W. D. H.

Nitrogen Retention after Feeding on Urea. Reply to Abderhalden and Lampé. EDUARD GRAFE (*Zeitsch. physiol. Chem.*, 1913, **84**, 234—238).—Polemical. The author maintains the correctness of his earlier conclusions. W. D. H.

Influence of Caffeine on Creatine and Creatinine Metabolism. WILLIAM SALANT and J. B. RIEGER (*Proc. Amer. Soc. Biol. Chem.*, 1912-13, xxxv; *J. Biol. Chem.*, **14**).—Caffeine causes a moderate increase in the urinary creatine in fed rabbits, but a large increase during inanition; in some experiments, however, neither creatine nor creatinine were affected. Experiments on dogs gave negative results. W. D. H.

Metabolism of Nitrogenous Sugar Derivatives. JAMES ARTHUR HEWITT (*Biochem. J.*, 1913, **7**, 207—210).—Dextrose-*p*-phenetidide given by the mouth or by injection is not toxic in amounts up to 4 grams per kilo. of body weight. It produces no effect on nitrogenous metabolism, but a reducing substance appears in the urine. Some escapes oxidation in the body; *p*-phenetidine in amounts of 0·1 gram per kilo. of body weight is highly toxic. W. D. H.

The Action of Carbon Dioxide on Metabolism. Autolysis and Metabolism. VI. ERNST LAQUEUR (*Zeitsch. physiol. Chem.*, 1913, **84**, 117—160).—The nitrogenous metabolism was investigated on rabbits during a milk diet and inanition. Carbon dioxide slows and deepens the breathing; little or no narcotic action was observed. Nitrogenous metabolism was unaffected by a carbon dioxide percentage up to 7%. At 10% the output of nitrogen was increased,

at 13% very markedly so. In half the experiments this was accompanied by retention of water. The high tension of the gas is regarded as the cause of the increased decomposition of tissue-protein, possibly because the activity of autolytic enzymes is heightened. W. D. H.

Synthetic Powers of Animal Cells. The Action of Sodium Nitrate on Nitrogenous Metabolism. EMIL ABDERHALDEN and PAUL HIRSCH (*Zeitsch. physiol. Chem.*, 1913, **84**, 189—206).—Nitrogen given in the form of sodium nitrate is excreted quantitatively in the urine; it takes no direct part in protein metabolism. In two cases, however, there was retention of nitrogen, which did not correspond with the nitrogen given in the form of sodium nitrate. This is important as showing that nitrogen retention may be the result of the administration of nitrogenous materials which do not participate in metabolism. W. D. H.

Utilisation of Ammonia Nitrogen in Protein Metabolism. ALONZO E. TAYLOR and A. I. RINGER (*Proc. Amer. Soc. Biol. Chem.*, 1912–13, xxvi—xxvii; *J. Biol. Chem.*, **14**).—The findings of Grafe and of Abderhalden are confirmed, that starving and diabetic animals may retain a considerable part of the nitrogen ingested as ammonium carbonate. W. D. H.

Nitrogenous Assimilation on Feeding on Small Amounts of Protein and Large Amounts of Ammonium Salts and Urea. EDUARD GRAFE (*Zeitsch. physiol. Chem.*, 1913, **84**, 69—96).—The favourable action of ammonium salts and urea given by the mouth in pigs in causing retention of nitrogen is supported by further experimental data. By themselves, however, they do not maintain nitrogenous equilibrium over prolonged periods, but in combination with a small amount of protein they do. In other words, they have a protein sparing action. Whether their nitrogen is converted into protein or not is discussed, but no definite conclusion reached. The paper concludes with polemics against Abderhalden and Lampé, whose experiments are held to support and not disprove the author's contentions. W. D. H.

The Location of Protein Synthesis and the Production of Nitrogenous Equilibrium with Minimal Amounts of Proteins of Varying Decomposibilities. HANS STECK (*Biochem. Zeitsch.*, 1913, **49**, 195—224).—It has been assumed that the chief seat of synthesis of proteins is in the mucous membrane of the small intestine. If this is the case, those proteins which most readily undergo enzymatic hydrolysis into their constituent amino-acids will be the most efficient in maintaining nitrogenous equilibrium (that is, will maintain equilibrium when ingested in the smallest quantity), provided that the energy needs of the organism are sufficiently satisfied by the caloric value of the fats and carbohydrates. The reason for this assumption is that the majority of the amino-acids necessary for protein synthesis will be present at

the same time in the intestine in those proteins which are readily hydrolysed. The method of experiment adopted by the author was to place himself on a diet of sufficient caloric value and nearly free from nitrogen, and then to estimate the nitrogen loss. On this diet various proteins were superimposed, and the quantity was ascertained in each case, which is just necessary to restore the nitrogenous equilibrium. It was found that after three days of protein-free diet, the superimposition of small quantities of beef, egg-albumin, and caseinogen could restore equilibrium, but the amounts bore no relationship to their decomposability by proteoclastic ferments. The conclusion is drawn therefore, that protein synthesis takes place in parts of the organism other than the small intestine. From the amounts of nitrogen secreted in the after period, it appears that the ingestion of these proteins results in protein synthesis in the organism. Hæmoglobin, when ingested in small quantities, was inefficient in maintaining nitrogenous equilibrium. S. B. S.

The Influence of the Plane of the Protein Intake on Nitrogen Retention in the Pig. ELMER V. MCCOLLUM (*Proc. Amer. Soc. Biol. Chem.*, 1912–13, xxxiii—xxxiv; *J. Biol. Chem.*, **14**).—The retention of nitrogen at all levels, except 7·5 times the endogenous level, was in close agıeement, whether the proteins given were derived from wheat, oats, or maize. At five times this level, 10% of the ingested nitrogen was retained; at 7·5, 12—17%; at 10, 15, and 20, the retention was 21—24%. W. D. H.

Metabolic End-Products of the Lipoid Nitrogen of Egg-yolk. ELMER V. MCCOLLUM and H. STEENBOCK (*Proc. Amer. Soc. Biol. Chem.*, 1912–13, xliv—xlv; *J. Biol. Chem.*, **14**).—A pig was fed for a week on 220 grams of dry egg-yolk and 35 grams of starch per diem. The nitrogen intake was 11·65 grams daily; of this, 0·65 gram was lipoid nitrogen. The urinary nitrogen varied from 5 to 6 grams; of this 30 to 40% was in the form of ammonia, and only 35—45% as urea. The urine contained 0·3 gram of nitrogen as substituted amines. The demethylation of substituted amines is evidently not readily accomplished in the pig's body. W. D. H.

The Biological Value of α-Nucleic Acid. G. ALLESANDRO BROSSA (*Chem. Zentr.*, 1912, ii, 2123; from *Arch. Anat. Physiol.* (*Physiol. Abt.*), 1912, 191—196).—A dog and two hens were reduced to a nitrogen-free diet balanced by increased amounts of carbohydrates and fats, and then supplied with α-nucleic acid. Estimation of nitrogen in the excreted substances showed that 60—80% of the nucleic acid, a compound which is far removed from the proteins, had been absorbed. J. C. W.

Resorption of Bromide from the Intestine. STEFAN VON BOGDÁNDY (*Zeitsch. physiol. Chem.*, 1913, **84**, 15—17).—To study the resorption of bromide from the intestine, the blood stream was limited to the intestine, heart, and lungs, and the haloids in it determined before and after injection of sodium bromide. The

bromide is shown to aggregate in the blood in a very short interval; part of the sodium chloride of the blood is replaced by bromide.
E. F. A.

The Fate of Protein Cleavage Products in the Intestine. EMIL ABDERHALDEN, ARNO ED. LAMPÉ, and EFIM S. LONDON (*Zeitsch. physiol. Chem.*, 1913, **84**, 213—217).—Accepting the view that in absorption protein cleavage products enter the blood stream as amino-acids and ammonia, there still remains the possibility that the lacteals may be a channel for protein absorption. In two series of experiments on dogs, the lymph during digestion of meat was found to contain more nitrogen but less amino-acid than during hunger; the amount of ammonia was but little altered. Further work in this direction is promised.
W. D. H.

The Absorption of Magnesium Sulphate Solutions in the Small Intestine, and the Mode of Action of Saline Purgatives. RUDOLF COBET (*Pflüger's Archiv*, 1913, **150**, 325—360).—The relative importance of physical and physiological factors in the causation of purgation by salines is discussed. Magnesium sulphate causes a great increase of secretion in the intestines; the sodium chloride of the intestinal juice poured out is re-absorbed in the lower reaches of the gut, but the fluid portion is not; the sulphate itself is badly absorbed.
W. D. H.

Intestinal Obstruction. A Toxic Substance in the Intestinal Mucosa. GEORGE H. WHIPPLE (*Proc. Amer. Soc. Biol. Chem.*, 1912–13, xxxii—xxxiii; *J. Biol. Chem.*, **14**).—Closed loops of the small intestine yield what normal mucosa does not yield, a toxic substance which causes low blood-pressure, vomiting, diarrhœa, collapse, and death. If the mucosa is first destroyed by sodium fluoride, no toxic substance is formed.
W. D. H.

The Influence of Function on the Lime Requirements of Animals. H. STEENBOCK and EDWIN B. HART (*J. Biol. Chem.*, 1913, **14**, 59—73).—In the non-pregnant animal a daily intake of 0·3 gram of CaO in the pig, and 0·4 in the goat per 100 lbs. of body-weight covers metabolic losses; but mammary activity is a severe drain on the skeletal lime, and the allowance in the food should be three or, better, six times greater, for increase of food entails large losses of lime in the intestine.
W. D. H.

The Effect of a High Magnesium Intake on Calcium Retention in Swine. EDWIN B. HART and H. STEENBOCK (*J. Biol. Chem.*, 1913, **14**, 75—80).—Bran is not a good bone-producer, on account of its low lime content. Magnesium salts added to a pig's ration increase the urinary calcium, but this is counteracted by di-potassium hydrogen phosphate. The inter-relations existing between the mineral elements are important factors in nutrition.
W. D. H.

The Behaviour of Plasteins in the Animal Body. ERICH VON KNAFFL-LENZ and ERNST P. PICK (*Arch. expt. Path. Pharm.*, 1913, **71**, 407—425).—Plasteins act as antigens, but the immune material generated is not specific. The specificity of the original proteins is thus destroyed during digestion. It further makes no difference what variety of pepsin is employed in their formation. Plasteins do not produce the phenomena of anaphylaxis.

W. D. H.

The Influence of the Composition and Amount of the Mineral Content of the Ration on Growth. ELMER V. McCOLLUM and MARGUERITE DAVIS (*Proc. Amer. Soc. Biol. Chem.*, 1912–13, xl; *J. Biol. Chem.*, **14**).—Young rats do not grow when fed on wheat kernel only, but the addition of salts so as to make the ration like that of milk or egg-yolk produced normal growth.

W. D. H.

The Chemical Changes Occurring in Meats during Drying in a Vacuum. L. H. DAVIS and A. D. EMMETT (*Proc. Amer. Soc. Biol. Chem.*, 1912–13, xlii; *J. Biol. Chem.*, **14**).—Calculating the data for fresh and desiccated meats to the dry basis, using the two values for dry substance (the vacuum and the oven-heated), the results agree closely for the various constituents, the differences being greatest in the fat, as was to be expected. W. D. H.

The Presence of Choline or Allied Bases in the Saliva of the Horse. JULES HOUDAS (*Compt. rend.*, 1913, **156**, 824—826).—Schulze and Trier (A., 1912, ii, 1203) having demonstrated the presence of choline and allied bases in all plants, the author has examined the saliva of horses for the presence of these substances therein, using Bouchardat's reagent to recognise them. Specimens of saliva were obtained from horses under varying conditions and at different times after feeding and with varying diet, and in all cases either choline or bases of the same group were found to be present. W G.

The Central Nervous System under Normal and Pathological Conditions. V. Biochemical Studies on Brain Swelling: (*a*) Acute Brain Swelling and the Colloidal Theory of Œdema. GIACOMO PIGHINI, PIETRO BARBIERI, and DOMENICO CARBONE (*Biochem. Zeitsch.*, 1913, **49**, 293—316).—According to the theory of M. Fischer, œdema is due essentially to imbibition of water, which, in the case of proteins, takes place more readily in the presence of alkalis and bases, and is inhibited by salts. The authors discuss the subject of brain swelling from the clinical and pathological point of view, and suggest as a possible cause for the imbibition of water by the brain an increase of acid in the circulation. They have, however, failed to substantiate the hypothesis, as the injection of acids under varying conditions into animals (rabbits) did not produce œdema. S. B. S.

The Fatty Acids of the Human Brain. EGERTON CHARLES GREY (*Biochem. J.*, 1913, **7**, 148—156).—At least 25% of the solid fatty acids of the brain are hydroxy-acids; of these, three have been isolated: $C_{17}H_{34}O_3$ or $C_{22}H_{44}O_4$, m. p. 100—101°; $C_{25}H_{50}O_3$, m. p. 91·0°; and $C_{20}H_4O_3$, m. p. 73·5°, and two at least are monohydroxy-acids, and therefore are not produced artificially by oxidation of unsaturated fatty acids. The unsaturated acids include oleic, linoleic, and linolenic acids; also an acid still more unsaturated, to which the name *clupanodenic acid* is given; it combines with 12 atoms of bromine. Another is a solid, $C_{18}H_{34}O_2$ or $C_{18}H_{36}O_2$, m. p. 42°; this is probably an isomeride of oleic acid. The saturated acids are stearic, palmitic, myristic, and Thudichum's neurostearic acid, m. p. 51—52°. The resemblance between the hydroxy-acids of the brain and those of lanoline is additional evidence of the relationship of nervous tissues to other tissues of epiblastic origin.

W. D. H.

Action of Various Influences on the Mammalian Heart V. H. K. MOORHOUSE (*Amer. J. Physiol.*, 1913, **31**, 421—438).—Isolated strips of the cat's auricle beat spontaneously in a bath of oxygenated Ringer's solution; the rhythm and effect of temperature are approximately equal in coronary, nodal, and septal strips. Drugs which act on the vagus are more effective on strips which do not contain nodal muscle. Drugs which act on sympathetic nerve-endings produce an equal effect on all these kinds of strip, but the acceleration lasts longest in septal strips. The sino-auricular node does not exhibit any specially reactive properties to various influences affecting rhythm.

W. D. H.

The Action of Oxalic Acid on the Frog's Heart. OSKAR GROS (*Arch. expt. Path. Pharm.*, 1913, **71**, 395—406).—A solution of sodium oxalate added to Ringer's solution soon stops the heart of the frog in diastole. Its activity is restored by washing out with a calcium-free solution. Sodium citrate acts more powerfully in the same way, although its power to precipitate calcium is less. It is held that the removal of the calcium is not the cause of the action, but that oxalates and citrates have a specific harmful effect on cardiac tissue.

W. D. H.

Diastases. II. Sugar Formation in the Frog's Liver. I. IVAR BANG (*Biochem. Zeitsch.*, 1913, **49**, 40—86).—The experiments were carried out with both *Rana esculenta* and *R. fusca.* Sugar was estimated in separate lobes of the liver. As a rule, one lobe was separated from the others, and the sugar was estimated immediately, whilst the other lobes were allowed to remain in Ringer's fluid and the sugar was estimated after several hours. The amounts of sugar free and existing in the separate lobes from the same animal were also ascertained, and the limits of variation determined. From the alterations in weight after keeping in Ringer's solution, which were found to be small, the conclusion was drawn that the liver still survives even after prolonged keeping in the Ringer

fluid, it being assumed that the organ is not killed, whilst its osmotic properties remain intact. Other reasons are also given for assuming that the organ survives after prolonged immersion in Ringer's solution. After keeping in this liquid, the livers show an increase of reducing sugar (found both in the organ itself and in the fluid in which it is immersed), the amount of which is larger than the variations in the lobes from the same animal. The conclusion was therefore drawn that the surviving liver is capable of producing sugars. The mechanism of this sugar production was studied. It is not due to the diastase of the blood, as there is no appreciable difference between the amounts produced in a liver containing blood and one that has been perfused (from the portal vein). There is, however, a considerable difference between the sugar production by the crushed liver paste and by the intact cells, according to whether the organs have been perfused or not. If they have not been perfused, the paste produces much more sugar, owing to the fact that the diastase of the blood can then act; where they have been perfused, the difference between the sugar production by the paste and intact cells is very much diminished. This is additional evidence of the fact that the sugar production by the surviving liver is not due essentially to the diastase of the blood. The facts indicate that it is due to a liver enzyme. In the case of *Rana esculenta*, the treatment of the liver with alcohol reduces the sugar-producing power of the liver, which can, however, be restored by addition of sodium chloride; in fact, when the liver has been treated in this way, the sugar-producing power is increased beyond that of the original intact liver. This fact is explained by the hypothesis that the alcohol removes some lipoid-like substance which exerts an inhibitory action on the sugar-producing power. As the addition of the alcoholic extract does not inhibit this power exerted by the extracted liver and salt, it is assumed that the inhibitory substances only exert their action when in some form of combination, which is broken up on treatment with alcohol, but not restored on the addition of the alcoholic extract. The same phenomena were not observed in the livers of *R. fusca*, which, unlike those of *R. esculenta*, do not appear to contain a large store of enzyme or pro-enzyme, which can be activated by the addition of salt. S. B. S.

Diastases. III. Sugar Formation in the Frog's Liver. II. IVAR BANG (*Biochem. Zeitsch.*, 1913, **49**, 81—119).—Adrenaline increases the sugar-producing power of the liver, in quantities which are insufficient to kill the organ. Details are given of Overton's experiments on the irritability of muscles after treatment with adrenaline which justify the conclusion as to the relative non-toxicity of the adrenaline solutions employed. A detailed account is given of the action of adrenaline on the sugar production of the liver under varied conditions. In the case of *R. fusca*, the increased production appears to be due to the reduction of the acidity of the medium, and the effect can be imitated by the use of neutral phosphate solutions. Furthermore, the accelerating effect of the adrena-

line in these cases can be antagonised by the presence of minute amounts of free hydrochloric acid. In the case of *R. esculenta*, the action of adrenaline appears to be exerted on the intracellular lipoids, which in combination inhibit the diastatic action of the organ (compare preceding abstract). The adrenaline action in this case can be imitated by treating the liver with narcotics (for example, alcohol), which can also break down the lipoid complex. There is no evidence that adrenaline causes new production of enzyme; it appears only to activate the pre-existing ferment.

S. B. S.

The Formation of Glycogen from Glyceraldehyde in the Liver. JAKOB PARNAS (*Zentr. Physiol.*, 1912, **26**, 671—672).—Perfusion of the tortoise's liver with glyceraldehyde in Ringer's solution leads to the deposition of glycogen therein, at the rate of about 50 mg. reckoned as dextrose per hour per 10 grams of liver. Whether this is due to condensation, or oxidation through the stages of glyceric acid, glycolaldehydecarboxylic acid, and glycolaldehyde is uncertain; the view that dextrose is katabolised into glyceraldehyde in the body is also unsettled. W. D. H.

The Importance of Cholesterol in the Organism. LEONHARD WACKER and WERNER HUECK (*Arch. expt. Path. Pharm.*, 1913, **71**, 373—394).—The methods of estimation of cholesterol are discussed, but the microscopic examination of the adrenal cortex gives a good indication of the amount present. In this situation free cholesterol is an integral and stable cell constituent, but the cholesterol in the condition of ester is variable and labile. It is here that the polarising microscope is especially useful. In arterial sclerosis, chronic kidney disease, diabetes, and during pregnancy the amount of cholesterol esters increases, but in long-continued infectious disease, septic processes, chronic ulcer, cancer, and tubercle it falls. In the acute stages of infectious diseases, it increases. The amount in the blood varies directly as that in the suprarenal; this is regarded as important, for cholesterol plays a rôle in the natural protective processes of the body. W. D. H.

The Iodine-containing Complex of Thyreo-globulin. FRED C. KOCH (*J. Biol. Chem.*, 1913, **14**, 101—116).—The full activity of thyroid tissue (measured by Hunt's method) is contained in the thyreo-globulin fraction. The full activity per iodine unit is still present in the metaprotein fraction from this globulin, although the iodine in this fraction is increased three-fold. Other products of hydrolysis (proteoses and iodothyrin) show a decrease in activity per unit of iodine. The amino-acid fractions contain very little iodine, and are either inactive or nearly so. Tetra-iodohistidine anhydride and iodotryptophan have no activity. W. D. H.

Some Phosphatides of Human Placenta. I. and II. C. SAKAKI (*Biochem. Zeitsch.*, 1913, **49**, 317—325, 326—332).—The placenta was extracted with alcohol at 60°. A white substance

only sparingly soluble in cold alcohol was isolated, which was very similar in properties to the diaminophosphatide isolated by Thierfelder and Stern from egg-yolk. Its composition was intermediate between that of *apo*myelin and sphingomyelin, as isolated by Thudichum. A preliminary account of other products is given. No evidence as to the existence of jecorin was obtained.

In the second paper, a preliminary account is given of various fractions, none of which can be claimed to be a pure product.

S. B. S.

Muscular Contraction; Influence of Non-electrolytes, Electrolytes, and Osmotic Pressure. GEORGES KLEEFELD (*Bull. Acad. roy. Belg.*, 1913, 91—180).—The principal views of J. Loeb on the antagonism between calcium ions and those of potassium and sodium, as well as on the toxicity of sodium ions, are confirmed; perfusion with calcium chloride extinguishes muscular excitability; sodium nitrate has the same effect, and potassium is sometimes indifferent; at other times it abolishes excitability. Certain non-electrolytes (sucrose, dextrose) are capable of determining rhythmic contractions. Calcium is sometimes an excitant of contractility, and is able to render contractile muscles treated with sodium citrate. Calcium can exist in the perfusion fluids far above the normal amount without suppressing excitability. By the method of Lapicque-Weiss it can be shown, however, that electrical irritability can diminish, even although the muscle executes normal contractions. Contractility and irritability cannot be regarded as identical.

W. D. H.

Amount of Creatine in Muscles of Various Animals and in Different Types of Muscles. MARIO CABELLA (*Zeitsch. physiol. Chem.*, 1913, **84**, 29—38).—Creatine is always present in the muscle tissue of vertebrates. The amount varies with the nature of the muscle; it is most in striped voluntary muscle, less in heart muscle, and least in unstriped muscle. In birds (hens, ducks) the amount of creatine in the breast muscles is considerably larger than that in the limb muscles.

Similar differences in the amount of creatine are found in the individual muscles of any one animal. These differences persist whether referred to the weight of fresh muscle or dried muscle, or expressed as creatine nitrogen in terms of the total nitrogen. This nitrogen factor lies between 3 and 4 for the voluntary muscles of mammals, birds, fishes, and the heart muscle of the ox. It is from 4 to 5 for the breast muscle of birds, and about 1 for the heart muscle of the hen and the smooth muscle of the ox.

Creatine could not be obtained from the muscular tissue of the mantle or the arms of the octopus.

E. F. A.

Muscle-Creatine. Dialysis of Creatine from Dog's Muscle H. T. LEO and PAUL E. HOWE (*Proc. Amer. Soc. Biol. Chem.*, 1912–13, xliii; *J. Biol. Chem.*, **14**).—Creatine dialyses out from muscle into water, Ringer's solution, and various strengths of sodium chloride

solution. Hydrochloric acid delayed the diffusion, alcohol increased it. The experiments offer no definite evidence as to the way in which creatine is held in the muscle. W. D. H.

The Action of Potassium Chloride on Frog's Muscle. RICHARD SIEBECK (*Pflüger's Archiv*, 1913, **150**, 316—324).—Neutral isotonic solutions of potassium chloride render muscles rapidly inexcitable; the muscles increase in weight. Even after some hours, when there is a 20% increase in weight, the action is completely reversible. Organs the structure of which is destroyed by freezing and thawing, do not swell in solutions of potassium chloride, but swell in alkaline solutions. An acid reaction causes in muscle either in Ringer's or a potassium chloride solution no marked reversible effect; but the swelling is increased by faradic stimulation, an alkaline reaction, or by narcosis. W. D. H.

Connective Tissues of Limulus. HAROLD C. BRADLEY (*Proc. Amer. Soc. Biol. Chem.*, 1912-13, xl—xli; *J. Biol. Chem.*, **14**).—The cartilage-like tissue yields a sclero-protein which is insoluble in water and the ordinary solvents. It is insoluble in pepsin hydrochloric acid, but digests readily in a tryptic mixture. It gives the usual protein reactions, but no gelatin was obtained. The white, fibrous tissue within the carapace is also composed of a non-collagenous sclero-protein. It digests readily in a peptic, but very slowly in a tryptic, mixture. W. D. H.

The Secretion of Pigments by Annelids. K. KSCHISCHKOWSKI (*Chem. Zentr.*, 1913, i, 40; from *Zentr. Physiol.*, 1912, **26**, 528—532). —Under certain conditions, *Lumbriconereis impatiens* secretes a lilac-red pigment, which gives an orange solution in ether and a pink in chloroform. The secretion is provoked in a specific way by solutions of potassium salts which are isotonic with a 3·5% solution of sodium chloride. If the organisms are narcotised or kept in isotonic solutions free from potassium salts for some time, the pigment reaction does not occur for several days. J. C. W.

The Rôle of Glycogen, Lecithides, and Fats in the Reproductive Organs of Echinoderms. BENJAMIN MOORE, EDWARD WHITLEY, and ALFRED ADAMS (*Biochem. J.*, 1913, **7**, 127—141).—The male and female reproductive glands in echinoderms contain large amounts of reserve metabolic products, such as glycogen, fat, and lecithides. These reserves are only slowly used up, if at all, when the animal is deprived of food. In such glands no sugar formation occurs in a period of two days after death. The fatty substances are highly unsaturated, thus resembling liver oils. W. D. H.

The Basic and Acidic Proteins of the Sperm of Echinus esculentus. Direct Measurements of the Osmotic Pressure of a Protamine or Histone. BENJAMIN MOORE, EDWARD WHITLEY, and ARTHUR WEBSTER (*Biochem. J.*, 1913, **7**, 142—147).—A substance

was separated from the ripe male gonads of *Echinus esculentus*, which had properties intermediate between those of a histamine and a histone. Its molecular weight calculated from its osmotic pressure is 8780. Its action on ova and cell division was tested, but the results were negative. W. D. H.

Anoxybiose and Chemical Polarity. (Mme.) ANNA DRZEWINA and GEORGES BOHN (*Compt. rend.*, 1913, **156**, 810—812).—*Prostheceraeus* and *Convoluta* when placed in tubes deprived of oxygen for six hours and then returned to aerated water, in all cases exhibit the phenomenon that the anterior extremity has possessed a greater resistance to the privation of oxygen than the posterior extremity, the latter becoming disintegrated when returned to water, whilst the heads live and can be seen swimming about. This differentiation the authors compare with chemical polarity. W. G.

The Composition of Human Bile. ERNST VON CZYHLARZ, ADOLF FUCHS, and OTTO VON FÜRTH (*Biochem. Zeitsch.*, 1913, **49**, 120—129).—Details are given for the estimation of the following constituents of the bile: Total solids, pigment (colorimetric method), cholesterol (colorimetric method with chloroform and acetic anhydride), higher fatty acids, mucin, bile acids (as cholic acid). Typical analyses are given of bile obtained from the bladder and from fistulæ. Administration of cholesterol *per os* appeared to increase, not the amount of cholesterol, but that of the bile acids in the bile obtained from a fistula. S. B. S.

Secretin and Vaso-dilatin. L. LAUNOY and KARL OECHSLIN (*Compt. rend.*, 1913, **156**, 962—965).—By repeated precipitation by absolute alcohol from aqueous solution the authors have obtained the secretin of Bayliss and Starling (A., 1902, ii, 275, 613; 1903, ii, 316) in a solid state as a non-hygroscopic, white powder, very soluble in water, having an alkaline reaction and a very marked exciting influence on the secretion of pancreatic juice, but no depressing effect. Further, on concentrating the alcohol used for the above precipitation, they obtained a yellow, hygroscopic powder, soluble in water, and having a strongly alkaline reaction. Its aqueous solution only produces feeble secretion excitation, but is strongly depressant. It corresponds with the "depressor substance" mentioned by Bayliss and Starling (*loc. cit.*). This shows that Popielski's vaso-dilatin (compare A., 1912, ii, 593) is distinct from the above secretin. W. G.

An Attempt to Estimate the Vitamine-fraction in Milk. CASIMIR FUNK (*Biochem. J.*, 1913, **7**, 211—213).—In milk freed from protein the vitamine fraction is precipitable by phosphotungstic acid; the amount of vitamine ($C_{17}H_{20}O_7N_2$) is about 1 to 2·5 mg. per litre. The filtrate still contains nitrogen, which probably represents allantoin. If milk is freed from fat by the centrifuge, about half the vitamine and allantoin is lost. Both allantoin and vitamine are destroyed by boiling. W. D. H.

The Secretion of the Two Kidneys. RAPHAEL LÉPINE and RAYMOND BOULUD (*Compt. rend.*, 1913, **156**, 754—756).—An examination of the amount of urine flowing from each of the kidneys of a healthy dog and a determination of the urea, sugar, and chlorides present in each case. In every case there was a greater flow from the right side, and the urine from this side was richer in chlorides and sugar. The nitrogen-urea coefficient was the same for both sides. These differences are stated to be due partly to a difference in the secretion activity, but principally to differences in resorption of the urinary constituents by the two kidneys. W. G.

The Extremes of Variation of the Concentration of Hydrogen Ions in Human Urine. LAWRENCE J. HENDERSON and WALTER W. PALMER (*J. Biol. Chem.*, 1913, **14**, 81—85).—After a dose of 10 grams of monosodium phosphate there is a slight increase of hydrogen ion concentration in the urine. Larger quantities of acid phosphate or of hydrochloric acid produce a similar effect, but the acidity is never as great as in many pathological conditions. A more alkaline urine is produced by sodium hydrogen carbonate, but beyond a certain point even after large doses of alkali the reaction of the urine does not change. In a large number of observations the highest acidity exceeded 4·70; the highest alkalinity 8·70. This corresponds with a range of 1:10,000 in the concentration of hydrogen and hydroxyl ions. The actual variation in normal people is at least 0·5 gram-molecule. In pathological states the variation is greater. In most acid urines, the urinary acids are in large measure free; in most alkaline urines they are almost completely combined with bases. W. D. H.

Diastase in the Urine of Infants. ERNST MAYER (*Biochem. Zeitsch.*, 1913, **49**, 165—167).—Diastase is seldom completely absent from the urine of breast-fed children. In the first three months, however, it does not exceed 5 units (in Wohlgemuth's system). There is no appreciable increase in the next three months. Between the sixth and ninth month the values vary between 2·5 and more than 20 units, after which period higher values are obtained. The amount is, however, affected by pathological complications.

S. B. S.

Excretion of Purine Katabolites in Sundry Types of Mammalia. MAURICE H. GIVENS and ANDREW HUNTER (*Proc. Amer. Soc. Biol. Chem.*, 1912—13, xxiv—xxv; *J. Biol. Chem.*, **14**).—Allantoin is a regular constituent of the urine of rabbit, horse, pig, cow, cat, dog, coyote, monkey, and man. To this list may be added the opossum, guinea-pig, porcupine, sheep, and racoon. In man the figure is smallest. Uricolytic power is greatest in carnivora; then follow rodents, ungulates, and marsupials in the order named. It is practically absent in man. W. D. H.

Estimation of Amylolytic Ferments in the Urine as a Measure of Certain Pathological Conditions. DUDLEY CORBETT (*Quart. J. Med.*, 1913, **6**, 351—383).—The amount of ferment passed

by a given individual in twenty-four hours' urine is fairly constant, varying between 6·6 and 33 Wohlgemuth units, the average being 10—20°. It is also present in blood serum, the average amount being 10 units. The quantity in the urine is unaffected by the diet, the reaction of the urine, the presence of bacteria, and other abnormal constituents, with the exception of blood. The amount in the urine does not appreciably diminish if the urine is kept in the presence of toluene. The amount in the urine of an infant fed on milk is very small, but rises on the administration of starchy food. When the amount of ferment in the serum exceeds that of the urine, there is a renal deficiency, as the ferment is readily excreted by normal kidneys. High readings were never obtained in pure cases of renal disease. High readings (up to 100 or even more) were found in certain acute infective conditions, in pancreatic disease, in certain forms of eclampsia, and in one case of "acidosis" in a child. All cases of undoubted pancreatic disease, whether due to malignant or inflammatory processes, gave high readings, and the test may therefore be of value for diagnosis of such conditions. In diabetics on strict diet, the readings were generally subnormal. In severe cases the readings were lower than in the milder forms, but in these conditions the excessive amount of urine excreted must be taken into account. S. B. S.

Sarcolactic Acid and the Theory of Diabetes. R. T. Woodyatt (*Proc. Amer. Soc. Biol. Chem.*, 1912–13, xxxviii; *J. Biol. Chem.*, **14**).—A theory is proposed that the internal secretion of the pancreas dissociates dextrose and perhaps other hexoses, and that the presence of lactic acid is evidence of such dissociation. In pancreatic diabetes there is lessened dissociation and less lactic acid in the tissues. W. D. H.

The Behaviour of Blood Sugar in Normal and Pathological Cases. VII. The Blood Sugar in Diabetes Mellitus. Fr. Rolly and Fr. Oppermann (*Biochem. Zeitsch.*, 1913, **49**, 278—292. Compare this vol., i, 425).—No direct relationship was found between the amount of blood-sugar and glycosuria in diabetes. It was found that only in the case of severe diabetes did ingestion of proteins cause a rise both of blood-sugar and glycosuria. The blood sugar content did not increase either in the case of carnivora (dogs) or herbivora after administration of proteins. The administration of meat and carbohydrate foods caused a greater amount of glycosuria in diabetics than a similar diet in which the meat was replaced by vegetable proteins. S. B. S.

Sulphur Metabolism. I. The Urinary Sulphur Partition in Various Diseases. N. Stadtmüller, Max Kahn, and Jacob Rosenbloom (*Proc. Amer. Soc. Biol. Chem.*, 1912–13, xliv; *J. Biol. Chem.*, **14**).—High proportions of neutral sulphur were passed in nearly all cases of diabetes, in all cases of cancer, in one case of nephritis (out of two), and in the one case examined of hypopituitarism. W. D. H.

The Intestinal Flora. The Possible Production of Ptomaines in Acid Medium. ALBERT BERTHELOT and D. M. BERTRAND (*Compt. rend.*, 1913, **156**, 1027—1030. Compare A., 1912, ii, 668).—*Bacillus aminophilus intestinalis*, sown on media containing histidine and peptone, to which were added, instead of dextrose, amounts of lactic acid varying from 0·5 to 5 per 1000, shows marked culture and formation of 4-β-aminoethylglyoxaline, even with 3 per 1000 of acid present. Thus, in the intestinal flora of persons exhibiting, at the same time, symptoms of enteritis and colitis, their fæces being acid, the *B. aminophilus* may be found capable of attacking histidine even in a slightly acid medium. This bacterium is capable of acting in the intestine as a simple lactic ferment without forming any toxic base, but it can, in certain cases, produce aminoethylglyoxaline equally well in neutral or alkaline medium, or in the presence of acids elaborated by other microbes, and its attack is not limited solely to histidine. W. G.

The Action of Aloin on Metabolism. The Physiology of Artificially Produced Gout and Fever. M. BERRÁR (*Biochem. Zeitsch.*, 1913, **49**, 426—446).—It has already been shown by Kossá, that administration of aloin to birds produces increased output of uric acid, which, in cases where the action of the kidneys is inefficient, leads to the production of an artificial gout. The researches on aloin have now been extended to mammals. Quantities of 0·1 to 0·2 gram per kilo. of body weight, administered to dogs, produces an increase of temperature and increased metabolism, which at the height of action can be double the normal. Both the gaseous metabolism and the output of various products in the urine and fæces were investigated. The substances forming the source of the increased energy production were those most readily at the disposition of the organism at the time of the administration of the drug. In the starving animal, the fat and proteins served chiefly for this purpose, whereas in the case of an animal which had received a diet rich in carbohydrates, these substances were mostly drawn upon, their metabolism increasing from 150 to 500%, the normal value. No distinct relationship was ascertained between the amounts of different products employed to meet the increased energy needs. S. B. S.

Use of the Oxydase Reaction in the Differentiation of Acute Leucæmias. JOHN SHAW DUNN (*Quart. J. Med.*, 1913, **6**, 293—308).—The occurrence of a positive indophenol-oxydase reaction in large, non-granular cells in acute leucæmia is a certain proof of their myeloid nature, and enables a diagnosis of acute myeloid leucæmia to be readily made from a blood examination. The reaction is negative in the more embryonic forms of marrow-cells, and in small myoblasts, and is probably always negative in the most typical stage of large myoblasts with uniformly dense basophil reticular protoplasm. When the reaction is positive in these large, non-granular cells, it is associated with alterations in the protoplasm, which are recognisable by ordinary staining

methods, and indicate stages of ripening towards the granular myelocytes. Cases of acute myeloid leucæmia may occur in which the type of blood-formation is so embryonic that the oxydase reaction is valueless for differential diagrams; but even in such cases the histological characters of the large leucocytes may render a diagnosis possible. S. B. S.

Narcosis. BRUNO KISCH (*Zeitsch. Biol.*, 1913, **60**, 399—456).—The action of photodynamic materials (eosin, methylene-blue) is increased in *Colpidia* by the addition of alcohol, ether, or chloroform. Dilute alcohol, however, acting for short periods, sometimes has the opposite effect so far as eosin is concerned. Narcosis in these animals is markedly affected by light. In *Spirostomum* the action of increased oxygen tension is increased by light, and there is a rise in the oxygen consumed in *Opalina*. The effect of light and oxygen on *Spirostomum* is inhibited by narcotics, but this is not seen in *Opalina*. The movements of these animals are paralysed by narcotics, but not in a reversible way. W. D. H.

Gastric Juice in Malignant and Non-malignant Diseases of the Stomach and Duodenum. SAMUEL B. SCHRYVER and CHARLES SINGER (*Quart. J. Med.*, 1912, **6**, 71—81; 1913, **6**, 309—350).—Hans Fischer and Neuberg have suggested that the capacity of gastric juice to hydrolyse glycyl-tryptophan is diagnostic of cancer. The authors have investigated the action of gastric juices on Witte's peptone, and have shown, by the use of Sörensen's formaldehyde titration method, that in certain cases the gastric juice contains a peptolytic ferment. This was found in about 6½% of the cases examined, all of which were taken from patients suffering from grave gastric disorder. It is only found when free hydrochloric acid is absent, and where the peptic powder is low, or even absent. It is not diagnostic of malignancy, as in the majority of cases of undoubted cancer the ferment was absent. It is most commonly associated with gastric dilatation and atrophy of the walls of the stomach, and is probably of intracellular origin.

Investigations were also carried out with the object of interpreting the analyses of gastric juice as regards the titration numbers obtained when methyl-orange and phenolphthalein are used as indicators. If B denotes the number of c.c. of $N/10$-sodium hydroxide necessary to neutralise 10 c.c. of gastric juice to phenolphthalein, and C the number of c.c. of alkali required to neutralise the same amount to methyl-orange, and A the number of c.c. of $N/10$-ammonia produced when 10 c.c. of the juice are incinerated by Kjeldahl's method with sulphuric acid, then $(C-B)/A$ was found to be a constant for any given amino-acid or mixtures of amino-acids or digestion products. $(C-B)/A \times 10$ has been designated the "nitrogen factor," and this is approximately a constant, and equal to about 2·4 for all cases of normal gastric juice. It is higher than that of gluten which has been digested for about one hour with pepsin in $N/20$-hydrochloric acid and pepsin of the same strength as that normally found in gastric juice, but is about equal to that

of a digest of an Ewald test-meal produced under similar conditions. The results indicate that the hydrochloric acid is not excreted in the form of an organic precursor. In cases of pyloric obstruction the "nitrogen factor" rises to 2·8 and more, and these high numbers are practically diagnostic for this condition. In cases of carcinoma of the body of the stomach, free mineral acid is absent, and pepsin is almost always absent, the analyses indicating almost complete achylia. In ulcers of the body of the stomach, the analyses vary, but complete achylia, such as is found in cases of carcinoma, is infrequent. Sometimes the analyses in this condition are not far removed from normal. In cancer of the pylorus, as opposed to cancer of the body of the stomach, the analyses are generally nearly normal; it is only when this condition is accompanied by distension and obstruction that the analytical numbers are sub-normal. The composition of the juice appears therefore to be affected rather by the site than the character of the lesion. Analytical numbers higher than normal are characteristic of pyloric and duodenal ulcers. Attention is called to the value of pepsin estimations, and to certain low values of the pepsin, when the hydrochloric acid secreted is normal or even high. For the purpose of pepsin estimation, the Fuld-Levison edestin method was employed. S. B. S.

The Entrance of Iodine into Diseased Tissues. H. GIDEON WELLS and O. F. HEDENBURG (*Proc. Amer. Soc. Biol. Chem.*, 1912–13, xxxvi—xxxvii; *J. Biol. Chem.*, **14**).—Necrotic tissues, whether caused by tuberculosis or not, are more permeable to iodine, and therefore contain more than healthy tissues when iodine is given. W. D. H.

Pharmacological Investigations of Ammonium Chloride. RODOLFO MENEGUZZI (*Chem. Zentr.*, 1913, i, 1046; from *Arch. Farmacol. sperim.*, 1912, **14**, 411—420).—The injection of ammonium chloride into the veins of a rabbit caused a retardation in the pulse-beats and an increase in the blood pressure, whilst the breathing was quickened at first, but suddenly ceased. A $1/40N$-solution had a toxic action on the fresh gastrocnemius of a frog, but weaker solutions were without effect. J. C. W.

Behaviour of Mercury [in the Organism]. ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1913, **84**, 67—68).—Polemical. Compare Buchtala (this vol., i, 318). E. F. A.

The Injection of Salts of Radium. HENRI DOMINICI, (Mme.) SIMONE LABORDE, and ALBERT LABORDE (*Compt. rend.*, 1913, **156**, 1107—1109).—A study of the intravenous and intramuscular injection of soluble and insoluble salts of radium, which shows that they persist for a long time in the organism. In the case of the insoluble salts injected into the muscles the greater portion of the radium remains at the point of injection, whereas with the soluble salts it is diffused throughout the organism. The bony tissue retains an appreciable quantity of the radium injected as radium bromide, thus bringing radium into line with calcium and strontium in this respect. W. G.

Thorium-*X* in Biology and Pathology. J. PLESCH, LÁSZLÓ KARCZAG, and BRUNO KEETMAN (*Chem. Zentr.*, 1913, i, 318 , from *Zeitsch. exper. Path. Ther.*, 1912, **12**, 1—84).—The behaviour and distribution of thorium-*X* in the animal organism are described. The measurements were made by estimating the α- or γ-radiation. About 80% is retained in the body, roughly two-thirds being stored in the bones, and most of the remainder in the liver. The toxicity varies considerably for different animals, and a lethal dose for a man is calculated at 10,000 electrostatic units, whilst a therapeutic dose should not exceed 1000 units. The symptoms accompanying the administration of thorium-*X* vary. The respiration of healthy subjects is not affected, but in cases of cardiac weakness or pneumonia the blood pressure is reduced. The preparation has a clinical application in metabolism, circulation and blood troubles, and in infectious diseases. J. C. W.

Action of Thorium-*X* on the Circulation. THEODOR A. MAASS and J. PLESCH (*Chem. Zentr.*, 1913, i, 318; from *Zeitsch. exper. Path. Ther.*, 1912, **12**, 85—94).—Experiments on the isolated heart of a frog show that, like radium emanation, thorium-*X* increases the diastolic relaxation of the heart. J. C. W.

Experimental and Histological Investigation of the Action of Thorium-*X* on the Animal Organism. A. PAPPENHEIM and J. PLESCH (*Chem. Zentr.*, 1913, i, 318 ; from *Zeitsch. exper. Path. Ther.*, 1912, **12**, 95—107).—The results of the action of thorium-*X* on the animal organism are to be referred to dilation of the blood vessels accompanied by bleeding and poisoning of the cells. Thorium-*X* is also a poison to the leucocytes of the marrow of the bones and to the kidney and liver epithelia. J. C. W.

Pharmacological Differences between *cis*- and *trans*-Isomerides. HEINRICH DRESER (*Verh. Ges. deut. Naturforsch. Aerzte*, 1913, 122—123).—The following figures give before the / the lethal dose, and after the / the dose which is no longer lethal, in the case of frogs (F) and white mice (M). The doses were injected under the skin, and are given in percentage-weights of the animal used. Atropic acid, F, 0·45/0·40; M, 0·0054/0·0022. Ordinary cinnamic acid, F, 0·30/0·25; M, 0·19/0·166. *allo*Cinnamic acid, F, 0·46/0·42; M, 0·2/0·175. *trans-o*-Coumaric acid, F, 0·45/0·40; M, 0·30/0·278. *cis*Coumarinic acid, F, 0·084/0·0745; M, 0·01/0·0051. *trans-o*-Methoxycinnamic acid, F, 0·20/0·15; M, 0·07/0·04. *cis-o*-Methoxycinnamic acid, F, 0·7/0·5; M, 0·15/0·111.

The lethal doses are smaller for warm-blooded than for cold-blooded animals (compare atropic acid). The *cis*-isomeride is less poisonous than the *trans*-isomeride; the exception shown by coumaric and coumarinic acids is due to the fact that the latter gives the very poisonous coumarin in the organism. The introduction of phenolic hydroxyl into the ortho-position in *trans*-cinnamic acid decreases, whereas the methoxy-group increases, the toxicity.

The results show that no assumptions as to the pharmacological action of a substance can be based on chemical isomerism.

T. S. P.

Pyruvic Acid Glycosuria. II. The Question of Sugar Formation from Pyruvic Acid. PAUL MAYER (*Biochem. Zeitsch.*, 1913, **49**, 486—501).—If pyruvic acid in suitable doses is administered to rabbits and dogs with total phloridzin diabetes, it causes an injury to the kidneys, which are rendered less permeable to nitrogenous substances and sugar. The administration in these cases results therefore in a diminution of both sugar and nitrogen in the urine. Even in cases where no injury to the kidneys could be ascertained, the administration of pyruvic acid led to no extra output of sugar. The experiments with animals with phloridzin diabetes offer, therefore, no solution of the problem as to whether pyruvic acid can be regarded as a sugar former in the body.

S. B. S.

The Action of Methyl Alcohol on the Circulating Blood. SOICHIRO MIURA (*Biochem. Zeitsch.*, 1913, **49**, 144—151).—In two only out of five experiments (on four rabbits and one dog) did injection of methyl alcohol produce anæmia. There was observed a diminution of lymphocytes and an increase in the number of pseudo-eosinophile or neutrophile corpuscles and also hæmoglobinuria. The methyl alcohol appears to act toxically on the blood-forming apparatus.

S. B. S.

Caffeine Hyperglycæmia. THOR STENSTRÖM (*Biochem. Zeitsch.*, 1913, **49**, 225—231).—It has been assumed that caffeine preparations produce glycosuria by acting on the kidneys. If this is the case, then no hyperglycæmia should result. The author now shows, by experiments on rabbits, employing Bang's microchemical method of sugar estimation, that administration of caffeine derivatives leads to increase of sugar in the blood, which commences about an hour after administration, rises to a maximum and then falls. In two cases, after the maximum period there was a second very rapid rise and fall, which was accompanied by convulsions in the animals, which subsequently died. The conclusion is drawn that the glycosuria produced by caffeine preparations is not due to the action on the kidneys.

S. B. S.

The Behaviour of Dextrose-Resorcinol in the Animal Organism. LUCIANO PIGORINI (*Chem. Zentr.*, 1913, i, 319; from *Arch. Farmacol. sperim.*, 1912, **14**, 353—358).—The additive compound of dextrose and resorcinol (Fischer and Jennings, A., 1894, i, 397) is without harm to the frog or the guinea-pig, and is excreted unchanged, whereas resorcinol or mixtures of resorcinol and dextrose have a toxic action.

J. C. W.

The Destruction of α-Hydroxypropaldehyde and Methylglyoxal by Animal Organs. CARL NEUBERG (*Biochem. Zeitsch.*, 1913, **49**, 502—506).—It has been suggested that pyruvic

acid, as an intermediary product of sugar fermentation, can be formed by the Cannizzaro reaction from methylglyoxal. Equations are given showing that this substance can yield on hydrolysis (1) pyruvic acid and acetol, or (2) pyruvic acid and α-hydroxypropaldehyde, (3) pyruvic acid only. It was therefore of interest to investigate the behaviour of methylglyoxal and α-hydroxypropaldehyde when these substances are treated with various ferments from yeast or animal organs. Experiments show that with liver paste, both substances are destroyed, the former more rapidly than the latter. *p*-Nitrophenylhydrazine acetate was employed to detect their presence in the mixture, after the proteins had been precipitated by colloidal ferric hydroxide. More lactic acid was found in the incubation mixture than the organs alone would yield. The actual course of the reactions discussed has not, however, been yet entirely elucidated. S. B. S.

The Behaviour of Ferric Iodoparanucleate in the Organism. ERNST SALKOWSKI (*Biochem. Zeitsch.*, 1913, **49**, 152—164).—By the action of iodine on ferric paranucleate (triferrin), a product can be obtained which contains about 8% of organically combined iodine. It causes no toxic symptoms when administered to dogs and rabbits. On administration *per os*, the iodine, even in large doses, is completely absorbed into the system, whereas the iron is only partly absorbed. The iron content of the liver can be increased threefold after administration of iodotriferrin. No organically combined iodine could be detected in the body, after ingestion of the medicament, and the iodine appears to be excreted chiefly as alkali iodide, with a small quantity as an iodo-derivative of an aromatic acid. The iodine excretions last for three days after administration of the drug. S. B. S.

Enzyme Concerned with the Formation of Hydroxy-acids from Ketonic Aldehydes. HENRY D. DAKIN and HAROLD W. DUDLEY (*J. Biol. Chem.*, 1913, **14**, 155—157).—Phenylglyoxal administered to rabbits in doses of 1—1·5 grams per kilo. leads to the excretion of about half a gram of optically active *l*-mandelic acid and about 0·75 gram of hippuric acid. No phenylglyoxylic acid was detected. Aqueous extracts of various animal tissues contain an enzyme capable of converting phenylglyoxal into mandelic acid, the action of which is readily inhibited by heat.

By analogy, methylglyoxal should be converted into lactic acid, and an enzyme extract prepared from dog's liver is shown to effect this change.

Phenylglyoxal readily combines with histidine, arginine, ornithine, and lysine to give sparingly soluble yellow substances. E. F. A.

The Influence of Phloridzin on Dogs with Eck's Fistula. JOSHUA E. SWEET and A. I. RINGER (*J. Biol. Chem.*, 1913, **14**, 135—138). —Phloridzin produces glycosuria in dogs with Eck's fistula exactly as in normal dogs. The power of gluconeogenesis is not lessened. W. D. H.

The Influence of Phloridzin on a Splenectomised Dog. JOSHUA H. AUSTIN and A. I. RINGER (*J. Biol. Chem.*, 1913, **14**, 139—140). —In dogs minus a spleen the effect of phloridzin exactly resembled those produced in normal animals. W. D. H.

Lead Compounds in the Organism. ANTONIO RIVA (*Chem. Zentr.*, 1913, i, 1047—1048; from *Arch. Farmacol. sperim.*, 1912, **14**, 406—410).—The lead-poisoned liver of a dog was extracted by physiological salt solution, and the filtrate, containing the albumins, globulins, and nucleoproteins, was evaporated to dryness. Lead was only found in the globulin, apparently in combination, since it persisted after repeated dialysis. A globulin from horse serum showed a great affinity for lead. J. C. W.

The Action of Dyes in Conjunction with Poisons and Medicaments. JOSEF SELLEI (*Biochem. Zeitsch.*, 1913, **49**, 466—478). —The mixture of dyes with poisons increases in many cases the toxicity of the latter, even although the dye is by itself practically inert. The dyes chiefly used were vitalneugelb, chrysoidin, methyl-orange, etc., which were combined with, amongst other substances, mercuric chloride, gold chloride, platinum chloride, and other metallic chlorides. Sodium vanadate mixed with a certain quantity of eosin is very toxic, but an increase of eosin in the mixture above a definite limit appears to diminish the toxicity. Other combinations of dyes with metallic poisons are less toxic than the metallic poisons alone. The influence of methylene-blue on the toxicity of copper salts was investigated. The most toxic of these, namely, cupric chloride, loses its toxic power most readily on mixture with the dye, whereas potassium cupric tartrate, which is the least toxic, acts in the presence of methylene-blue most toxically. The mixtures of dyes with the copper salts produce convulsions in the animals (guinea pigs); they also act as strong irritants at the place of injection. The author discusses the theory of the action of dyes. S. B. S.

Influence of Poisons on the Isolated Heart of the Fish W. I. BERESIN (*Pflüger's Archiv*, 1913, **150**, 549—568).—The heart of the fish (hake) lends itself very well to physiological experimentation. Details are given of the method employed for isolating the heart, and the perfusion apparatus (a modification of Locke's) employed. If poisons are added to the perfusion fluid (Locke's fluid) their effects are readily observable. The poisons used were strophanthine, erythrophlein, caffeine, adrenaline, nicotine, pilocarpine, chloroform, ether, hydrocyanic acid, quinine, and veratrine. The effects are practically identical with those already known from work on the heart of the frog or the mammal; a few differences of detail were noted in one or two instances. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

The Phosphorus Compounds formed by Amylomyces Rouxii. R. GOUPIL (*Compt. rend.*, 1913, **156**, 959—962).—*Amylomyces Rouxii* contains combined phosphorus in three states, two organic and one inorganic. The organic compounds are normal constituents of the living tissue, and their formation corresponds with the period of active growth. Of these two compounds one only is soluble in, and extracted by, ether, and is of a lecithin-like nature, whilst the second, which can be extracted by sodium hydroxide and reprecipitation by acids, possesses all the properties of a nucleic acid, and appears to be built up from the lecithin compound. The inorganic phosphates result from the degradation of the organic phosphorus compounds as the plant grows old. W. G.

The Precipitation of Calcium Carbonate in the Sea by Marine Bacteria. G. HAROLD DREW (*J. Marine Biol. Assoc.*, 1913, **9**, 479—524).—The large, chalky, mud flats forming the Great Bahama Bank, and those near the Florida Keys, are now being precipitated by the action of *B. calcis* on the calcium salts dissolved in sea water. This or similar bacteria may have been an important factor in the formation of various chalk strata and oolitic rocks in addition to the part played by shells of foraminifera, etc. If this is correct, these strata must have been precipitated in shallow seas at tropical temperature. Bacterial denitrification is also far more rapid in tropical than in temperate waters; hence plankton and algæ growth is relatively scarce in the former. More extensive observations on the distribution of bacteria at different places and depths are, however, necessary. W. D. H.

Alcoholic Fermentation of Lactic Acid. PIERRE MAZÉ (*Compt. rend.*, 1913, **156**, 1101—1104).—A study of the fermentation of lactic acid by a bacillus, capable of fermenting sugars and polyatomic alcohols, and comparable in its physiological properties to the *B. ethacetosuccinicus* of Frankland and Frew (T., 1892, **61**, 254). An examination of the results points to two parallel fermentation processes taking place on the lactic acid:

$$(1)\ C_3H_6O_3 + O = CH_3{\cdot}CO_2H + H{\cdot}CO_2H.$$
$$(2)\ C_3H_6O_3 = C_2H_5{\cdot}OH + CO_2.$$

The ratio of acetic acid to formic acid in the product is, however, as 5 : 1, the alcohol formed in (2) undergoing further oxidation, and this is confirmed by the value of the respiratory quotient. No pyruvic acid could be detected in any of the cultures at any stage. W. G.

An Acid-producing Enzyme in Bacterium lactis acidi. E. G. HASTINGS and EDWIN B. HART (*Proc. Amer. Soc. Biol. Chem.*, 1912–13, xxxviii—xxxix; *J. Biol. Chem.*, **14**).—The enzyme in question acts on lactose, and the acid produced is probably lactic. W. D. H.

Employment of Lactic Acid and Lactic Acid Bacteria in the Pickling of Cucumbers. ALEXANDER KOSSOWICZ [with L. VON GRÖLLER] (*Chem. Zentr.*, 1913, i, 640; from *Zeitsch. Gärungsphysiol. Mykologie*, 1912, **2**, 78–80).—The presence of small quantities of lactic acid in cucumber sap or asparagine-sugar solutions prevents the development of bacteria of the *Mesentericus* group. J. C. W.

A New Thermophilic Bacterium. ADOLF AMBROŽ (*Centr. Bakt. Par.*, 1913, ii, **37**, 3—16).—A sporogenous, facultative anaerobic organism, *Denitrobacterium thermophilum*, was obtained from soil and found to have the capacity of growing vigorously at 60—70°, and of decomposing nitrates with the liberation of free nitrogen. Analysis of cultures in nutrient bouillon, containing 0·5% potassium nitrate, showed that about 25% of the total nitrogen was lost during an incubation period of fourteen days at 60—65°. The gases were found to consist of nitrogen and oxides of nitrogen, the former being partly derived from the organic nitrogen compounds in the bouillon. H. B. H.

The Mechanism of Alcoholic Fermentation. ALEXANDER VON LEBEDEV (*Ber.*, 1913, **46**, 850—851).—Polemical. A reply to Kostytschev (this vol., i, 323), stating that there is nothing essentially new in the latter's views. D. F. T.

The Rate of Fermentation by Growing Yeast Cells. ARTHUR SLATOR (*Biochem. J.*, 1913, **7**, 197—203).—Various methods for estimating the rate of growth and fermentation are given, some of which are possible when the organism is growing on a solid medium. The rate of growth developing in wort-gelatin follows the logarithmic law. W. D. H.

Chemical Composition and Formation of Enzymes. VIII. Simultaneous Variation in Amount of Invertase and Fermenting Enzyme in Living Yeast. HANS VON EULER and DAVID JOHANSSON (*Zeitsch. physiol. Chem.*, 1913, **84**, 97—108. Compare A., 1912, ii, 376, 970).—As the result of the previous treatment of the yeast in solutions containing mineral salts and sucrose or invert sugar there is an increase in the inverting power. This change cannot be regarded as an adaptation to environment, since the increase is the same whether the previous treatment is with sucrose or invert sugar. Neither is it due to a general increase in the vital activity of the cell, since the treatment materially lessens the fermentative activity. It is regarded as a special property due to causes as yet unknown. E. F. A.

The Enzymes of Washed Zymin and Dried Yeast (Lebedev). I. Carboxylase. ARTHUR HARDEN (*Bio.-Chem. J.*, 1913, **7**, 214—217). —If zymin and Lebedev's dried yeast are washed free from co-enzyme they are incapable of fermenting dextrose, but they readily decompose pyruvic acid into carbon dioxide and acetaldehyde, provided that the acidity of the solution is kept low.
W. D. H.

Action of Free Ammonia on Yeast. Comparison with Other Bases. THOMAS BOKORNY (*Chem. Zentr.*, 1913, i, 641—642; from *Allg. Brauer Hopfen Zeit.*, 1912, **52**, 2867—2869).—Seeds of cress, barley, wheat, hemp and vetch, and peas and scarlet runners were allowed to germinate in ammonia solutions from 0·1 to 0·01%. Only at the lower dilution did germination proceed, and even then, at a slower rate than in control experiments. Ammonia to the extent of 0·5% in a good culture solution prevented the growth of yeast, whilst potassium hydroxide in the same dilution had no effect. Yeast apparently combines with ammonia, for it was found that 12 grams of yeast with a dry weight of 3·6 grams contained 0·374 gram of the base. Hydroxylamine and phenylhydrazine hydrochlorides were poisonous to yeast in 0·1% solutions, whilst hydrazine hydrate in 0·002% and phenylhydrazine in 0·001% solutions entirely prevented any fungoid growth. J. C. W.

Microchemical Detection of Potassium in Yeast and Other Cells. THOMAS BOKORNY (*Chem. Zentr.*, 1913, i, 640—641; from *Allg. Brauer Hopfen Zeit.*, 1913, **52**, 113—114).—In order to make the potassium cobaltinitrite precipitate more visible it is blackened by means of ammonium sulphide. It is possible to detect one part of potassium in 5000 at 8° by this method. Potassium could only be found in the cell sap of yeast, but the conclusion is not to be drawn that it is not present in the protoplasm or nucleus in the form of a potassium protein compound. Potassium is necessary for the development of yeast. J. C. W.

Action of Certain Metallic Salts on the Development of Yeast and the Germination of Barley. THOMAS BOKORNY (*Chem. Zentr.*, 1913, i, 641; from *Allg. Brauer Hopfen Zeit.*, 1912, **52**, 1905—1906).—The reproduction of yeast was not influenced by the presence of even 4% of potassium dihydrogen phosphate in the culture solution, neither did the ash contain more phosphorus. Cæsium sulphate was found to be harmful to barley seedlings, even in the dilution of 0·05%, but 0·01% of that salt or 0·2% of rubidium sulphate proved to be beneficial, whilst potassium chloride in 0·05% solution did not accelerate germination, and in strong solutions was injurious. J. C. W.

Action of Uranium, Molybdenum, and Vanadium Salts on Yeast and Other Micro-organisms. THOMAS BOKORNY (*Chem Zentr.*, 1913, i, 641; from *Allg. Brauer Hopfen Zeit.*, 1912, **52**, 709—710. Compare A., 1912, ii, 1201).—During fermentations in presence of ammonium molybdate, the liquid acquired a blue colour, due to the action of that salt on hydrolysis products of sucrose, particularly on lævulose. J. C. W.

Influence of Different Substances on the Germination of Vegetable Seeds. I, II, and III. THOMAS BOKORNY (*Biochem. Zeitsch.*, 1913, **50**, 1—48, 49—86, 87—118).—Potassium chloride is somewhat injurious to plants in 0·25% solutions, whilst the nitrate

is very injurious in 1% solutions, and may retard growth even in 0·1% solutions. Calcium nitrate (1%) is only slightly injurious, and sodium nitrate somewhat more so; 0·1% solutions of both salts are without injurious effects. Even 0·1% solutions of ammonium nitrate retard germination. Whilst rubidium sulphate is only slightly injurious in 0·5% solutions, cæsium and lithium sulphates are injurious in 0·1 and 0·05% solutions respectively.

Germination is quickened by cæsium, lithium, and rubidium sulphates in 0·01, 0·05, and 0·2% solutions respectively. The germination of barley was promoted by 0·005% of carbon disulphide; beans and lentils by 0·01% potassium chromate; cress by 0·0005% mercuric chloride; barley and cress by 0·0025% and 0·005% copper sulphate respectively; cress by 0·005% of phenylhydrazine; barley and cress by 0·0025% of aniline; barley by 0·01% of hydroxylamine; and peas, lentils, and barley by 0·001% of hydrofluoric acid.

It would seem that most poisons stimulate growth when diluted to certain points. Since a slight increase in concentration causes injury and a slightly increased dilution renders the substances inactive, it is doubtful whether this property of poisons can have any practical importance. N. H. J. M.

Action of Manganese Dioxide and of Other Metallic Compounds on the Germination of Seeds. Ugo Varvaro (*Chem. Zentr.*, 1913, i, 546—547; from *Staz. sperim. agrar. ital.*, 1912, **45**, 917—929).—The oxides of manganese, iron, uranium, cerium, copper, zinc, aluminium, cadmium, and mercury hinder the germination of beans, and are poisonous, even in small doses, to horse beans. The oxides of zinc, lead, copper, cadmium, aluminium, and uranium are stimulants to maize. J. C. W.

Formation of Pentosans in the Germination of Seeds. Luigi Bernardini and F. Galluccio (*Chem. Zentr.*, 1913, i, 179; from *Staz. sperim. agrar., ital.*, 1912, **45**, 874—884).—The pentosans developed by seeds germinating in the dark and in the light have been estimated by Tollens's and Krüger's phloroglucinol method, and the cellulose by König's glycerol-sulphuric acid method. The results show that the production of pentosans is slow in the dark, but rapid in the light, whilst the cellulose content rises at first in the dark, only to fall off rapidly as germination proceeds, but increases steadily in the light. J. C. W.

Respiration of Plants as Hydrolytic Oxidation. Vladimir I. Palladin (*Ber. deut. botan. Ges.*, 1913, **31**, 80—82).—Alkaline solutions of the respiration chromogens absorb atmospheric oxygen vigorously with production of brownish-red pigments. During alcoholic fermentation, hence in the first anaerobic stage of respiration, substances are formed which readily give up their hydrogen to the respiration pigment, by which it is oxidised to water by means of atmospheric oxygen.

The respiration chromogens, like the leuco-compounds, give up

their hydrogen to the absorbed oxygen, producing a pigment and water. The oxygen absorbed during respiration is employed, therefore, as previously shown, in removing hydrogen from the plants.

The hydrogen liberated after the hydrolytic oxidation of dextrose, which in higher plants is oxidised to water and in yeast is eliminated as ethyl alcohol, is given up by anaerobic bacteria to the surrounding gaseous medium. N. H. J. M.

Causes of Growth of Plants. G. A. BOROVIKOV (*Biochem. Zeitsch.*, 1913, **50**, 119—128. Compare this vol., i, 324).—Salts which are readily hydrolysed are favourable to growth owing to the presence of acids, and consequently of hydrogen ions. The weaker the base the more easily is it hydrolysed, and the stronger the action of the salt. In solutions of salts of strong organic bases, growth is not quickened because hydrolysis is less, and because such bases have a greater retarding effect than weak bases, such as caffeine, carbamide, and glycine. The quickening or retarding of growth seems to be due to unequal degrees of hydration of the plasma colloids. The conditions which are favourable to the *ionisation* of the protein also bring about greater hydration of the plasma colloids. Acids are favourable to plants, whilst metals and bases diminish the protein ionisation by neutralising the protein. N. H. J. M.

Formaldehyde and Plant Syntheses. HERMANN DECKER (*Annalen*, 1913, **396**, 336).—The hypothesis of the action of formaldehyde as a methylating agent in the formation of plant substances, advanced by Decker and Becker (this vol., i, 291), was suggested by Pictet eight years ago. C. S.

Plants which Require Sodium. WINTHROP J. V. OSTERHOUT (*Bot. Gaz.*, 1912, **54**, 532—536).—Sodium was found to be as necessary for the marine plants employed as for animals, and its replacement in sea-water by ammonium, potassium, cæsium, lithium, magnesium, calcium, and strontium is injurious. The best substitutes are the elements which predominate in sea water, magnesium, calcium, and potassium.

The behaviour of various species indicates that each salt has a specific action. N. H. J. M.

Antagonistic Action of Chemical Substances on Fungi. Chemical Preservation. THOMAS BOKORNY (*Cent. Bakt. Par.*, 1913, ii, **37**, 168—267).—Numerous experiments are described on the action of various inorganic and organic substances on fungi, yeasts, etc. The results are summarised in tables. N. H. J. M.

Assimilation of Nitrites by Moulds. ALEXANDER KOSSOWICZ (*Chem. Zentr.*, 1913, i, 640; from *Zeitsch. Gärungsphysiol. Mykologie*, 1912, **2**, 55—58).—Ten moulds have been found to subsist with nitrites as their source of nitrogen, and since in only two cases could ammonia be detected, the conclusion is drawn that the

nitrite ion is assimilated directly, without reduction. In good culture media, moderate concentrations of nitrites are not poisonous to moulds. J. C. W.

Decomposition of Carbamide, Uric Acid, Hippuric Acid, and Glycine by Moulds. II. ALEXANDER KOSSOWICZ (*Chem. Zentr.*, 1913, i, 640; from *Zeitsch. Gärungsphysiol. Mykologie*, 1912, **2**, 51—55).—Several of the well-known moulds are able to make glycine or hippuric acid their sole source of nitrogen in presence of mannitol or dextrose, some of them producing ammonia. Certain moulds can depend on uric acid, hippuric acid, or glycine for their combined source of carbon and nitrogen. J. C. W.

Chemistry of the Higher Fungi. IX. Galls Produced by Exobasidium Vaccinii, Woron., on Rhododendron ferrugineum, L. JULIUS ZELLNER (*Monatsh.*, 1913, **34**, 311—319. Compare A., 1912, ii, 196).—The galls and the leaves on which they are found have been examined, and shown to contain the same constituents, the former containing a larger proportion of water-soluble substances, except tannin, and a smaller proportion of matter insoluble in water, than the leaves. On this and other grounds, it is suggested that the formation of galls on leaves is similar in character to the production and ripening of fruits.

The galls and the leaves were extracted in turn with light petroleum, ether, 95% alcohol and water, and the composition of these extracts was as follows: The galls yielded 1·71% to light petroleum; the product was a thick, semi-crystalline oil, having acid number 93·4, saponification number 165·1, and containing 12·5% of unsaponification matter, composed of (*a*) a *substance*, m. p. 129—130°, $[\alpha]_D^{18} - 29·4°$, crystallising in colourless needles, and (*b*) a *substance*, m. p. above 280° (decomp.), much less soluble than the foregoing; both these products are phytosterols. The fatty acids of the oil are semi-solid. The leaves yielded 9·2% to light petroleum; the extract had acid number 60, saponification number 150, and contained the same two phytosterols as the gall extract, and also much resin and terpenes.

The ether extract of the galls amounted to 2·68%, and consisted of tannin and resin. The leaves yielded 8·34% to ether, and this extract also consisted of tannin and resin, the latter being somewhat different from that in the galls.

The alcohol extract of the galls amounted to 39·1%, and consisted of phlobaphen, dextrose, lævulose, tannin, and organic acids. The leaves yielded 32·6% to alcohol, and this extract consisted chiefly of tannin with some phlobaphen and a small amount of sugar.

The aqueous extract of the galls amounted to 13·32%; it contained some tannin, but was mostly gummy carbohydrate; no starch was present. The leaves gave only 1·7% of aqueous extract of similar composition to the foregoing, but containing some starch.

All the foregoing yields are expressed as percentages of the original material dried at 100°. T. A. H.

Chemistry of the Higher Fungi. X. JULIUS ZELLNER (*Monatsh.*, 1913, **34**, 321—336).—In this portion four fungi are dealt with, the method of investigation being the same as that described in the preceding abstract.

Armillaria mellea, Vahl.—The light petroleum extract was a semi-crystalline, thick, brown oil, having acid number 89·1, saponification number 179·6, iodine number 94·2, and containing notable amounts of lecithin and 4·5% of unsaponifiable matter, the latter consisting of a yellow resin and some ergosterol. The fatty acids were mostly liquid, but yielded when kept a mixture of crystalline acids, m. p. 62°, and acid number 210°. The ether extract contained some amorphous matter and ergosterol, m. p. 155°, $[\alpha]_D$ $-114·8°$ in chloroform, which gave an acetyl derivative, m. p. 169°. No cerebrin was found. The alcoholic extract deposited after a time mannitol, m. p. 169—170° (possibly contaminated with mycose), dextrose, choline ?, and matter precipitated by lead acetate.

Lactarius piperatus, L. (compare Thörner, A., 1880, 44; Bissinger, A., 1884, 480; Chodat and Chuit, A., 1890, 80; Gérard, A., 1891, 606; and Bougault and Charaux, A., 1912, ii, 289).—The light petroleum extract amounted to 5·9%, and was a solid, yellow fat, having acid number 121·3 and saponification number 200·2. The unsaponifiable matter was separated into (1) a substance, m. p. 146—150°, probably a mixture of ergosterols; (2) a yellow resin; and (3) a sparingly soluble substance, m. p. 150° (approx. decomp.). This extract also contained lecithin. The fatty acids included some liquid acids, but the principal constituent was stearic acid, which was isolated in quantity (*loc. cit.*). The ether extract amounted to 1·2%, and consisted of yellow resin. The alcoholic extract contained mannitol (possibly contaminated with inositol), dextrose, and choline (compare Bourquelot, A., 1890, 103).

Pholiota squarrosa, Müll.—The light petroleum extract (3·8%) was a semi-solid, yellowish-brown fat, having acid number 51·8, saponification number 168·3, containing lecithin and 12·9% of unsaponifiable matter. From the latter a resin and a mixture of ergosterols, m. p. 159 (approx.), crystallising in colourless leaflets, were isolated. The ether extract resembled the foregoing in composition. The alcoholic extract contained mannitol, mycose, dextrose, choline, phlobaphen, and indefinite amorphous matter soluble in alcohol, but not in water.

Polyporus betulinus.—The light petroleum extract amounted to 3·5%, and had acid number 96·3, saponification number 155·0, iodine number 98·6, and contained 17·8% of unsaponifiable matter composed of a mixture of ergosterols, m. p. 139—144°, $[\alpha]_D$ $-97·6°$, crystallising in needles or leaflets, cerebrin, resin, and gum. The ether extract was resinous, and contained a *substance*, $C_{31}H_{50}O_5$, m. p. 250° (approx. decomp.), which is probably an alcohol and is named *polyporol*. The alcoholic extract contained phlobaphen, mannitol, dextrose, traces of choline, and indefinite substances precipitated by lead acetate and other salts. The aqueous extract contained potassium phosphate and a carbohydrate, giving a pale

greyish-blue coloration with iodine, and readily hydrolysed by dilute hydrochloric acid. Winterstein's para*iso*dextran (A., 1895, i, 323) could not be obtained. T. A. H.

Extraction of the Colouring Matter from the Cherry and Investigations of its Properties. GIULIO MASONI (*Chem. Zentr.*, 1913, i, 546; from *Staz. sperim. agrar. ital.*, 1912, **45**, 885—907).—The pigment may be extracted from fresh or dried cherries by means of water or alcohol with the help of a little tartaric or hydrochloric acid. The aqueous extract may be cleared by gelatin, and is violet-red and not very stable, whereas the alcoholic extract is clear, pure red in colour, and remains unaffected by heat or light. The dye may be applied to wool or food-stuffs. Its presence in wine may be detected, after clearing the liquid with lead acetate, by the addition of alum, when a violet coloration is produced, pure wines remaining colourless. J. C. W.

Chemical Examination of Euphorbia pilulifera. FREDERICK B. POWER and HENRY BROWNING, jun. (*Pharm. J.*, 1913, [iv], **36**, 506—510).—A complete chemical examination of the entire plant, collected in Fiji, has been made. None of the definite constituents isolated has any specific physiological action, so that such therapeutical value as the plant possesses cannot depend on any single definite substance. An alcoholic extract of the plant was steam-distilled, and yielded (1) a volatile oil, b. p. 235—260°, giving the colour reaction of furfuraldehyde; (2) a portion soluble in water; (3) a resinous portion, insoluble in water; the two latter portions of the extract were then examined by methods which are described in detail, and gave the following products:

Portion Soluble in Water.—This yielded gallic acid, quercetin, a small amount of jambulol (see also below), and a phenolic *substance*, $C_{28}H_{18}O_5$, which crystallised in microscopic clusters of needles, and decomposed, but did not melt, at 340°. There was also present a lævorotatory sugar, which yielded *d*-phenylglucosazone, some amorphous glucosidic matter, traces of an alkaloidal substance, together with indefinite oily and extractive matters.

Portion Insoluble in Water.—This yielded melissic acid, ceryl alcohol, triacontane, a *phytosterol*, m. p. 132—133°, crystallising in flattened needles, and giving an *acetyl* derivative, m. p. 122—123°; a *phytosterolin*, $C_{33}H_{56}O_6$(?), m. p. 297° (decomp.), crystallising in colourless needles, and yielding an *acetyl* derivative, m. p. 161—162°, crystallising in flattened needles; jambulol (T., 1911, **99**, 962, and A., 1912, ii, 480), and a mixture of palmitic, oleic, and linoleic acids. In addition, a monohydric alcohol, *euphosterol*, $C_{25}H_{39}\cdot OH$, m. p. 274—275°, was obtained. This crystallises from petroleum in needles, gives the colour reaction characteristic of this class of substances (T., 1909, **95**, 739; 1912, **101**, 2425), and is optically inactive. It yields an *acetyl* derivative, m. p. 295—297°, $[\alpha]_D$ +8·2° in chloroform, and this on bromination in cold chloroform gives *bromoacetyleuphosterol*, m. p. 183—186°, crystallising in small needles from a mixture of alcohol and ethyl acetate.

Euphosterol is probably accompanied by other alcohols of the same series, since in recrystallising the acetyl derivative two other fractions, m. p. 205—210° and m. p. 230—260°, were obtained.
T. A. H.

Causes of the Natural Changes in the Latex of Hevea Brasiliensis. G. STAFFORD WHITBY (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 147—157).—Experiments are described which have been made in order to ascertain the nature of the changes which are involved in the coagulation of the latex of *Hevea Brasiliensis* when this is left in contact with the air. The observations indicate that coagulation is brought about by an enzyme (probably a protease). Anærobic decomposition occurs in those portions which are out of contact with the air, and evidence has also been obtained which indicates the presence of an oxydase, to which the name, *hevease*, is applied.

A fourth factor in the coagulation process consists in ærobic decomposition, which occurs in the later stages, and gives rise to an alkaline mucus which causes the latex to become milky. The relative importance of these four independent processes depends very largely on the conditions under which coagulation of the latex occurs.
H. M. D.

Herbage Studies. II. Variation in Lotus Corniculatus and Trifolium repens (Cyanophoric Plants). HENRY E. ARMSTRONG, E. FRANKLAND ARMSTRONG, and EDWARD HORTON (*Proc. Roy Soc.*, 1913, *B*, **86**, 262—269).—It is established that in addition to the common widely distributed cyanophoric form of *Lotus corniculatus*, a botanically indistinguishable form exists, in which the power of producing the cyanophoric glucoside is all but suppressed. *Lotus major* is uniformly cyanophoric. The normal form of *L. corniculatus* contains both glucoside and the correlated enzyme, a second form is rich in enzyme, but contains mere traces of the glucoside, whilst in the third form the amount of both glucoside and enzyme is very small.

The conclusion is drawn that the above differences are due to the presence or absence of definite factors rather than the consequence of the operation of special conditions of environment.

Whereas cultivated white clover (*Trifolium repens*) is without cyanide, wild white clover always contains a cyanophoric glucoside.

The determination of the enzymic activity of a number of specimens of *Trifolium repens* showed that all were moderately active towards salicin, but that the cultivated variety alone was practically without action on linamarin and prunasin.

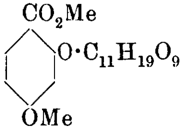
The bearing of the chemical peculiarities of the two types of clover on their value as food materials is discussed. E. F. A.

Chemistry of Peat Moss (Sphagna). JOSEF IBELE (*Ber. deut. bot. Ges.*, 1913, **31**, 74—77).—When *Sphagnum papillisum* is oxidised with hydrogen peroxide a substance soluble in sodium hydroxide

solution is obtained, which becomes insoluble when precipitated with acid and dried. Formic acid and ammonia are also formed.

Sphagnum dissolves almost completely in hydrochloric acid containing antimony trichloride. Ammonia is liberated, but no methylamine could be detected. N. H. J. M.

Glucosides and Oils of the Primrose. A. GORIS, M. MASCRÉ, and CH. VISCHNIAC (*Chem. Zentr.*, 1913, i, 310—311; from *Bull. Sci. Pharmacol.*, 1912, **19**, 577—598, 648—670; *Wiss. ind. Ber. Roure-Bertrand fils*, 1912, **6**, 3—73. Compare A., 1910, ii, 63).—The crude glucosides which form about one part per thousand of the roots of *Primula officinalis* may be separated by fractionation from a mixture of ethyl acetate and alcohol. Primverin (I), $C_{20}H_{28}O_{13}$, m. p. 206° (corr.), $[\alpha]_D$ $-71°53'$, yields on hydrolysis with dilute acids, *methyl β-methoxyresorcylate*, $C_9H_{10}O_4$, m. p. 49°, which develops a violet-red colour with ferric chloride, and two molecular proportions of monoses. The enzyme primverase, however, produces the biose, *primverose*, $C_{11}H_{20}O_{10}$, m. p. 209—210°, which exhibits multirotation; $[\alpha]_D$ $+23°1'$, $-2°3'$ after twenty-four hours (1·846 grams in 75 c.c. H_2O), $+23°11'$, $-3°17'$ after twenty-four hours (1·35 grams in 26 c.c. of water). It reduces Fehling's solution (0·0673 gram = 77 mg. Cu), forms an *osazone* in light yellow needles, m. p. 204—207°, and contains a pentose, apparently in combination with a hexose.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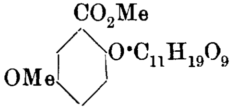
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Primulaverin, $C_{20}H_{28}O_{13},2H_2O$, m. p. 163° (corr.), $[\alpha]_D$ $-66°65'$, yields on hydrolysis the same sugars and *methyl* m-*methoxysalicylate*, mixed with methyl β-methoxyresorcylate. It has not yet been obtained pure, but the true primulaverin would have the formula II.

The ethereal oils of the primrose root contain the above esters, whilst the oil from the flowers contains, in addition, over 10% of an unhydrolysable substance. J. C. W.

Willow Bark. I. GEORGEI GEORGEVITSCH POVARNIN and A. BARABANOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 267—271).—The authors have examined the barks of a number of willows, including hybrids, with the object of classifying them according to their chemical reactions. Tannides of two distinct types occur in the barks (see following abstract). T. H. P.

Willow Bark. II. GEORGEI G. POVARNIN and N. SHURAVLEV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 271—283. Compare preceding abstract).—The bark of the hybrid willow, *Salix alba* × *S. viminalis*, contains, in addition to phlobaphens, two tannides which are char-

acterised by their reactions with ferric chloride and with ammoniacal copper sulphate. The tannide of *S. alba* is a tannoside, and may be separated from that of *S. viminalis*, which contains free sugar, by its different solubility in a mixture of methyl alcohol and ether. The former gives anhydro- and oxy-phlobaphens, and it contains protocatechuic acid, whilst the tannide of *S. viminalis* contains pyrogallol, but the principal decomposition products are phlobaphen and sugar. T. H. P.

Manuring of Cultivated Plants by means of Carbon Dioxide. ADOLPH HANSEN (*Chem. Zentr.*, 1912, ii, 2135; from *Naturw. Rundsch.*, 1912, **27**, 547—550).—It was noticed that the vegetation in the neighbourhood of a natural carbonic acid spring was particularly fine, and the administration of carbon dioxide to cultivated plants is found to increase the dry weight considerably. It is suggested that the gas is loosely combined with the chlorophyll in the same way as oxygen is united to the pigment of the blood.
J. C. W.

Importance of the Potassium in Felspar for Plants. EDWIN BLANCK (*J. Landw.*, 1913, **61**, 1—10. Compare *ibid.*, 1912, **60**, 97).—Pot experiments in which oats were manured with various potassium minerals. Previous results, indicating that the tubes are more suitable as sources of potassium for plants, are confirmed.

Plagioclase gave much better results than microlin and orthoclase, which were almost without effect. N. H. J. M.

History of Maize Sugar. PH. DE VILMORIN and FERDINAND LEVALLOIS (*Bull. Soc. chim.*, 1913, [iv], **13**, 294—304).—The authors give an extensive review of the efforts which have been made to extract a crystallisable sugar from maize on the industrial scale, special reference being made to the work of Pallas and to the recent investigations of Stewart and of Heckel (*Compt. rend.*, 1912, **155**, 686).

A series of experiments have been made on maize from Verrières and from Antibes, the conditions, however, being rather unfavourable. In these circumstances, the juice from maize from which the ears had been removed during growth was found to contain 10% of sucrose, whilst a greater proportion could be extracted from sugar maize. From the industrial point of view, the extreme rapidity, both of formation and of decomposition of sugar in maize, constitutes a serious difficulty, which, however, could possibly be obviated to some extent by the systematic employment of different varieties of maize. H. W.

Respiration and Metabolism in Ruminants. NATHAN ZUNTZ, RICHARD VON DER HEIDE, KLEIN, I. VON MARKOFF, FÜRST VON DSCHANDIERI, and DJADKOW (*Landw. Versuchs-Stat.*, 1913; **79-80**, 781—814).—The utilisation of foods by cattle varies according to the mechanical condition of the mixture, and the same food will give different results when given in conjunction with other foods. An experiment is described in which potatoes were compared with

the corresponding amount of potato slump to which starch was added to replace that which had been lost; whilst malt and yeast were added to the potatoes. Although the two foods had practically the same composition, the results with starch were essentially different from those with potatoes. When starch is given in conjunction with hay, the crude fibre, protein, and fat are digested in diminished amounts. In the case of the non-nitrogenous extract the amount in the fæces was diminished by the starch. This does not, however, indicate better resorption, as there is no doubt that the extractive substances were lost by fermentation. The comparison of food and fæces is misleading in the case of ruminants.

It is desirable in feeding experiments to estimate the amount of oxygen utilised as well as the amounts of respired nitrogen and carbon dioxide. A method for estimating the oxygen is described.

The various estimations in respiration experiments should be made at short intervals.

Methods for investigating the fermentation processes of the rumen are discussed. N. H. J. M.

Employment of Dialysis in the Estimation of the Oxidising Power of Soils. JOSEF KÖNIG, JULIUS HASENBÄUMER, and K. GLENK (*Landw. Versuchs-Stat*, 1913, **79–80**, 491—539).—Several soils were subjected to dialysis, and the amounts of organic matter, calcium, magnesium, potassium, phosphoric acid, and sulphuric acid in the solutions estimated. It was found that soils which were heated at 150° yielded considerably more soluble matter than soils which had not been heated; similar results, but less marked, were obtained with soils dried, under reduced pressure, at 95—98°. Clearer indications of the changes which soils undergo when heated, and even when air-dried, were obtained by estimating the electrolytic conductivity. The results indicate that in the ordinary drying of soils the colloidal state is in part destroyed.

The amounts of carbon dioxide produced in six different soils, and in the same soils with small amounts of dextrose and urea respectively, were estimated daily for three weeks; and at the end of the experiment the amounts of ammonia and nitrates and the numbers of bacteria were estimated (compare Hutchinson and Marr, A., 1911, ii, 430). As regards nitrification, the urea was almost completely nitrified in the loamy soil, whilst the clay soil showed very slight nitrification. Addition of dextrose considerably increased the number of bacteria in all the soils. Electrolytic conductivity was increased by urea and diminished by dextrose.

The results of pot experiments with oats showed that heating the soil at 95—98° in a vacuum increased both the total growth and the mineral constituents. Addition of dextrose and gum arabic to loamy sand and loam diminished the yield of grain and straw.

N. H. J. M.

Colloidal Substances in Soil Solutions. Production of Soda in Soils. Alkali and Salt Soils. K. K. GEDROIZ (*Bied. Zentr.*, 1913, **42**, 76—79; from *J. exper. Landw.*, 1912, **13**, 421).—The amount of colloids in soil extracts (except alkali soil extracts)

was found to vary from 0·0018 to 0·0200%, and in Russian arable soils from 0·0058 to 0·0147%. The dry matter dissolved by water amounted to 0·0385 to 0·0591%. The coagulation of such small amounts of colloidal substances can have very little effect on the physical properties of the soils; and the changes brought about by frost, electrolytes, and liming, etc., are attributed to their influence on substances mechanically suspended in the soils, especially the gels.

In the case of alkali soils the total colloids, mineral and organic, varied from 0·0990 to 0·4494%; in such soils coagulation of the colloids may influence the physical properties of the soil.

In typical alkali soils, nearly free from chlorides and sulphates, the amount of soda in successive extracts decreases much more slowly than would be the case if only pre-existing soda were dissolved. In alkali soils containing much sodium chloride, but little sulphate, alkalinity begins only after some of the chloride is washed out.

A loamy, black soil, treated with sodium chloride and calcium carbonate, failed to yield appreciable amounts of soda, and only small amounts were produced by treatment with sodium sulphate and calcium carbonate. Under the combined influence of sodium chloride and sulphate, alkaline, dark-coloured solutions were obtained after the removal of most of the chloride and sulphate; in presence of calcium carbonate the soil yielded soda. The conclusion is drawn that the soda is produced from zeolites. The production of soda is hindered by excessive amounts of sodium chloride and sulphate. N. H. J. M.

The Fertilising Action of Sulphur. A. DEMOLON (*Compt. rend.*, 1913, **156**, 725—728).—Further experiments with sulphur (compare A., 1912, ii, 382) show that it can act as a useful addition to farmyard manure as a fertiliser, but that its action diminishes and vanishes in the presence of a large amount of organic and mineral fertilisers. Potatoes benefit most by the addition of sulphur. On light lands it has an injurious effect on cereals. Addition of sulphur in amount equal to the nitrogen supplied has given the same results as a complete mineral fertiliser. The fertilising action of the sulphur is due (*a*) to its action on the soil bacteria, (*b*) to its progressive transformation into sulphuric acid. W. G.

[Manurial] Action of Different Forms of Nitrogen. W. SCHNEIDEWIND (*Bied. Zentr.*, 1913, **42**, 101—110; from *Arb. deut. Landw.-ges.*, Heft. 217).—Pot and field experiments on the action of sodium and calcium nitrates, calcium nitrite, ammonium salts, calcium cyanamide, and urine. On the whole the best results were obtained with sodium and calcium nitrates. Ammonium salts were not regular in their action; in one case, both on dry and wet soils, ammonium salts gave better results than nitrate. Both with oats and potatoes, nitrates and ammonium salts gave the same results. Calcium cyanamide acted most favourably when applied in the autumn for winter cereals. Urine was unsatisfactory both on light and loamy soils. The effect of calcium nitrite was variable.

The application of large amounts of manure to light soils in the autumn is useless; ammonium salts and calcium cyanamide may, however, be applied to soils of better quality. N. H. J. M.

Influence of Ammonium Sulphate on the Phosphate Manuring of Oats. EILHARD A. MITSCHERLICH and W. SIMMERMACHER (*Landw. Versuchs-Stat.*, 1913, **79–80**, 71—96).—Addition of ammonium, sodium, and magnesium sulphates considerably increased the solubility of the phosphoric acid of di- and tri-calcium phosphates, whilst in presence of calcium phosphate the solubility is diminished.

The results of vegetation experiments, in which oats were manured with di- and tri-calcium phosphates, showed that the addition of small amounts of ammonium sulphate increased the amounts of phosphoric acid assimilated even in presence of considerable amounts of soluble salts which would be acting in the same direction.

In the case of superphosphate and basic slag, addition of ammonium sulphate was without effect on the assimilation of the phosphoric acid by oats. N. H. J. M.

Manuring with Sodium Salts. BERNHARD SCHULZE (*Landw. Versuchs-Stat.*, 1913, **79–80**, 431—448).—Sodium is utilised by plants, and may take the place of potassium to a certain extent. The sodium of sodium chloride is taken up by plants with great rapidity; and, as it is not absorbed by soils to the same extent as potassium, its manurial action lasts longer if not washed out of the soil.

Whilst potassium salts decompose sodium zeolites in the soil, sodium salts have a very slight action, if any at all, on potassium zeolites. N. H. J. M.

Lime Rich in Silica as Manure. HEINRICH IMMENDORFF (*Landw. Versuchs-Stat.*, 1913, **79–80**, 891—901).—Different soils were rubbed in a mortar with lime and water, and then put on to glass plates to dry in order to ascertain whether any hardening of the soil takes place owing to the presence of silica. The limes employed contained from 0·03 to 19·51% of soluble silica (Portland cement). The same soils were treated with water alone for comparison.

The results showed that no hardening of the soil takes place when lime containing large amounts of soluble silica are employed. Hydrated silica may itself have a favourable effect on the soil by increasing its absorptive power. N. H. J. M.

Organic Chemistry.

Composition of Mineral Oils of High Boiling Point. I. The Viscous Components of Mineral Oils of High Boiling Point. JULIUS MARCUSSON (*Chem. Zeit.*, 1913, **37**, 533—534).—Previous investigations (*ibid.*, 1911, **35**, 729) have shown that the more viscous portion of mineral oils (naphthenes, polynaphthenes, paraffins, and olefines) is that which does not react with formaldehyde and sulphuric acid, whilst the reacting portion (benzene derivatives, unsaturated naphthenes, and terpenes) is comparatively mobile. Paraffins have small viscosity, whilst that of naphthenes is greater than that of paraffins of the same molecular weight. The viscosity of mineral oils cannot therefore be attributed to the presence of paraffins. This is confirmed by the fact that the viscosity of lubricating oils can be raised by removal of solid paraffins and lowered by their addition. Olefines are present in too small amount to exert a distinct effect on the viscosity, so that the diminution in viscosity effected by treating oils with fuming nitric acid at $-10°$ must be attributed to the destruction of polynaphthenes. The viscosity must therefore be due to the presence of naphthenes and polynaphthenes. The former are mainly present in the portions distilling below 300°, so that in oils of high b. p. and high viscosity, the chief saturated hydrocarbons are polynaphthenes. This is confirmed by analysis of a heavy Russian machine oil, which, before purification, contained C = 85·79% and H = 12·78%, whilst after treatment with formaldehyde and sulphuric acid, the figures obtained were C = 85·41%, H = 13·07%, which correspond with the results to be expected from a mixture of condensed naphthenes. Further confirmation is found in the high molecular weight of machine oils, which ranges from 300 to 400 with a mean value of about 350, corresponding with compounds containing twenty-five atoms of carbon in the molecule.

Highly viscous oxygen compounds are present in nearly all machine oils, but, generally, in such small amount that their effect is inconsiderable.

The present communication deals only with machine oils. Cylinder oils are under investigation. H. W.

Composition of Mineral Oils of High Boiling Point. II. Components of Liquid Paraffin and their Behaviour towards Aluminium Chloride. JULIUS MARCUSSON and C. VIELITZ (*Chem. Zeit.*, 1913, **37**, 550—553).—The so-called liquid paraffin is generally regarded as a mixture of liquid hydrocarbons of the paraffin series. This view, however, appears improbable, since the substance is usually obtained from Russian oils which are comparatively poor in such hydrocarbons.

Two specimens of liquid paraffin were employed, having D_4^{20} 0·8827, 0·8858, n^{20} 1·4797, 1·4799, specific viscosity at 20°, 23·0, 29·9,

$[\alpha]_D$ +2·13, 2·35, respectively. The density and refractive index indicate that hydrocarbons of the paraffin series cannot be the main components of the mixture, whilst ultimate analysis points to the presence of polynaphthenes.

In order to decide whether the optical activity is attributable to *iso*paraffins or polynaphthenes, a specimen of liquid paraffin was fractionated under greatly reduced pressure. Density, viscosity, refractive index, and optical activity were found to increase with increasing b. p. of the fraction. Since the fraction, b. p. 255—277°/4 mm., was completely liquid and only yielded a trace of precipitate when cooled with alcohol–ether to −20°, it appears improbable that *iso*paraffins can be the cause of activity. This is confirmed by the results of an ultimate analysis, and further by the fact that optical activity is not lost when liquid paraffin is subjected to energetic treatment with fuming nitric acid. Activity must therefore be due to the presence of polynaphthenes, which is in accord with the observation of Bushong and Humphrey (*Chem. Zeit.*, 1912, **36**, 1139) that optically active naphthenic acids are present in mineral oil.

The optically active constituents of liquid paraffin are stable towards fuming sulphuric or fuming nitric acid, but are readily inactivated by aluminium chloride. When a solution of liquid paraffin in carbon disulphide was heated on the water-bath during three hours with aluminium chloride and the residue left after removal of the solvent was extracted with light petroleum, a colourless oil was obtained, which possessed feeble optical activity and considerably lower density, refractive index, and viscosity than the original material. From that portion of the reaction product which was insoluble in light petroleum, a viscous, brown substance was obtained, solutions of which were too deeply coloured to permit polarimetric observation. In the absence of any solvent, similar inactivation was observed. With light petroleum as solvent, however, the recovered oil had nearly the same properties as the original specimen. This difference is probably attributable to the fact that the yellowish-white additive product formed from liquid paraffin and aluminium chloride is practically insoluble in light petroleum, whilst it is appreciably soluble in carbon disulphide and also in liquid paraffin. In the first case, therefore, the liquid paraffin becomes practically protected from further action of aluminium chloride.

Finally, a series of experiments has been performed on the action of aluminium chloride on different optically active substances dissolved in carbon disulphide. Camphor and castor oil were not affected. Rosin oil, oil of turpentine, cholesterol, and the unsaponifiable portions of wool grease yielded black masses from which optically inactive products were extracted by light petroleum. H. W.

Structure of Acetylene. ALBERT P. MATHEWS (*J. Physical Chem.*, 1913, **17**, 320—321. Compare this vol, ii, 494).—The total number of valencies in acetylene calculated from the critical data by the author's formula is ten. The formula of acetylene at its critical point is therefore $H—C\equiv C—H$, and not $C=C=H_2$. R. J. C.

Preparation of $\beta\gamma$-Dihalogen *iso*Pentanes by the Chlorination of β-Halogen *iso*Pentane. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 257600).—When the vapours of monohalogenated tertiary *iso*pentanes are treated with chlorine (or bromine), they readily furnish a satisfactory yield of the technically important $\beta\gamma$-dihalogen *iso*-pentanes, and the preparation of $\beta\gamma$-dichloro*iso*pentane, b. p. 60°/60 mm., from β-chloro*iso*pentane is described. F. M. G. M.

The Preparation of Carbon Tetraiodide. MARCEL LANTENOIS (*Compt. rend.*, 1913, **156**, 1385—1387).—A critical study of the various methods recommended for the preparation of carbon tetraiodide (compare Spindler, A., 1886, 434; Moissan, A., 1891, 1420; Robineau and Rollin, A., 1895, i, 123). The author adopts Spindler's method, but prefers to replace the calcium iodide with lithium iodide, which gives a very pure product on heating it with excess of carbon tetrachloride in a vacuum in a sealed tube at 90—92° for five days. The best solvents for carbon tetraiodide are benzene, acetone, and carbon disulphide. W. G.

Higher Tertiary Alcohols Derived from Palmitic and Stearic Esters. HUGH RYAN and THOMAS DILLON (*Proc. Roy. Irish Acad.*, 1912, *B*, **29**, 235—245).—A series of tertiary alcohols has been prepared by the action of Grignard's reagents on esters of palmitic and stearic acid. The latter were readily obtained by the addition of a few c.c. of concentrated sulphuric acid to a hot solution of the acid in excess of the requisite alcohol, the yields in every case being more than 90% of the quantity theoretically obtainable. The following esters were obtained in this manner: methyl palmitate, needles, m. p. 28°; ethyl palmitate, long needles, m. p. 24·2°; n-*propyl palmitate*, needles, m. p. 18·8—19·2°; methyl stearate, needles, m. p. 38°; ethyl stearate, needles, m. p. 31°; n-*propyl stearate*, prisms, m. p. 28·6°.

For the preparation of tertiary alcohols, the solid ester was added in small portions to an ethereal solution of the necessary Grignard's reagent. There were thus obtained: *dimethylpentadecylcarbinol*, $C_{18}H_{38}O$, needles, m. p. 35°; *diethylpentadecylcarbinol*, curved needles, m. p. 34—35°; *diphenylpentadecylcarbinol*, prisms, m. p. 47—48°; *dimethylheptadecylcarbinol*, needles, m. p. 44—45°; *diethylheptadecylcarbinol*, needles, m. p. 44—45°; *dipropylheptadecylcarbinol*, needles, m. p. 28—30°; *diphenylheptadecylcarbinol*, long, curved needles, m. p. 58°. The action of an ethereal solution of magnesium naphthyl bromide on methyl stearate led to the formation of *naphthyl heptadecyl ketone*, $C_{17}H_{35}\cdot CO\cdot C_{10}H_7$, m. p. 55°.

Diethylheptadecylcarbinyl acetate was obtained as an oily liquid, which solidified when placed in iced water, by the action of acetyl chloride on diethylheptadecylcarbinol.

Dimethylpentadecylcarbinol, when heated on the sand-bath with sodium acetate and acetic anhydride, yielded a mixture of the corresponding *acetate* and unsaturated hydrocarbon. A similar result was obtained with diethylheptadecylcarbinol.

Dimethylheptadecylcarbinol was apparently not affected when heated with potash-lime at 250°. At 300°, however, unsaturated substances

were produced, but no evolution of hydrogen was observed. Diphenylheptadecylcarbinol similarly yielded unsaturated substances at 300°.

H. W.

Basic Properties of Oxygen. II. OTTO MAASS and DOUGLAS MCINTOSH (*J. Amer. Chem. Soc.*, 1913, **35**, 535—543).—In an earlier paper (A., 1912, i, 825) it has been shown that the compounds formed by the union of halogens or halogen hydrides with organic substances containing oxygen differ in many respects from molecular aggregates containing water or alcohol of crystallisation. In order to ascertain whether such compounds exist in solution, conductivity determinations have been made of the two-component systems of hydrochloric acid with ethyl and methyl ethers and with ethyl and methyl alcohols over the complete concentration range at $-89°$. The results are compared with the freezing-point curves of the different systems. In the case of methyl ether, two compounds are formed, namely, Me_2O,HCl and $Me_2O,4HCl$ (?). With ethyl ether, three compounds are produced: Et_2O,HCl, m. p. $-92°$; $Et_2O,2HCl$, m. p. $-88°$; and $Et_2O,5HCl$, m. p. $-89°$. Methyl and ethyl alcohols each yield only one compound, namely, $MeOH,HCl$, m. p. $-62°$, and $EtOH,HCl$, m. p. $-65°$. The conductivity curves indicate the probability of the existence of compounds in solution.

E. G.

A Derivative of Quinquevalent Tungsten. ARTHUR FISCHER and LOUIS MICHIELS (*Zeitsch. anorg. Chem.*, 1913, **81**, 102—115. Compare this vol., ii, 513).—The electrolysis of a solution of tungsten hexachloride in absolute alcohol gives at the platinum cathode a green, crystalline compound, $C_6H_{16}O_3Cl_2W$. It is decomposed by hot alcohol, but may be recrystallised from a mixture of alcohol and chloroform at 60°, cooling in ice. The compound forms bright green leaflets, with metallic lustre and slight fluorescence. It is slowly decomposed by hot water, yields the blue oxide when strongly heated, and gives the iodoform reaction. More than two-thirds of the carbon is evolved on heating in the form of ethylene. Oxidation with permanganate indicates that the tungsten is quinquevalent. The reactions indicate the composition $WCl_2(OEt)_3$, but the molecular weight is double this, and the exact constitution is uncertain.

C. H. D.

Catalytic Actions of Colloidal Metals of the Platinum Group. IX. The Hydrogenation of Egg-lecithin. CARL PAAL and HERMANN OEHME (*Ber.*, 1913, **46**, 1297—1304).—As in previous experiments with certain fats (A., 1908, i, 599; 1909, i, 358), so also it has been found possible to reduce egg-lecithin to a crystalline substance. Merck's reddish-brown, wax-like egg-lecithin had the iodine value, 55·3, but the volume of hydrogen absorbed in presence of colloidal palladium in 90% alcoholic solution was higher than this value would predict, being about 59 c.c. instead of 48·4 c.c. per 1 gram. The *hydrolecithin* partly separates from the solution, and may be recrystallised from chloroform and acetone as a white powder which sinters at 83—84°. On hydrolysis with barium hydroxide, it gave glycerol, phosphoric acid, and choline, which was identified as the

aurichloride, whilst the fatty acids recovered from the soap were found, after fractional crystallisation, to contain chiefly stearic acid, which would arise from the unsaturated C_{18}-acids of egg-lecithin. The presence of small quantities of acids of lower molecular weight, probably myristic, decoic, or lauric acids, showed that the substance and consequently the starting material were not quite homogeneous. Egg-lecithin is, however, chiefly a palmityl-linolyl-lecithin, and the analysis of the hydrolecithin agreed fairly well with $C_{42}H_{86}O_9NP$, the formula of a palmityl-stearyl-lecithin. J. C. W.

Uranyl Formate. GASTON COURTOIS (*Bull. Soc. chim.*, 1913, [iv], **13**, 449—454).—The properties of *uranyl formate*, $(HCO)_2UO_2,H_2O$, which is obtained in non-deliquescent, yellow octahedra by digesting the hydrated oxide, UO_3,H_2O, with dilute formic acid at 80°, are very different in many respects from those described by Œchsner de Coninck and Raynaud (this vol., i, 333). When crystallised from ice water, it still contains $1H_2O$, and it is not dehydrated by prolonged sojourn in a vacuum desiccator. When dried in this manner, it is stable up to 100°, loses water at 150°, but also formic acid. A moist sample loses water and formic acid at 100°, and becomes insoluble. The solubilities are 7·2% in water at 15°, 4·9% in methyl alcohol at 18°, only slightly soluble in concentrated formic acid or alcohol, insoluble in other organic media.

The concentrated solution slowly deposits a *basic* salt in the cold and dark, quickly on boiling, in the form of yellowish-white, truncated prisms of the composition $(HCO)_2UO_2,H_2O$, $UO_3,2H_2O$. Prolonged boiling with water results in the acid, UO_3,H_2O. When exposed to light for some time, dilute solutions of the formate gradually deposit this basic salt mixed with a small amount of a violet hydrate of uranoso-uranic oxide. Even in methyl alcohol no brown uranium oxide was obtained, but the above violet substance, which was transformed into the pale yellow oxide, $UO_3,2H_2O$, in the air, and into the yellowish-white acid, UO_3,H_2O, on boiling with water.

J. C. W.

Molecular Association of Acetic Acid. ÉMILE BAUD (*Bull. Soc. chim.*, 1913, [iv], **13**, 435—438).—According to the surface tension measurements of Ramsay and Shields (A., 1894, ii, 179), acetic acid exists in double molecules at the ordinary temperature. This was found to be the case when the acid is mixed with some organic solvents (A., 1912, ii, 233, 331, 1147), and is again confirmed by cryoscopic measurements in nitro- and chloro-benzene. The fact holds good even for strong solutions, from which it follows that the pure acid is bimolecular, and that the solvent has no associating influence in these cases.

Formic acid, however, like water, has a dissociating effect and the unimolecular value is obtained. The freezing-point curve for mixtures of the two acids does not indicate the formation of a compound, but it is assumed that combination does take place, since the heat absorbed on mixing the two substances is much less than the heat of dissociation of the double molecules. An equilibrium between the double molecules

and the mixed molecules, $(C_2H_4O_2)_2 + (CH_2O_2)_2 \rightleftarrows 2(C_2H_4O_2,CH_2O_2)$, would require that in a dilute solution of acetic acid in formic acid, the acetic acid molecule would produce two molecules of the mixed acid and cause an excessive depression of the freezing point, leading, therefore, to the unimolecular value for the molecular weight.

J. C. W.

Margaric Acid and its Relations to Palmitic and Stearic Acids. ROBERT F. RUTTAN (*8th Inter. Cong. Appl. Chem.*, 1912, **25**, 431—442).—The history of margaric acid is related, a method of preparing the acid by the Grignard reaction is described, and the chief constants of the acid are recorded in comparison with those of palmitic and stearic acids.

When cetyl iodide is treated with magnesium in ether, in presence of iodine as a catalyst, micaceous crystals of the organo-magnesium compound separate. If the mixture is then treated with carbon dioxide, a mixture of ditriacontane and margaric acid is formed, the yield of the acid being 50% of the theoretical under the best conditions, which include the use of dry reagents throughout the operations. A method for the separation of the hydrocarbon and acid is described. Margaric acid crystallises in colourless, bulky, shining plates, melts at 59·9—60° (corr.), and solidifies at 58·8°. It has D 0·8532 at its melting point, $n = 1{\cdot}4342$ at 60°, and the coefficient of expansion is $6{\cdot}65 \times 10^{-4}$ at 60—80°. The following quantities (grams) dissolve in 100 grams of dry alcohol at the temperatures named: 0°, 1·53; 5·4°, 2·42; 10°, 4·12; 15°, 6·72; 21°, 13·4; 28°, 32·14. Methyl margarate, m. p. 29°, forms waxy scales. Ethyl margarate, m. p. 27·5°, crystallises in waxy plates. *Ethylene margarohydrin*, m. p. 53·2°, forms pearly scales, and *ethylene dimargarate*, m. p. 70·4°, glistening plates.

T. A. H.

Saponification of Triglycerides. JULIUS MEYER (*Chem. Zeit.*, 1913, **37**, 541—542).—The author criticises the experiments of Fortini (A., 1912, i, 826) on the saponification of triolein with alkali hydroxide in alcohol. The latter found that the curves obtained by plotting (1) quantity of triglyceride hydrolysed against time, or (2) acetyl number against time, were composed of three parts corresponding with (*a*) formation of diglyceride; (*b*) formation of monoglyceride, and (*c*) formation of free fatty acid.

According to the author, the amount of alkali consumed is not a measure of the quantity of triglyceride saponified, since a portion of it is used in decomposing di- and mono-glycerides (compare Kellner, A., 1909, i, 357, 548, 759). Also, by plotting alkali consumed against time, a continuous curve is obtained in the saponification of triacetin in homogeneous solution by 0·01 and 0·02*N* potassium hydroxide (Meyer, A., 1909, ii, 803). Further, the determination of the acetyl number after definite intervals of time is not a satisfactory method of following the course of the reaction, since, particularly with the unsaturated oleic acid and its glycerides, this number depends greatly on the conditions under which the determination is executed, and is further complicated by the decomposition of the triglyceride into olein

acetate and glycerol occurring with intermediate formation of di- and mono-glycerides (compare Kremann, A., 1905, ii, 630; 1908, i, 120; Fanto and Stritar, 1908, i, 499). H. W.

The Behaviour of Paints Under the Conditions of Practice, with Special Reference to the Aspersions Cast on Lead Paints. HENRY E. ARMSTRONG and C. A. KLEIN (*J. Soc. Chem. Ind.*, 1913, **32**, 320—331).—This communication is, to a great extent, critical and polemical against the work of Baly (*The Oil and Colour Trades Journal*, 1911, 1518; A., 1912, i, 533), and the report of Breton in connexion with lead paints. The experimental part deals with the formation of volatile products from linseed and other oils and the ordinary materials used in making paints, and with the test for lead in the volatile products, if any, from paint materials. The leaf of the common shrub, *Aucuba Japonica*, or the spotted Japanese laurel, is used as a test for volatile products, in the presence of which it blackens more or less rapidly.

The conclusions arrived at are: The vapours produced during the drying of white-lead pastes and paints do not contain lead. The vapours given off as paints dry consist of turpentine for the most part, together with oxidation products of the oil; the latter are common to paints generally containing oil so treated that it will dry. The oxidation products formed from the oil during drying are harmless under the conditions of practice. The toxic effects sometimes experienced from drying paints are to be ascribed to turpentine; in many cases effects which have been regarded as due to lead-poisoning are attributable to other causes, especially to turpentine. The dangers attending the use of lead compounds are only the well-known mechanical dangers. T. S. P.

Cerebronic Acid. II. PHŒBUS A. LEVENE and C. J. WEST (*J. Biol. Chem.*, 1913, **14**, 257—266. Compare A., 1912, i, 936).—Previous work indicated that cerebronic acid has the structure of an α-hydroxypentacosoic acid; on reduction the acid formed a hydrocarbon, m. p. 54—57°. According to Krafft and Marie, *n*-pentacosane has m. p. 53·5—54°. The experiments were repeated with a larger supply of material, and the melting point came out at the latter figure. By reduction of the acid, $C_{24}H_{48}O_2$, obtained by oxidation of cerebronic acid, a hydrocarbon, melting at 51—52°, was obtained, which is the melting point of normal tetracosane. Cerebronic acid is a α-hydroxy-*n*-pentacosoic acid.

Acetylcerebronic acid, $C_{25}H_{49}O_3$, obtained by the action of acetic anhydride on cerebronic acid, is a white, crystalline solid, m. p. 55·5—56°, and solidifies at 53—54°. W. D. H.

Formation of β-Ketone Esters by the Application of Reformatsky's Reaction. TREAT B. JOHNSON (*J. Amer. Chem. Soc.*, 1913, **35**, 582—585).—Fittig and Daimler (A., 1887, 361) have shown that ethyl chloroacetate reacts with ethyl oxalate in presence of amalgamated zinc with formation of ethyl ketipate. Reformatsky, in his work on the synthesis of dibasic hydroxy-acids (A., 1896, i, 206)

found that ethyl α-bromopropionate reacts with ethyl formate with production of ethyl β-hydroxy-αα-dimethylglutarate, but he obtained no evidence of the formation of ethyl formylpropionate corresponding with Fittig and Daimler's ethyl ketipate. In attempting, however, to prepare ethyl β-hydroxyglutarate from ethyl formate and ethyl chloroacetate (A., 1899, i, 516), he obtained ethyl trimesate as the chief product of the reaction, this having been formed by a condensation of ethyl formylacetate. The production of ethyl formylacetate and ethyl ketipate are analogous, and represent the first stage of Reformatsky's synthesis.

These results suggested that perhaps other esters besides ethyl formate and ethyl oxalate might undergo similar condensations with esters of halogen-substituted acids, and this has been found to be the case. The reaction has been applied to ethyl ethoxyacetate, ethyl α-ethoxypropionate, ethyl bromoacetate, and ethyl α-bromopropionate, and the following esters have been obtained: *Ethyl γ-ethoxyacetoacetate*, $OEt\cdot CH_2\cdot CO\cdot CH_2\cdot CO_2Et$, b. p. 110°/20—21 mm., 116—120°/26—27 mm., 120—125°/30 mm., and 130—136°/45 mm. *Ethyl γ-ethoxy-α-methylacetoacetate*, $OEt\cdot CH_2\cdot CO\cdot CHMe\cdot CO_2Et$, b. p. 113—116°/18—20 mm., and 116°/24 mm. *Ethyl γ-ethoxy-γ-methylacetoacetate*, $OEt\cdot CHMe\cdot CO\cdot CH_2\cdot CO_2Et$, b. p. 110—115°/19 mm. *Ethyl γ-ethoxy-αγ-dimethylacetoacetate*, $OEt\cdot CHMe\cdot CO\cdot CHMe\cdot CO_2Et$, b. p. 108—115°/16 mm. E. G.

Real and Supposititious Oxalomalonic Esters and Applicability of Methanetricarboxylic Ester for Synthetic Purposes.

ROLAND SCHOLL and WILHELM EGERER (*Annalen*, 1913, **397**, 301—366).—The triethyl oxalomalonate (ethyl ketoethanetricarboxylate) and corresponding acid described by Kurrein (A., 1905, i, 413) are a mixture of ethyl oxalate and malonate, and a mixture of hydrated oxalic acid and malonic acid respectively. Also the substance, b. p. 220°/10 mm., obtained by Bouveault in 1898 from ethyl sodiomalonate and ethyl oxalic chloride, and described by him as triethyl oxalomalonate, $CO_2Et\cdot CO\cdot CH(CO_2Et)_2$, cannot be this compound, as the sequel proves.

[With EMIL HEUSER.]—Methyl dichloromethoxyacetate,

$$OMe\cdot CCl_2\cdot CO_2Me,$$

which is obtained in 80—90% yield by heating methyl oxalate and phosphorus pentachloride ($1\frac{1}{2}$ mols.) at 130—135° for thirty hours, is converted into methyl chloropyruvate, $CO_2Me\cdot COCl$, to the extent of 60% by heating it with a small quantity of platinum black in a bath at 200° until the temperature cannot be raised above 140—160°; the methyl oxalic chloride, b. p. 117—118°, is then removed by distillation, and the residue again heated, a quantity of platinum black being again added if necessary.

Methyl sodiomalonate and methyl chloropyruvate in equal molecular quantities react in dry ether in a freezing mixture to form methyl malonate and *methyl dioxalomalonate* (*methyl αγ-diketopropane-αββγ-tetracarboxylate*), $C(CO_2Me)_2(CO\cdot CO_2Me)_2$; after the removal of the ether by a current of air at 25°, the residue is vigorously shaken with ice-water, by which all products are dissolved except the tetracarboxylate.

Methyl dioxalomalonate, m. p. 97·5—98°, colourless needles or prisms, which can be also prepared in a similar manner from methyl chloropyruvate and methyl sodio-oxalomalonate (see below), is unattacked by alkaline potassium permanganate or by bromine, and is therefore not an *O*-derivative, $CO_2Me{\cdot}CO{\cdot}C(CO_2Me){:}C(OMe){\cdot}O{\cdot}CO{\cdot}CO_2Me$ or

$$C(CO_2Me)_2{:}C(CO_2Me){\cdot}O{\cdot}CO{\cdot}CO_2Me,$$

but is a very reactive substance in other ways. It is decomposed by water, slowly at the ordinary temperature and rapidly by heating, into oxalic acid and methyl malonate. It is decomposed in the same manner by boiling methyl alcohol, with or without potassium hydroxide. Ammonia, phenylhydrazine, and aniline also decompose the tetracarboxylate, producing methyl malonate and oxamide, oxalic acid diphenylhydrazide, or methyl oxanilate respectively.

By heating at 180—200°, methyl dioxalomalonate loses carbon monoxide and is converted into *methyl oxalomethanetricarboxylate* (*methyl ketoethanetetracarboxylate*), $CO_2Me{\cdot}CO{\cdot}C(CO_2Me)_3$, m. p. 91—92°, b. p. 285—286° or 179—180°/15 mm., colourless plates, which is also prepared by heating methyl chloropyruvate and methyl sodiomethanetricarboxylate in benzene (see below). The ester is remarkably stable when heated, being almost unchanged after boiling for one and a-half hours. It does not give a coloration with alcoholic ferric chloride. When boiled with methyl alcohol, the ester is rapidly converted into methyl oxalate and *methyl methanetricarboxylate*, $CH(CO_2Me)_3$, m. p. 45—46°, b. p. 242·7° (corr.) or 128°/15 mm., colourless prisms. Methyl methanetricarboxylate is also obtained by heating a suspension of methyl sodiomalonate in benzene with methyl chloroformate; it is soluble in dilute sodium hydroxide or carbonate, and forms with methyl-alcoholic sodium methoxide a *sodio*-derivative, $C_7H_9O_6Na$, colourless needles. Methyl methanetricarboxylate exists as the ketonic modification in the crystalline state, but when fused or in alcoholic solution it is partly changed to the enolic form, since the reddish-brown coloration produced by ferric chloride gradually becomes more intense.

Many attempts have been made to prepare methyl oxalomalonate (methyl ketoethane-$\alpha\alpha\beta$-tricarboxylate) from methyl sodiomalonate and methyl chloropyruvate under different conditions of temperature and concentration, but the principal product is always methyl dioxalomalonate. The desired ester, however, has been obtained from methyl dioxalomalonate by careful decomposition with methyl alcohol or methyl sodiomalonate. The preparation is difficult because methyl oxalomalonate itself is decomposed into methyl oxalate and methyl malonate by methyl alcohol. A 10% solution of methyl dioxalomalonate in benzene is kept with an equal molecular quantity of methyl alcohol for thirty days at the ordinary temperature, or at least four days at 50°, the product is distilled under about 12 mm. pressure, and the ethereal extract of the residue is fractionally crystallised, whereby *methyl oxalomalonate*, $CO_2Me{\cdot}CO{\cdot}CH(CO_2Me)_2$, m. p. 49—50°, colourless needles, is obtained, the yield being about 50% of the amount ascertained volumetrically (see below). The ester is also obtained by treating a suspension of methyl sodiomalonate (2 mols.) in benzene at 50° with methyl dioxalomalonate (1 mol.), removing the yellow precipitate (sodio-derivatives of methyl oxalomalonate and methyl

malonate), suspending it in ether at 0°, and treating it with dilute sulphuric acid at 0°; the ester is obtained from the ethereal solution. A third method of preparing methyl oxalomalonate from methyl sodiomalonate and methyl chloropyruvate is described.

Methyl oxalomalonate forms colourless solutions in aqueous sodium hydroxide or carbonate, and does not react in ether with sodium. At 120—130° it decomposes quantitatively into carbon monoxide and methyl methanetricarboxylate, and thus reacts as the ketonic modification. By titration with alcoholic bromine and β-naphthol by Meyer's method, it is shown that the ester is entirely enolic in alcohol or benzene, but contains about 7%, 21%, and 94% (?) of the ketonic modification in chloroform, acetone, and glacial acetic acid respectively. Meyer's method can also be employed to show that the maximum (molecular) percentage of methyl oxalomalonate obtained from equal molecular quantities of methyl alcohol and methyl dioxalomalonate in benzene (at 18° or at 50°) is about 71%.

The series of ethyl esters corresponding with the preceding methyl esters has been prepared. Ethyl sodiomalonate and ethyl chloropyruvate react in ether to form ethyl malonate and a mixture of ethyl oxalo- and dioxalo-malonates, from which the latter cannot be isolated. By distillation under 15 mm. pressure, the mixture decomposes, evolves carbon monoxide, and produces *ethyl methanetricarboxylate*, $CH(CO_2Et)_3$, m. p. 28·5°, and *ethyl oxalomethanetricarboxylate*, $CO_2Et{\cdot}CO{\cdot}C(CO_2Et)_3$, b. p. 191—192°/15 mm. (Bouveault's so-called ethyl oxalomalonate).

By treating an ethereal solution of the preceding mixture of ethyl oxalo- and dioxalo-malonates with sodium, *ethyl sodio-oxalomalonate*, $C_{11}H_{15}O_7Na$, is obtained as a white precipitate, from which *ethyl oxalomalonate*, D_4^{17} 1·1147, is obtained. Ethyl oxalomalonate is soluble in dilute sodium hydroxide or carbonate, but is not attacked by sodium except in the presence of a little ethyl malonate. It develops a red coloration with alcoholic ferric chloride, decomposes by heating into carbon monoxide and ethyl methanetricarboxylate, and is decomposed by water or phenylhydrazine in the same manner as the methyl ester.

Ethyl dioxalomalonate, $C(CO_2Et)_2(CO{\cdot}CO_2Et)_2$, is obtained from ethyl chloropyruvate and ethyl sodio-oxalomalonate in ether, and decomposes by heating.

Conrad and Guthzeit, Michael, and others have tried to utilise methanetricarboxylic esters for synthetic purposes. Their efforts have been unsuccessful, since they used alcohol, by which alkyl methanetricarboxylates are decomposed into alkyl malonates. In the absence of alcohol, alkyl sodiomethanetricarboxylates can be used for synthetic purposes as effectively as ethyl sodioacetoacetate or sodiomalonate, higher temperatures, however, being necessary.

Dimethyl ethyl methanetricarboxylate, $CO_2Et{\cdot}CH(CO_2Me)_2$, prepared from methyl sodiomalonate and ethyl chloroformate, has b. p. 240—241°, or 138—139°/12 mm., and forms with sodium ethoxide a white *sodio*-derivative. Ethyl sodiomethanetricarboxylate reacts with methyl iodide at 140° to form *ethyl ethane-aaa-tricarboxylate*, $CMe(CO_2Et)_3$, b. p. 250°, or 130°/11 mm., and with ethyl iodide, in a

similar manner, to form *ethyl propane-aaa-tricarboxylate*, $CEt(CO_2Et)_3$, b. p. 258°, or 146°/17 mm.; the latter ester, which has a bitter taste, is converted into ethyl carbonate and ethyl sodioethylmalonate by alcoholic sodium ethoxide.

Ethyl sodiomethanetricarboxylate and acetyl chloride react, finally on the water-bath, to form *ethyl acetylmethanetricarboxylate* (*ethyl β-ketopropane-aaa-tricarboxylate*), $C(CO_2Et)_3\cdot COMe$, b. p. 253° or 147—148°/14 mm., and with benzoyl chloride to form *ethyl benzoylmethanetricarboxylate*, $C_{17}H_{20}O_7$, b. p. 214°/14 mm. Methyl sodiomethanetricarboxylate and methyl chloro-formate react at 120° to form *methyl methanetetracarboxylate*, $C(CO_2Me)_4$, m. p. 74—75°, b. p. 295° (corr.)/735 mm., or 163°/12 mm., colourless, tasteless needles, which is not attacked by alkaline potassium permanganate or by bromine, and is converted into malonic acid by dilute sulphuric acid and into methyl carbonate and methyl sodiomethanetricarboxylate by alcoholic sodium methoxide. *Dimethyl diethyl methanetetracarboxylate*, b. p. 293°, or 167°/11 mm., and *ethyl methanetetracarboxylate*, m. p. 13·5°, b. p. 304° (corr.)/735 mm., or 173·5°/12 mm., D_4^{17} 1·0886, both of which have a bitter taste, are also described.

Ethyl oxalomethanetricarboxylate (see above) is also obtained from ethyl sodiomethanetricarboxylate and ethyl chloropyruvate in benzene.

C. S.

Effect of Heating Paraformaldehyde with a Trace of Sulphuric Acid. JOHN G. M. DUNLOP (*Proc. Camb. Phil. Soc.*, 1913, **17**, 180—181).—When a mixture of paraformaldehyde and sulphuric acid is heated at 115° in a sealed tube, bent in such a manner that one end is heated while the other end is kept cool by immersion in a beaker of water, a mobile distillate is obtained, which, when fractionated, yields methyl formate and a liquid, b. p. 95—96°, still under investigation, which appears to be a polymeride of formaldehyde. The yield of methyl formate is very variable and depends on the amount of sulphuric acid and also on the temperature. With about six drops of sulphuric acid to ten grams of trioxymethylene, a yield of about one to two grams of ester appears to be usual. With five grams of acid to the same weight of trioxymethylene, great charring takes place and practically no ester is formed. H. W.

Methylation of *iso*Valerone by means of Sodamide and Methyl Iodide. Tetramethyl*iso*valerone or βγγεεζ-Hexamethylheptan-δ-one. ALBIN HALLER and EDOUARD BAUER (*Compt. rend.*, 1913, **156**, 1295—1298. Compare this vol., i, 488).—By the action of sodamide on *iso*valerone dissolved in benzene, followed by addition of methyl iodide according to the usual method, a liquid was obtained which, after twice repeating this methylation, gave, on fractional distillation, *βγεζ-tetramethylheptan-δ-one*, b. p. 76—78°/13 mm., yielding only traces of an oxime, and *βγγεζ-pentamethylheptan-δ-one*, b. p. 88—89°/13 mm., which gave no oxime, and was not decomposed on boiling with sodamide in benzene. The last substance on further methylation with sodamide and methyl iodide in toluene yielded *βγγεεζ-hexamethylheptan-δ-one*, b. p. 107—109°/14 mm., which gave

neither oxime nor semicarbazone, and was not decomposed by sodamide in boiling toluene. On reduction with sodium in alcohol, it yielded the corresponding *βγγεεζ-hexamethylheptan-δ-ol*, b. p. 115—117°/13 mm., giving a *phenylurethane*, m. p. 91—92°. W. G.

Reactions of Methylene. IV. The Decomposition of Ketens at High Temperature. HERMANN STAUDINGER and R. ENDLE (*Ber.*, 1913, **46**, 1437—1442. Compare A., 1912, i, 245).—Since it has been shown (this vol., i, 604) that dicarbon dioxide is incapable of existence, but decomposes into carbon monoxide with rupture of the ethylenic bond, whilst, generally, ethylene derivatives are remarkably stable towards heat, the authors have been led to examine the behaviour of ketens at high temperatures, as these substances form an intermediate link between dicarbon dioxide and the true ethylene derivatives.

The experiments were performed in a quartz tube closed at one end at which the substance was placed. In the middle of the tube a silver spiral was placed which could be maintained at 600—700°. The tube was further connected with a suitable condensing arrangement. Previous to an experiment the tube was exhausted. The substance was then vaporised, and the vapours conducted over the heated spiral.

Diphenylketen, when heated in the above manner, yielded fluorene in accordance with the scheme:

$$(C_6H_5)_2C{:}CO \longrightarrow \begin{matrix}C_6H_5\\C_6H_5\end{matrix}{>}C{<} + CO \longrightarrow \begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}{>}CH_2 + CO.$$

Dimethylketen, obtained by heating tetramethyldiketo*cyclo*butane, gave propylene and tetramethylethylene:

$$CMe_2{:}CO \longrightarrow CMe_2{<} \longrightarrow CH_3{\cdot}CH{:}CH_2;\ 2CMe{<} \longrightarrow CMe_2{:}CMe_2.$$

In similar circumstances, diphenylethylene and tetraphenylethylene were not altered, whilst only slight decomposition occurred with diphenyldichloroethylene. Diphenylmethane also underwent no change. At 250°, diphenylbromomethane was converted into tetraphenylethylene and hydrogen bromide. When the silver spiral was replaced by fragments of porcelain, diphenylbromomethane and diphenylchloromethane yielded at 700° tetraphenylethylene instead of fluorene, so that possibly the course of the reaction depends on the contact material.

Phenylcarbimide and phenylthiocarbimide were not affected by a silver spiral at 700°, or by a platinum spiral heated to glowing. H. W.

Esterification of Dihydroxyacetone with Phosphates. ALEXANDER VON LEBEDEV (*Zeitsch. physiol. Chem.*, 1913, **84**, 305).—Polemical (compare Euler and Johansson, A., 1912, i, 750). E. F. A.

The Action of Ultraviolet Light on Sucrose. YNGVE DALSTRÖM (*Arkiv. Kem. Min. Geol.*, 1913, **4**, No. 30, 1—14).—The source of ultraviolet light was an arc burning between carbon or iron electrodes. The apparatus was similar to that used by Euler and

Ohlsén (A., 1911, i, 524), the temperature being 70°. The progress of any reaction taking place was followed by observing the change in rotation of the solutions used, and by titrating any acid formed with standard barium hydroxide solution.

The action of the light of short wave-length produced by the above-mentioned arcs consists, in the first instance, in the formation of an organic acid, which then brings about the hydrolysis of the remaining sucrose. Any direct action of the ultraviolet light on the hydrolysis can only be very small.
T. S. P.

Action of Reducing Agents on the Chloraloses. MAURICE HANRIOT and ANDRÉ KLING (*Compt. rend.*, 1913, **156**, 1380—1382).—α- and β-Chloralose and galactochloralose are reduced in aqueous solution by aluminium activated with mercury, one of the chlorine atoms being replaced by hydrogen, and the products obtained are the same as in the action of ammonia on the chloraloses (compare A., 1911, i, 524, 525). In alkaline solution, sodium amalgam removes a second atom of chlorine, and from α-chloralose a *compound*, $C_7H_{11}O_6\cdot CH_2Cl$, m. p. 168°, is obtained. β-Chloralose yields a similar *compound*, m. p. 166°, giving a *dibenzoyl* derivative, needles, m. p. 149°, and on oxidation with nitric acid it yields a non-crystalline substance giving with hydrazine hydrate a *compound*, $C_7H_7O_5Cl,N_2H_4$, white needles, m. p. 170°.

Sodium in liquid ammonia removes the third chlorine atom from the chloralose, but the product of the action could not be crystallised, the action seeming to lead to the destruction of the chloralose nucleus.
W. G.

Pseudo-crystals of Starch and Crystals of Dextrose. GIOVANNI MALFITANO and (Mlle.) A. N. MOSCHKOV (*Compt. rend.*, 1913, **156**, 1412—1415. Compare A., 1910, i, 301, 817).—The so-called crystals of starch, when examined microscopically, although resembling crystals of dextrose fairly closely, are found not to have a true crystalline form. These particles of starch have not the polyhedric form, neither do they exhibit the phenomenon of birefringence.
W. G.

The Molecular Size of Dextrin-β. WILHELM BILTZ and WILHELM TRUTHE (*Ber.*, 1913, **46**, 1377—1380. Compare Pringsheim and Langhans, A., 1912, i, 832).—The osmotic pressures exerted by dilute solutions of dextrin-β in a cell composed of collodion impregnated with copper ferrocyanide have been measured directly, and the calculated molecular weights plotted against concentration. By extrapolation for infinite dilution, the value 950 ± 50 is obtained, which confirms the expectation that dextrin-β is a hexa-amylose. The fact that the curve rises rapidly with increasing concentration is not due so much to association as to the time required to reach equilibrium, for higher pressures and therefore lower molecular weights are obtained when the water column is allowed to sink to position than when it is made to rise. The method is being described

in another place. The results obtained for similar substances compare favourably with the values obtained by cryoscopic and other means. J. C. W.

Cellulose. Edward G. Parker (*J. Physical Chem.*, 1913, **17**, 219—229).—Lange's method of estimating cellulose by hydrolysing the non-celluloses with potassium hydroxide, and the various modifications of it which have been proposed, give untrustworthy results, as the yield of normal cellulose varies with slight variations in the time of boiling, concentration of alkali, and temperature. By heating in a paraffin bath at 130—140° under reflux, after a certain interval of time the yield of normal cellulose from absorbent cotton became constant. The time required for the hydrolysis of the non-celluloses was less with dilute potassium hydroxide within the limits used, a 1 or 2% solution requiring three hours and a 20% solution fifteen hours. It is suggested that the increased evolution of steam from the dilute solutions carried the non-celluloses more rapidly into suspension where the alkali could act on them.

The author's sample of cotton wool contained approximately 92—93% of normal cellulose, 4—5% of soluble cellulose, and 3·25% of water.

Samples of oxycellulose prepared by the action of hydrochloric acid and potassium chlorate and of cellulose reprecipitated from cuprammonium solution contain a much higher proportion of matter soluble in potassium hydroxide. It is suggested that the soluble part of cotton wool consists of oxy- and hydro-cellulose and that cotton reprecipitated from Schweitzer's reagent consists largely of oxycellulose. R. J. C.

Esters of Cellulose with Benzoic Acid and their Derivatives. G. J. Briggs (*Zeitsch. angew. Chem.*, 1913, **26**, 255—256).—Hauser and Muschner have stated (this vol., i, 363) that they were unable to prepare the dibenzoate and tetrabenzoate described by Cross and Bevan. The author gives in detail the methods which were employed in the preparation of these derivatives of cellulose. Both esters are obtained by treating alkali cellulose with a 5—10% solution of benzoyl chloride in benzene, and are separated, first by treating the crude product with chloroform or glacial acetic acid in which the tetrabenzoate dissolves, and then by treating the residue with a cuprammonium solution which removes the unattacked cellulose.
W. H. G.

Oxycellulose. R. Oertel (*Zeitsch. angew. Chem.*, 1913, **26**, 246—250).—The oxycelluloses prepared by the methods of Witz, Nastukoff, Vignon, or Faber and Tollens are not simple substances. An oxycellulose having properties differing from those already known and described in the literature is obtained by passing an electric current between platinum electrodes and through a solution of potassium chloride containing cellulose in suspension. Under this treatment a large proportion of the cellulose is decomposed and passes into solution, but if the electrolysis is not carried too far, a product

is obtained which is soluble in a 10% solution of sodium hydroxide and has a copper value of 21·0—29·6 according to the extent of the electrolysis, the reducing power becoming greater as the treatment is prolonged. If the electrolysis be carried sufficiently far, the product obtained dissolves in water, forming a stable, colloidal solution, and has a copper value as high as 39·5.

The oxycellulose prepared by the electrolytic method is rapidly destroyed by a hot solution of sodium hydroxide, and when dissolved in a cuprammonium solution gives a very limpid solution. It is converted by sulphuric acid into dextrose, but the yield is not so high as in the case of cellulose, for whereas 100 parts of the latter yield 111 parts of dextrose, 100 parts of oxycellulose yield only 100 parts of dextrose. Oxycellulose when acetylated, using zinc chloride as catalyst, yields an acetate, part of which is soluble in acetone and has $[\alpha]_D - 17^\circ$, and part in chloroform ($[\alpha]_D - 19^\circ$ to $- 20^\circ$); the proportion of acetyl radicle present in the product is not so high as in cellulose triacetate.

The yield of cellobiose acetate from oxycellulose is also not so great as from cellulose. W. H. G.

Formation of Humic Substances by the Action of Polypeptides on Sugars. LOUIS C. MAILLARD (*Compt. rend.*, 1913, **156**, 1159—1160. Compare A., 1912, i, 13, 169; this vol., i, 165).—Glycylglycine like glycine itself readily reacts with xylose and dextrose in the presence of water, with the evolution of carbon dioxide and formation of brown humus-like substances, which are insoluble in boiling water and dilute acids, but partly soluble in ammonia and potassium hydroxide, from which solutions they are reprecipitated on neutralisation. Three samples of commercial peptones behaved similarly with the sugars. W. G.

Some Tetramethylammonium Compounds. JAROSLAV MILBAUER (*J. pr. Chem.*, 1913, [ii], **87**, 397—403).—The following tetramethylammonium salts are described: *perchlorate*, white crystals (solubility in cold water 1·126 : 100); *permanganate*, purple-red, tetragonal crystals, which readily decompose on exposure to moist air, and explode violently when heated. The *dithionate*, prepared by the interaction of the sulphate and barium dithionate in aqueous solution, forms lustrous, transparent, colourless cubes and octahedra. The *thiocyanate* crystallises in white, felted needles, the *stannichloride* in white, microscopic octahedra, and the *stannibromide* in pale yellow, microscopic octahedra. The *borate*, $(NMe_4)_2B_4O_7,5H_2O$, forms strongly refractive, transparent crystals, probably belonging to the triclinic system. The *sulphide* and *fluoride* could not be obtained in a pure condition. F. B.

Non-equivalence of the Five Valencies of Nitrogen. JAKOB MEISENHEIMER (*Annalen*, 1913, **397**, 273—300).—The author's explanation of the existence of amine-oxides in enantiomorphous configurations (A., 1912, i, 25) tacitly assumes the non-equivalence of the five valencies of the nitrogen atom. Many facts can be quoted in support

of the assumption, but it has now been definitely proved. Trimethylamine oxide reacts additively with an alkyl iodide, and its hydrochloride reacts with sodium alkyloxide, as follows:

$$Me_3NO + RI \longrightarrow Me_3N{<}^{OR}_{I} \xrightarrow{NaOH} Me_3N{<}^{OR}_{OH} \text{ (I).}$$

$$Me_3NO + HCl \longrightarrow Me_3N{<}^{OH}_{Cl} \xrightarrow{NaOR} Me_3N{<}^{OH}_{OR} \text{ (II).}$$

The position of the halogen atom in the ammonium salt is occupied by OH in substance (I) and by OR in substance (II). Several such pairs of isomerides have been prepared, and in every case the two substances are fundamentally different. The substances have not been isolated in the solid state, but by the evaporation of its aqueous solution, substance (I) decomposes quantitatively into trimethylamine, an aldehyde, and water, whereas substance (II) yields trimethylamine oxide and the alcohol R·OH. Pairs of isomerides of the types $Me_3N{<}^{OR}_{OR'}$ and $Me_3N{<}^{OR'}_{OR}$ have also been obtained; the evaporation of their solutions yields trimethylamine, an alcohol, and one aldehyde, the aldehyde always being that corresponding with the alkyl group of the alkyloxy-group not attached to the unique "fifth" valency of the quinquevalent nitrogen atom. Consequently, the two alkyloxy-groups are not attached to the nitrogen atom in the same manner.

The author discusses the constitutions of the isomerides $Me_3N{<}^{OR}_{OR'}$, and $Me_3N{<}^{OR'}_{OR}$, and gives reasons for rejecting formulæ:

$$Me_3N{:}O{<}^{R}_{OR'}$$

and $Me_3N{:}O{<}^{R'}_{OR}$, $[Me_3NO] \ldots R{\cdot}OR'$ and $[Me_3NO] \ldots R'{\cdot}OR$, and $[Me_3N \ldots OR]OR'$ and $[Me_3N \ldots OR']OR$, based on the oxonium, oxonium-ammonium, and (Werner's) ammonium theories respectively. A modification of the last theory is adopted. In Werner's formula of ammonium chloride, the nitrogen atom still remains in a sense tervalent; the four hydrogen atoms are attached to the nitrogen atom each by an amount of affinity less than that corresponding with a principal valency, so that the group NH_4 has an amount of residual affinity whereby it functions as a univalent group and is attached to the acid radicle. Objections can be raised against this view (compare Moore and Winmill, T., 1912, **101**, 1673). The author is of opinion that in ammonium compounds the nitrogen is quinquevalent, all five atoms or groups being attached to it by principal valencies, four in an inner, the fifth in an outer, zone; the atom or group in the outer zone is not attached in any definite position, and therefore exerts no influence on the asymmetry of the molecule. The author's pairs of isomerides are consequently represented by the formulæ: $[Me_3N{\cdot}OR]{\cdot}OR'$ and $[Me_3N{\cdot}OR']{\cdot}OR$, which satisfactorily represent their behaviour.

[With Kurt Bratring.]—Hydrated trimethylamine oxide,

$$NMe_3O,2H_2O,$$

prepared best by Dunstan and Goulding's method (T., 1899, **75**, 1005), can be dehydrated by heating under 10—12 mm. at a tempera-

ture not exceeding 150° until the greater part of the water has been expelled; the temperature is then raised to 190—200°, when *trimethylamine oxide*, NMe_3O, sublimes in colourless needles, m. p. 208°, which are extremely hygroscopic. By boiling for three-quarters of an hour with ethyl iodide in ethyl alcohol or with propyl iodide in propyl alcohol, the anhydrous oxide is readily converted into additive *compounds*, $OEt·NMe_3I$, m. p. 122—125°, and $OPr·NMe_3I$, m. p. 145—147°, respectively, both colourless, crystalline substances. By treating a dilute aqueous solution of methoxytrimethylammonium iodide with silver oxide and subsequently with cold hydrochloric acid and evaporating, *methoxytrimethylammonium chloride*, $OMe·NMe_3Cl$, is obtained, but the evaporation of an alcoholic solution of the methoxytrimethylammonium hydroxide without the addition of hydrochloric acid results in the formation of trimethylamine (isolated as the platinichloride) and formaldehyde (isolated as the *p*-nitrophenylhydrazone). Similar results are obtained by the evaporation of alcoholic solutions of ethoxytrimethylammonium hydroxide and propoxytrimethylammonium hydroxide, acetaldehyde and propaldehyde, respectively, being formed. By treating trimethylamine oxide hydrochloride, dissolved in the necessary alcohol, with the calculated amount of sodium methoxide, ethoxide, or propoxide, *hydroxytrimethylammonium methoxide, ethoxide,* and *propoxide* respectively are produced, $OH·NMe_3·OR$. By evaporation of their alcoholic solutions, these substances yield no trimethylamine, and only a trace of an aldehyde; the residue in all three cases is converted into trimethylamine oxide hydrochloride by alcoholic hydrogen chloride.

[With J. Dodonow.]—*Tetramethylammonium ethoxide*,

$$NMe_4·OEt,EtOH,$$

hygroscopic crystals, is obtained by treating tetramethylammonium chloride in anhydrous alcohol with the calculated amount of sodium ethoxide, adding ether, and removing the sodium chloride by filtration and the solvent by evaporation in a vacuum at 40°. *Alkyloxytrimethylammonium alkyloxides*, $[NMe_3·OR]·OR'$, are obtained in alcoholic solution by treating alkyloxytrimethylammonium iodides with alcoholic sodium alkyloxides. The substances have not been isolated, but the products of their decomposition by the evaporation of their alcoholic solutions in a current of nitrogen have been examined. *Methoxytrimethylammonium ethoxide* and *methoxytrimethylammonium propoxide* each yield formaldehyde, *ethoxytrimethylammonium methoxide* and *ethoxytrimethylammonium propoxide* each yield acetaldehyde, whilst *propoxytrimethylammonium methoxide* yields propaldehyde.

[By the Author.]—It is probable that phosphonium compounds have a constitution similar to that of ammonium compounds suggested by the author; the existence of phosphorus pentachloride is not evidence against the probability, since the equivalence of the five chlorine atoms has not been proved. The additive compound of phosphenyl chloride and bromine, therefore, should be different from that of phosphenyl bromide and chlorine, the two substances having the constitutions $[PPhCl_2Br]Br$ and $[PPhBr_2Cl]Cl$ respectively. Experiment shows, however, that the two substances are identical.

C. S.

Action of Ethylene Dibromide, Methylene Iodide, and Iodine on Ethyl Aminocrotonate. ERICH BENARY (*Ber.*, 1913, **46**, 1375—1377).—Unlike chloroacetyl chloride, ethylene dibromide and methylene iodide do not form pyrrole derivatives on condensation with ethyl aminocrotonate in presence of pyridine, but they give rise to ethyl dihydrocollidinedicarboxylate and ethyl lutidinedicarboxylate respectively. When iodine is added to the sodium compound of ethylaminocrotonate in ether, *ethyl iodoaminocrotonate*, $NHI\cdot CMe\colon CH\cdot CO_2Et$, is obtained in soft leaflets, m. p. 83—84°, which are hydrolysed by dilute sulphuric acid to ethyl α-iodoacetoacetate (compare ethyl bromoaminocrotonate, Behrend, A., 1900, i, 210). J. C. W.

The Reaction Products of Ammonia on Ethyl Dicarbintetracarboxylate. ROLAND SCHOLL, KARL HOLDERMANN, and ARMIN LANGER (*Monatsh.*, 1913, **34**, 623—629).—Ethyl dicarbintetracarboxylate [ethyl ethylenetetracarboxylate] is best prepared by the method of Blank and Samson (A., 1899, i, 484). It reacts slowly with a saturated alcoholic solution of ammonia at the ordinary temperature, producing *ethyl α-aminoethane-ααββ-tetracarboxylate*,

$$NH_2\cdot C(CO_2Et)_2\cdot CH(CO_2Et)_2,$$

as an additive product. This is an oily liquid which dissociates into its two components when distilled under reduced pressure and also regenerates ethyl ethylenetetracarboxylate when treated with nitrous acid. The stability of the amino-acid towards acid and alkali is believed to be incompatible with the alternative structure suggested by the two reactions just cited (compare Meister, A., 1888, 675).

If a bomb tube containing a mixture of liquid ammonia and ethyl ethylenetetracarboxylate is kept sealed at the ordinary temperature for sixty hours, tablet or prismatic crystals of *α-aminoethane-ααββ-tetracarboxylamide*, $NH_2\cdot C(CO\cdot NH_2)_2\cdot CH(CO\cdot NH_2)_2$, separate. This substance is unstable and smells of ammonia; it is decomposed by water, and when heated alone, gradually decomposes with final carbonisation. D. F. T.

The Course of the Action of Ammonia on Ethyl Dicarbintetracarboxylate. ERNST PHILIPPI and ALFRED UHL (*Monatsh.*, 1913, **34**, 717—731. Compare preceding abstract).—The paper opens with a discussion of various theories as to the mechanism of amide formation.

Carefully dried ammonia was passed for twenty minutes, after all sign of heat evolution had disappeared, into a suspension of ethyl ethylenetetracarboxylate (ethyl dicarbintetracarboxylate) in absolute alcohol, and the resultant solution kept for three months; a yellowish-white, crystalline crust separated. The alcoholic mother liquid contained a little unaltered ester together with an oily additive *compound* of molecular proportions of ammonia and ester; *platinichloride*, yellow, microscopic, columnar crystals. The additive compound is believed to be *ethyl α-aminoethane-ααββ-tetracarboxylate*, the presence of the carboxyl groups having so increased the activity of the ethylenic linking of the original ester as to cause addition at this position; such addition of ammonia has been observed at the double bond of several ethylenic esters. When boiled for several hours with $2N$-hydrochloric

acid, carbon dioxide is set free, leaving the hydrochloride of aspartic acid. A solution of the additive compound in hydrochloric acid when treated with nitrous acid regenerates ethyl ethylenetetracarboxylate; this behaviour is explained by the primary formation of the expected hydroxy-compound, which immediately passes into the ethylenic ester with loss of a molecule of water. The solid crust obtained in the initial experiment consisted of *α-aminoethane-ααββ-tetracarboxylamide*, a hygroscopic, unstable substance which decomposes on moderate heating. Altogether 89·6% of the original ester could be accounted for in the products. D. F. T.

Internally Complex Metallic Salts of Derivatives of Oxalic Acid and of Triformaldoxime. KARL A. HOFMANN and UDO EHRHARDT (*Ber.*, 1913, **46**, 1457—1466).—Various amido-derivatives of oxalic acid have been examined in connexion with the power of formation of internally complex salts, because their structure is such as to suggest an easy formation of a ring composed of five atons. It is discovered that the stability of the complex salt depends on the number of amido- or imido-groups present, for, of the substances examined, oxamic acid shows least tendency, whilst oxalhydrazide shows the greatest tendency to formation of complex salts. This increase in tendency to form complex salts caused by the increase in supplementary valencies due to the nitrogen atoms accords well with the views of Ley (A., 1905, i, 175) as to the structure of such salts.

As criteria for the occurrence of internally complex salts were accepted an abnormal colour (usually intense), and stability towards alkali and acetic acid. The salts were prepared in each case in alkaline solution, and caused to crystallise by the addition of methyl alcohol.

Oxamic acid under the above conditions gave no complex salt with a nickel, iron, or manganese salt, but with copper acetate and concentrated potassium hydroxide solution, bluish-violet needles of a *potassium-copper* salt, $K_2(NH·CO·CO_2)_2Cu$, were obtained, which are decomposed by excessive alkali or by pure water, yielding copper oxide.

Oxamide gave no compound with iron or manganese, but yielded a *potassium-copper* salt, $K_2(NH·CO·CO·NH)_2Cu,1\frac{1}{2}H_2O$, reddish-violet needles, soluble in alkali to a violet-blue solution, which slowly decomposes, and a *potassium-nickel* salt, $K_2(NH·CO·CO·NH)_2Ni$, bright yellow plates soluble in dilute hydroxide solution to an unstable golden-yellow solution.

Oxalaminohydrazide yielded a *potassium-copper* salt, violet-red needles, $K_2(NH·NH·CO·CO·NH)_2Cu,2H_2O$, which, when moist, undergoes gradual decomposition into a basic copper oxamate, and a *potassium-nickel* salt, $K_2(NH·NH·CO·CO·NH)_2Ni$, golden-yellow rods, which dissolve in water to a reddish-yellow solution without decomposition (compare Kerp and Unger, A., 1897, i, 270; Schiff, A., 1902, i, 85).

Oxalhydrazide in strong alkali solution with nickel acetate gives a violet solution, but on crystallisation yellow, hexagonal prisms of a more complex product are obtained; the *potassium-copper* salt,

$$K_2(N_2H_2·CO·CO·N_2H_2)_2Cu,$$

forms bright brown needles, decomp. 270°, soluble in water to a greenish-yellow colour.

Hydroxyloxamide gives a *sodium-copper* salt,

$$Na_4(NH\cdot CO\cdot CO\cdot NO)_2Cu,4H_2O,$$

reddish-violet needles, and a *sodium-nickel* salt,

$$Na_4(NH\cdot CO\cdot CO\cdot NO)_2Ni,2H_2O,$$

orange-yellow, hexagonal prisms, which decomposes about 280°. From the composition of these two salts the authors are of the opinion that the salts are derived by displacement of hydroxylic hydrogen, and that under the influence of the alkali used in the process of preparation the $-CO\cdot NH_2$ group undergoes a preceding change into the structure $-C(:NH)OH$. With bivalent and tervalent iron, also, hydroxyloxamide gives yellowish-red alkaline solutions.

Oxalodihydroxamic acid gives a *potassium-copper* salt,

$$K_3(C_4N_4O_8H_3)Cu,$$

brownish-red needles, which decompose at 180°, and a *potassium-nickel* salt, $K_3(C_4N_4O_8H_3)Ni,H_2O$, brownish-yellow needles. Cobalt and iron salts in the presence of excess of alkali give reddish-yellow solutions with oxalodihydroxamic acid.

Formaldoxime is known to give deep colorations with copper, iron, and nickel solutions in the presence of potassium hydroxide (compare Dunstan, T., 1898, **73**, 353), but complex salts have now been isolated for the first time. The colour of the solutions is so intense that manganese, iron, and nickel can be detected at a dilution of one part in a million; the solution of the manganous salt is yellow, but rapidly oxidises in the air to a *manganic* salt, $(CH_2:NO)_3Mn,2H_2O$., blackish-brown, rectangular plates, which decompose above 220°, and give an intense reddish-brown solution in water. The almost colourless alkaline solution of the nickelous salt in a similar manner absorbs oxygen, yielding a deep brown solution of the *sodium-nickelic* salt,

$$Na_3(CH_2:NO)_6Ni,$$

steel-blue, lustrous crystals, which decompose near 225°. The volume of oxygen absorbed in the two previous oxidations was in good accord with the theoretical. In a similar manner the yellowish-red alkaline solution of the ferrous salt undergoes gradual oxidation to the deep violet-red solution of the sodium-ferric salt, which is better obtained by using a ferric salt directly; the *sodium-ferric* salt,

$$Na_2(CH_2:NO)_5Fe,H_2O,$$

forms blue, hexagonal plates, which decompose near 195°. The structure of these salts is believed to be analogous to that of the internally complex salts of the dioximes. D. F. T.

Synthesis of Parabanic and Substituted Parabanic Acids. HEINRICH BILTZ and ERNST TOPP (*Ber.*, 1913, **46**, 1387—1404).—The authors have effected the synthesis of parabanic and substituted parabanic acids by the action of oxalyl chloride on carbamide and substituted carbamides in ethereal or, more rarely, acetic anhydride solution. Reaction generally takes place smoothly, and the yields, particularly with doubly-substituted carbamides, are excellent. In the case of parabanic acid itself, and, possibly, of dimethylparabanic acid, however, the older methods are simpler and cheaper.

Parabanic acid was obtained in small yield by the action of a boiling ethereal solution of oxalyl chloride on carbamide, and was identified

by conversion into its silver salt. Oxalyldicarbamide, $C_4H_6O_4N_4$, m. p. 270—275° (decomp.), was isolated as by-product. Similar observations have been made by Bornwater (A., 1911, i, 617). Methylparabanic acid, m. p. 153—154°, b. p. 201—202°/13 mm., and oxalyldimethylcarbamide, m. p. 230—232° (decomp.), were similarly prepared from methylcarbamide. An attempt to prepare oxalyldimethylcarbamide by melting methylparabanic acid with methylcarbamide was unsuccessful. Boiling acetic anhydride converted methylparabanic acid into 3-acetyl-1-methylparabanic acid, m. p. 183—185°, which was also obtained by the action of oxalyl chloride on acetylmethylcarbamide. Cold aqueous hydrochloric acid was without action on it, whilst the hot reagent caused great decomposition. Saturation of an absolute alcoholic suspension of it with hydrogen chloride brought about the elimination of the acetyl group, methylparabanic acid being formed in almost quantitative yield.

Dimethylparabanic acid, leaflets, m. p. 154°, b. p. 148—150°/13 mm., was obtained in 70% yield from *s*-dimethylcarbamide and oxalyl chloride, and also from *s*-dimethylcarbamide and ethyl chloropyruvate.

Dimethylcarbamide hydrochloride, needles, m. p. 124°, was obtained by saturating a solution of *s*-dimethylcarbamide in ethyl acetate with hydrogen chloride. *Methylcarbamide hydrochloride*, prepared similarly, is very hygroscopic. It has m. p. about 85—87° after softening at about 70°, and evolves hydrogen chloride at about 125°.

Ethylparabanic acid, m. p. 127—128°, and *oxalyldiethylcarbamide*, needles, m. p. 220—222° (decomp.), were obtained from ethylcarbamide and oxalyl chloride. The properties of the first-named substance differ from those of the ethylparabanic acid described by Andreasch (A., 1898, i, 243).

9-Ethyluric acid glycol (A., 1910, i, 526) was oxidised by potassium dichromate and sulphuric acid to ethylparabanic acid. An attempt was also made to degrade the former substance to the latter in the manner adopted for 7 : 9-dimethyluric acid (Biltz and Krebs, A., 1910, i, 521). An aqueous solution of the glycol was converted by heat into 5-*hydroxy* - 3 - *ethylhydantoylcarbamide*, which was transformed into 3-*ethylcaffolide* and ammonium chloride when treated with hydrochloric acid and subsequently evaporated to dryness. When an aqueous solution of 3-ethylcaffolide was boiled, 5-*hydroxy*-3-*ethylhydantoylamide* was formed, which, when oxidised, yielded ethylparabanic acid. The intermediate products could not be obtained in the crystalline state, but the course of the degradation can be deduced from the final product and from the isolation of the by-products expected in the various stages.

Diethylparabanic acid, needles, m. p. 49—51°, b. p. 138—140°/13 mm., was obtained in 78% yield from *s*-diethylcarbamide and oxalyl chloride, and was identical with the product obtained by the degradation of 7 : 9-diethyluric acid glycol (A., 1911, i, 693). Diethylthioparabanic acid had b. p. 148—150°/13 mm.

Phenylparabanic acid, m. p. 213—214° after softening at 208° [Stojentin (A., 1885, 1196) gives m. p. 208°], diphenylparabanic acid, m. p. 202° after previous softening, *benzylparabanic acid*, m. p.

167—169°, and pp-*bisbromophenylparabanic acid*, $C_{15}H_8O_3N_2Br_2$, were prepared in an analogous manner.

Thiocarbamide reacted vigorously with oxalyl chloride at first, but, even in the presence of a considerable excess of the latter, was not completely converted into *thioparabanic acid*. By repeated crystallisation from ethyl acetate, the latter was obtained in yellowish-red, indistinct crystals, m. p. 215—220° (decomp.), and was further identified by conversion into the *silver* salt, $C_3O_2N_2SAg_2$, and transformation of the latter into 1 : 3-dimethylthioparabanic acid, m. p. 113—115° [Andreasch (A., 1881, 897) gives 112·5°], by means of methyl iodide. When desulphurised by means of hydrochloric or nitric acids, this substance yielded dimethylparabanic acid. Dimethylthioparabanic acid was also prepared by the action of oxalyl chloride on dimethylthiocarbamide, and then had m. p. 113—115°, after softening at 110°, b. p. 153—155°/13 mm.

The authors have also examined the "thioparabanic acid" obtained by Michael (A., 1894, i, 164) by the condensation of thiocarbamide with ethyl oxalate in the presence of sodium ethoxide. They find that it softens at 165°, and has m. p. 173—175° (decomp.). The fusion separates into two layers, the upper one of which begins to distil at about 190°. Since also this substance slowly yields a precipitate with calcium chloride and ammonia, even at the ordinary temperature, the authors are led to the conclusion that it is an additive compound of thiocarbamide and ethyl oxalate (compare Nencki, A., 1874, 981).

Ethylthioparabanic acid was obtained in small yield from ethylthiocarbamide and oxalyl chloride, the loss being chiefly attributable to the difficulty of separating the acid from unchanged ethylthiocarbamide by crystallisation. The observed m. p., 65—69°, is sufficiently close to that found by Andreasch (66°, *loc. cit.*) to prove the identity of the two products. Desulphurisation by means of a boiling alcoholic solution of silver nitrate converted ethylthioparabanic acid into ethylparabanic acid, m. p. 127—128°.

Diphenylthioparabanic acid, pale yellow needles, m. p. 228—230°, was obtained in 94% yield from *s*-diphenylcarbamide and ethereal oxalyl chloride. H. W.

Oxalyldicarbamide. HEINRICH BILTZ and ERNST TOPP (*Ber.*, 1913, **46**, 1404—1417. Compare preceding abstract, and also Bornwater, A., 1911, i, 617).—When an ethereal solution of oxalyl chloride reacts with finely-powdered carbamide, parabanic acid is formed together with a substance characterised by its very sparing solubility in ordinary solvents, to which the constitution $C_2O_2(NH{\cdot}CO{\cdot}NH_2)_2$ is ascribed. This latter substance differs from the oxalyldicarbamide prepared by Grimaux by the fusion of a mixture of parabanic acid and carbamide (A., 1880, 105) in that it gives no biuret reaction, whereas Grimaux's compound yields a faint violet coloration with potassium hydroxide and copper sulphate. Further, oxalyldicarbamide may also be obtained by the oxidation of allantoin in acid solution, 5-hydroxyallantoin being formed as an intermediate product :

$$CO<\begin{matrix}NH{\cdot}C(OH){\cdot}NH{\cdot}CO{\cdot}NH_2\\ NH{\cdot}CO\end{matrix} \longrightarrow C_2O_2(NH{\cdot}CO{\cdot}NH_2)_2.$$

The authors have made a comparative critical examination of these three products, and are led to the conclusion that they are probably identical. The coloration given by Grimaux's compound with potassium hydroxide and copper sulphate is probably due to the presence of some impurity, the nature of which could not be established, but which is neither biuret, oxamide, allantoxanic acid nor allantoxaidine. Certain differences, however, remain unexplained. Thus, oxalyldicarbamide, when acted on by hydriodic acid, yields hydantoin together with other products, whilst, in similar circumstances, Grimaux's compound gives a *substance*, $C_4H_5O_3N_3$, in small quantity. Also, potassium hydroxide transforms all three compounds mainly into oxaluric acid and oxalic acid, but differences are found among the by-products of the action.

Ponomarev's observation (A., 1885, 760) that concentrated potassium hydroxide converts Grimaux's compound into potassium allantoxanate is probably incorrect.

Oxalyldicarbamide was obtained by the oxidation of an aqueous solution of allantoin and sodium acetate by means of ammonium persulphate or by potassium permanganate in dilute acetic acid solution. A portion of the allantoin remained unattacked even when an excess of the oxidising agent was used, whilst, also, oxaluric acid was formed. The latter was isolated in the form of its *ammonium* salt, needles, decomposing at 243—245°, from which the free acid and also the silver salt were obtained.

Grimaux's compound was obtained by heating a mixture of parabanic acid and carbamide and purified by extraction with boiling water. Such preparations yielded with potassium hydroxide and copper sulphate violet colorations of varying intensity. By repeated solution of the product in concentrated sulphuric acid, re-precipitation by means of water, and subsequent repeated extraction with boiling water, substances were obtained which gave only a very faint violet coloration, but the impurity could not thus be completely removed.

All three preparations evolved ammonia at the ordinary temperature when treated with potassium hydroxide (D 1·1—1·4). Under similar conditions oxalyldimethylcarbamide evolved only methylamine, whilst oxalyldiethylcarbamide gave ethylamine. These substances must therefore have the formulæ $C_2O_2(NH{\cdot}CO{\cdot}NHMe)_2$ and $C_2O_2(NH{\cdot}CO{\cdot}NHEt)_2$ respectively.

When treated with potassium hydroxide under varying conditions, neither of the compounds yielded potassium allantoxanate. Specimens of oxalyldicarbamide, prepared from oxalyl chloride or from allantoin, yielded carbon dioxide, potassium oxalate, and potassium oxalurate. Grimaux's compound yielded mainly potassium oxalurate; sometimes, also, a potassium salt which crystallised in short prisms, became somewhat discoloured at 280°, but was not greatly decomposed at 360°. This salt was probably derived from the impurity which yields the violet coloration, since it gave a distinct violet colour with potassium hydroxide and copper sulphate. In one experiment a second potassium salt, prisms, was obtained, which, with hydrochloric acid, yielded the free acid. The latter was sparingly soluble in water, darkened from 275° onwards, but showed no decomposition point below 360°.

The three compounds were very stable towards acid, and no differences were observed in their behaviour in this respect. Oxalic acid, but no parabanic acid, was obtained from each by the action of boiling fuming nitric acid. Concentrated hydriodic acid (D 1·5) converted Grimaux's compound into oxalic acid. The formation of methyl- and ethyl-parabanic acids by the action of boiling glacial acetic acid on dimethyl- and diethyl-oxalyldicarbamide (compare previous abstract) must be attributed to the formation of the glyoxalone ring during the course of the action, since oxaluric acid itself is partly transformed into parabanic acid by prolonged treatment with boiling glacial acetic acid.

Hydantoin, m. p. 215—217°, and ammonium iodide were obtained by the action of fuming hydriodic acid (D 1·96) at 130—140° on oxalyldicarbamide obtained from oxalyl chloride or from allantoin. Under similar treatment, Grimaux's compound yielded a substance, $C_4H_5O_3N_3$, leaflets, m. p. 270—273° (decomp.), which behaved as a monobasic acid. The *ammonium* salt formed needles, which decomposed at 270—273°. The *silver* salt, $C_4H_4O_3N_3Ag$, was analysed, and appeared to contain a certain amount of silver united to nitrogen.

H. W.

Oxalyl Chloride. V. Oxalyl Bromide and Attempts to Prepare Dicarbon Dioxide. HERMANN STAUDINGER and E. ANTHES (*Ber.*, 1913, **46**, 1426—1437. Compare A., 1912, i, 567).—The authors have prepared oxalyl bromide, which they find to be more readily decomposed by heat and more reactive than the corresponding chloride. In the hope of isolating dicarbon dioxide, CO:CO, they have investigated the action of metals on it. Ready interaction occurs with both zinc and mercury, but in each case carbon monoxide is evolved, so that dicarbon dioxide is probably incapable of existence at the ordinary temperature. With potassium, or the liquid alloy of sodium and potassium, an explosive product is formed, to which the authors attribute the composition OK·C:C·OK.

Phosphorus pentabromide (2 mols.) reacts slowly with anhydrous oxalic acid (1 mol.). If the mixture is warmed, oxalyl bromide is not obtained, nor is the process improved by mixing the materials with sand. If, however, phosphoryl bromide is mixed with phosphorus pentabromide, the dried oxalic acid added, and the mixture maintained at 50° during one day and subsequently distilled, small quantities of oxalyl bromide are obtained. A better method consists in the treatment of well-cooled oxalyl chloride with hydrogen bromide (compare this vol., i, 616), when oxalyl bromide is obtained in 85% yield. It is a greenish-yellow liquid, b. p. 102—103°/720 mm., 16—17°/10 mm., m. p. −19·5°.

A boiling 20% ethereal solution of oxalyl chloride does not react with zinc even after addition of iodine, mercuric chloride, or a trace of water. In ethyl acetate solution, reaction occurs if the zinc has been activated by means of diphenylchloroacetyl chloride. Carbon monoxide is then formed. Mercury, sodium, silver, or magnesium turnings do not react with oxalyl chloride, but a brown precipitate is obtained with magnesium powder in the presence of ether, investigation of

which is incomplete. The vapour of oxalyl chloride is practically completely decomposed by silver at 200°, carbon monoxide being formed. With zinc practically no action occurs.

Oxalyl bromide, on the other hand, is readily decomposed by zinc or mercury at the ordinary temperature, carbon monoxide being formed. Mercurous bromide has no action on it at the ordinary temperature or at 100°. Sodium potassium amalgam reacts with oxalyl bromide without marked development of heat or alteration in appearance. The product, however, explodes violently when subjected to vibration. Attempts to cause potassium to react with oxalyl bromide vapour at 130° or in xylene solution were unsuccessful.

Oxalyl bromide gradually becomes pale reddish-brown when preserved, owing to separation of bromine, decomposition being catalysed by light. At 100° it is stable, but at 150—200° is decomposed into carbon monoxide, bromine, and carbonyl bromide. Oxalyl chloride, on the other hand, could be heated during eighteen hours at 200° without noticeable decomposition occurring; at 340° it is completely decomposed during seventy hours into carbon monoxide and carbonyl chloride.

Oxalyl bromide reacts readily with benzaldehyde in light petroleum solution, forming a white additive *product*, m. p. 131°, with decomposition into benzaldehyde, benzylidene bromide, and carbon monoxide. Under similar conditions an additive *product* is slowly formed from oxalyl chloride, which, when rapidly heated, has m. p. about 21·2°, but loses carbon monoxide at a lower temperature.

Oxalyl bromide reacts more readily than the corresponding chloride with dimethylaniline, dimethylaminobenzoic acid, crystal-violet and tetramethyldiaminobenzil being formed.

Oxalyl iodide could not be isolated by the action of hydrogen iodide on oxalyl chloride. Even at −80° only carbon monoxide and iodine were obtained. The latter substances were also produced quantitatively when a solution of oxalyl chloride in ethyl acetate was boiled with sodium iodide.

Unsuccessful attempts were also made to obtain diphenyloxalimino-bromide and iodide by the action of the requisite halogen acid on diphenyloxalimino-chloride, NPh:CCl·CCl:NPh. The bromide could not be obtained from oxanilide by the action of phosphorus tri- or penta-bromide. H. W.

An Ester of Hydrocobalticyanic Acid. CHARLES E. BOLSER and L. B. RICHARDSON (*J. Amer. Chem. Soc.*, 1913, **35**, 377—381).—By the action of ethyl iodide on silver cobalticyanide, suspended in alcohol, *ethyl dihydrogen cobalticyanide*, $EtH_2Co(CN)_6,H_2O$, has been obtained as a yellowish-white solid which loses its water of crystallisation at a little over 100° and becomes blue. On the addition of silver nitrate to a solution of the ester, *disilver ethyl cobalticyanide* is produced as a white precipitate; a *copper* salt was also obtained. When the ester is treated with sodium hydroxide, ethylcarbimide is evolved, indicating that the ethyl group in some, if not all, of the molecules is attached to nitrogen.

An attempt was made to prepare the corresponding ester of hydroferricyanic acid, but without success. E. G.

Reaction of Nitroprussides with Acetone. LIVIO CAMBI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 376—381).—In this reaction the production of the coloration is accompanied by the production of oximinoacetone, for it is possible to isolate in impure form a coloured salt which yields this compound on treatment with alkali. Analogous results were obtained in the case of acetophenone, a coloured salt being obtained which yielded oximinoacetophenone when treated with alkali. R. V. S.

Maximum Yield of Amines by the Reduction of Alkyl Cyanides. JITENDRA NATH RAKSHIT (*J. Amer. Chem. Soc.*, 1913, **35**, 444—446).—A study of the conditions under which amines are produced by the reduction of nitriles has shown that the best yields can be obtained by the following modification of Ladenburg's method.

The nitrile (5 c.c.) is dissolved in 75 c.c. of alcohol and the solution is introduced in successive quantities of 5 c.c. into a flask containing 5 grams of sodium and attached to a reflux condenser. The mixture is heated at 50—60°. After 20 c.c. of the solution have entered the flask, 5 c.c. of alcohol are added, and the amine evolved on distillation is absorbed in dilute hydrochloric acid. When the whole of the nitrile solution has been introduced, alcohol is added until a layer remains above the solid sodium ethoxide in the flask. When the evolution of hydrogen ceases, the condenser is removed and the flask is connected directly to the absorption apparatus and heated as long as alkaline vapour is produced. If necessary, a further quantity of alcohol is added and the distillation continued. The acid solution is evaporated to dryness on the water-bath, and the amine hydrochloride extracted from the residue with a mixture of alcohol (15 c.c.) and ether (10 c.c.).

The results of experiments with acetonitrile, propionitrile, and butyronitrile show that the amines can be obtained by this method in nearly quantitative yield. E. G.

Amylene-*iso*nitroamineoxime and -bisnitroso*iso*nitroamine. GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 225—231. Compare A., 1911, i, 186).—Cryoscopic molecular weight determinations on the β-nitrosohydroxylamino-β-methylbutan-γ-oneoxime previously described, and on its sodium salt indicate that the compound is probably a bisnitroso*iso*nitroamine. Its formation is probably preceded, however, by that of an *iso*nitroamineoxime which suffers rearrangement and polymerisation. In fact, the freshly prepared substance has m. p. 71°; later, or after recrystallisation, the m. p. is 82°, as formerly stated. Hence it is possible to proceed from oximes of the type $\dot{:}CX{\cdot}C{:}N{\cdot}OH$ to nitrosyl compounds, $:CX{\cdot}\dot{C}H{\cdot}NO$.

When the bisnitroso*iso*nitroamine is treated with sodium nitrite in aqueous solution, the bisnitroso-oxime, $(NO{\cdot}CMe_2{\cdot}CMe{:}NOH)_2$, is

formed; the crystals at first melt at 83°, but later on, or after recrystallisation, the m. p. is 140°; the substance is soluble in alkali hydroxides and in acids, and gives a blue coloration with diphenylamine and sulphuric acid.

The *iso*nitroamineoxime previously described yields an *ethyl* ester, $C_7H_{15}O_3N_3$, m. p. 119°, which is prepared by means of the *silver* salt.

The iso*nitroamine* of β-methylbutan-γ-one, $CMe_2(N_2O_2H)\cdot COMe$, is obtained by the action of hydrochloric acid on the sodium salt of the *iso*nitroamineoxime, or by the action of nitrous acid on β-hydroxylamino-β-methylbutan-γ-one (previously described); it forms large, tabular crystals, m. p. 62°, and gives a blue coloration with diphenylamine and sulphuric acid. The substance has acid properties and is fairly stable, but when heated above its m. p. decomposes, leaving a partially crystalline residue, from which a substance crystallising in quadrangular tablets, m. p. 99°, can be isolated. R. V. S.

Preparation of Fatty Acids and their Salts containing Arsenic and Phosphorus. FELIX HEINEMANN (D.R.-P. 257641).—When the unsaturated acids of the acetylene series are heated with the halogen derivatives of arsenic or phosphorus, they furnish acidic compounds having a high molecular weight and containing a halogen substituent in addition to phosphorus (or arsenic); they give rise to soluble alkali, and insoluble calcium and strontium salts.

The *compound* produced when stearolic acid and arsenic trichloride (1·5 parts) are heated together at 140° during six hours is obtained (by extraction with ether) as a viscous oil which gradually in part solidifies; it contains As = 11% and chlorine 6—7%; the *strontium* salt, a flesh-coloured powder, contains 12% As; the *calcium* salt is also mentioned.

The *compound* from behenolic acid and arsenic trichloride is a pale brown, viscous oil containing 8—9% As and 5—6% Cl; the *strontium* salt is a colourless powder.

When stearolic acid is heated with an equal quantity of phosphorus trichloride at 140° during fifteen hours, it furnishes two acidic *compounds*; one a viscous, brownish-yellow acid extractable with ether containing P = 4—5% and Cl = 8%; the other an orange-yellow resin insoluble in ether and containing P = 15%. The analogous *compound* from behenolic acid and phosphorus trichloride, and the *strontium* and *calcium* salts are also described, whilst the arsenic and phosphorus chlorides employed can be replaced by the corresponding bromides.

F. M. G. M.

The Benzene Problem. HANS VON LIEBIG (*J. pr. Chem.*, 1913, [ii], **87**, 393—397. Compare A., 1912, i, 686).—A reply to Gebhard's criticism (this vol., i, 28). F. B.

3 : 3-Dimethyl-[0,1,3]-*dicyclo*hexane. Its Synthesis and Behaviour on Catalytic Reduction. NICOLAI D. ZELINSKI and A. E. USPENSKI (*Ber.*, 1913, **46**, 1466—1474).—The starting point for this substance was 1 : 1-dimethyl*cyclo*hexane-3 : 5-dione, which was prepared by a slight modification of the process of Vorländer (A.,

1897, i, 275); this substance is reduced by the gradual addition of sodium to a hot solution in absolute alcohol with the formation of 1 : 1-*dimethyl*cyclo*hexane*-3 : 5-*diol*, a sweet substance which separates from a mixture of benzene and acetone in lustrous, colourless needles. By heating with phosphorus tribromide in a sealed tube at 110—120°, this glycol is converted into 3 : 5-*dibromo*-1 : 1-*dimethyl*cyclo*hexane*, a colourless liquid, b. p. 120—122°/12 mm., D_4^{18} 1·5865, n^{18} 1·5329, which can also be obtained, but less advantageously, by the action of hydrobromic acid on the glycol. Zinc dust acts readily on a warm aqueous-alcoholic solution of this dibromide with the formation of a second ring, the product being 3 : 3-*dimethyl*-[0,1,3]-bicyclo*hexane*,

$$CH_2<\begin{matrix}CH-CH_2\\ | \\ CH-CH_2\end{matrix}>CMe_2.$$

This substance is a colourless liquid, b. p. 115° (corr.), D_4^{20} 0·7962, n^{20} 1·4331, which reacts vigorously with dry bromine, but only slightly with sulphuric acid diluted with half its bulk of water or also with cold dilute potassium permanganate solution. The formation of hydrogen bromide in the first reaction and the lack of change with the other reagents indicate the saturated nature of the hydrocarbon; in fact, treatment with potassium permanganate solution was resorted to as a means of removing small quantities of an olefinic cyclic hydrocarbon impurity. For the purpose of comparison, the isomeric 1 : 1-dimethyl-Δ^3-*cyclo*hexene (Crossley and Renouf, T., 1905, **87**, 1491) was examined, and the following values obtained: b. p. 117—117·5° (corr.), D_4^{20} 0·7994, n^{20} 1·4430, the differences in the density and refractivity indicating the more saturated nature of the new substance.

When 3 : 3-dimethyl-[0,1,3]-*dicyclo*hexane is heated with hydriodic acid at 100—110°, an iodo-compound is obtained, which can be reduced in alcoholic solution by zinc dust, yielding a hydrocarbon which from its properties, b. p. 115—116°/760 mm., D_4^{20} 0·7703, n^{20} 1·4223, and its indifference towards permanganate and bromine is probably 1 : 1 : 3-*trimethyl*cyclo*pentane*. That the fission of the trimethylene ring has occurred thus and not at the 2 : 6 linking is evidenced by the distinct nature of the otherwise expected *gem*-dimethylhexamethylene (Crossley, *loc. cit.*). Reduction by hydrogen under the catalytic influence of platinum-black at 125°, or by palladium-black at 55—60°, followed a quite different course, the product, b. p. 109·5—110·5° (corr.), D_4^{20} 0·7403, n^{20} 1·4088, being probably 1-*methyl*-2-iso*butyl*cyclo*propane*. As might be expected (Zelinski, A., 1913, i, 254), reduction by hydrogen under the influence of nickel causes a more considerable change, and even with reduction at 95—100° the physical properties of the product indicate the admixture of the above *cyclo*propane derivative with an appreciable quantity of an octane. D. F. T.

Anhydrides of Aromatic Sulphonic Acids. HANS MEYER and KARL SCHLEGL (*Monatsh.*, 1913, **34**, 561—577).—The action of thionyl chloride on aromatic sulphonic acids presents another example of the very considerable effect of minute traces of foreign substances

on the course and products of a chemical change. The product may be, in this case, the sulphonic anhydride, the sulphonyl chloride, or a mixture of both; the variation is apparently due to traces of impurity in the thionyl chloride, but in the majority of cases investigated no trustworthy decision could be made as to the disturbing factor. The formation of chloride and anhydride appears to be concurrent.

The sulphonic acid anhydrides are colourless or pale yellow, crystalline solids, which are remarkably stable towards water and weak alkali. They react with alcohol, ammonia, and amines, producing the corresponding esters and amides; they can be sulphonated and nitrated. On account of their sparing solubility in indifferent organic solvents they can easily be separated from the very soluble acid chlorides. It is surprising that, although they are stable towards water in bulk, yet they become easily hydrated by moist solvents or by exposure to damp air. The thionyl chloride used for their preparation was purified by distillation over quinoline or dimethylaniline (compare Besthorn, A., 1909, i, 673), the remaining yellow coloration being removed by further successive distillations over linseed oil and pure bees-wax.

Benzenesulphonic acid when heated with excess of thionyl chloride passes into solution with loss of its water of crystallisation, and after further heating, the solution, when cooled, deposits a mixture of benzenesulphonyl chloride with the anhydride, m. p. 90—91° (Billeter, A., 1905, i, 584); the latter substance was usually the preponderating constituent, but occasionally, with apparently the same conditions, the case was the reverse. Silver benzenesulphonate reacts with thionyl chloride yielding the acid chloride as the sole product.

p-*Bromobenzenesulphonic anhydride*, obtained by heating the acid with thionyl chloride and pouring the reaction mixture into ice water, is a colourless, crystalline substance, m. p. 164—167° (decomp.).

2 : 5-Dibromobenzenesulphonic anhydride, obtained by a similar process to the last, is a crystalline powder (compare Rosenberg, A., 1886, 551).

m-*Nitrobenzenesulphonic anhydride*, obtained analogously, forms colourless crystals decomposing at 130—140°; the accompanying *chloride* had m. p. 58°.

p-*Toluenesulphonic anhydride*, crystals, m. p. 122—125°, is obtained together with the chloride by heating *p*-toluenesulphonic acid with pure thionyl chloride; if the thionyl chloride is not pure, the acid chloride is the sole product.

Mesitylenesulphonic anhydride is often obtained mixed with the corresponding chloride if mesitylenesulphonic acid is heated with commercial specimens of thionyl chloride. If the last substance has been purified the only product is the acid chloride, but the power to produce the anhydride is restored to the thionyl chloride by distilling it with sulphur chloride. Sodium mesitylenesulphonate behaves in the same curious manner with the various specimens of thionyl chloride.

ψ-Cumenesulphonic anhydride is obtained mixed with the corre-

sponding acid chloride under the reverse conditions to those observed in the last case. Purified thionyl chloride gives rise to a mixture of the acid anhydride and acid chloride, whilst the commercial substance yields the acid chloride only.

α-Naphthalenesulphonic anhydride could not be obtained as the corresponding acid and also the sodium salt of the acid were converted by thionyl chloride entirely into the acid chloride.

β-Naphthalenesulphonic anhydride, a pale yellow, crystalline substance, is obtained together with the *chloride*, m. p. 73—74°, by the interaction of β-naphthalenesulphonic acid and excess of thionyl chloride.

α-Anthraquinonesulphonic acid, yellow crystals, m. p. 210—211°, and also the β-isomeride are converted by thionyl chloride entirely into α- and β-anthraquinonesulphonyl chlorides, crystalline solids, m. p. 203—204° and 185—187° respectively.

2-Chloro-5-nitrobenzenesulphonic anhydride forms colourless crystals, m. p. 120—125° (decomp.).

Ethanesulphonic acid with thionyl chloride yielded the acid chloride, whilst 3-pyridinesulphonic acid failed to react. D. F. T.

Tridiphenylylmethyl. WILHELM SCHLENK (*Ber.*, 1913, **46**, 1475—1481. Compare A., 1910, i, 236).—In reply to Schmidlin (this vol., i, 32) it is stated that the tridiphenylylmethyl obtained earlier by the author (*loc. cit.*) is a homogeneous product, and that the supposed isomeride of Schmidlin is due to an impurity caused by the presence of 4:4′-dibromodiphenyl in the *p*-bromodiphenyl used. In the subsequent Grignard reaction by which the carbinol is produced, the former substance gives rise to 4:*4′-diphenylene-bis-[bidiphenylylcarbinol]*, $OH\cdot C(C_6H_4Ph)_2\cdot C_6H_4\cdot C_6H_4\cdot C(C_6H_4Ph)_2\cdot OH$, which, mixed with tridiphenylylcarbinol, constitutes Schmidlin's "β-tridiphenylylcarbinol."

4:4′-Diphenylene-bis-[-bidiphenylylcarbinol] can be obtained pure by the condensation of 4:4′-di-iododiphenyl with bisdiphenylylketone and also of ethyl diphenyl-4:4′-dicarboxylate with iododiphenyl, in each case by the Grignard process. The substance is being more closely investigated. D. F. T.

α-Naphthylbisdiphenylylmethyl. WILHELM SCHLENK and C. BORNHARDT (*Ber.*, 1913, **46**, 1482—1483).—Contrary to the opinion of Schmidlin and Bergmann (this vol., i, 46), *α-naphthylbisdiphenylylcarbinol*, $C_{10}H_7\cdot C(C_6H_4Ph)_2\cdot OH$, can be readily obtained by the action of magnesium α-naphthyl bromide on bisdiphenylyl ketone; it forms prismatic crystals, m. p. 228°, which give a bluish-violet solution in sulphuric acid. When heated with a mixture of acetyl chloride and benzene, it is converted into *chloro-α-naphthylbisdiphenylylmethane*, $C_{10}H_7\cdot C(C_6H_4Ph)_2Cl$, m. p. 214—216°, which gives a deep blue solution in molten phenol. If the chloro-compound is heated in benzene solution with copper bronze under an atmosphere of carbon dioxide, *α-naphthylbisdiphenylylmethyl* is obtained, which separates from its brownish-red benzene solution as a greyish-green, crystalline powder. As a

solution of this substance which has been converted into the peroxide by shaking with air does not regain any of its original colour on keeping, it is probable that the substance is almost entirely unimolecular. D. F. T.

Preparation of Aromatic Nitroamino-compounds. HEINRICH BART (D.R.-P. 258059).—When 3-nitro-4-hydroxyazobenzene-4′-sulphonic acid, $OH \cdot C_6H_3(NO_2) \cdot N:N \cdot C_6H_4 \cdot SO_3H$, is reduced with iodine and sulphurous acid (or phosphorus) it furnishes sulphanilic acid and 3-*nitro*-p-*aminophenol*, glistening. red needles, m. p. 127°, whilst 3-nitro-*p*-aminophenol, together with 4-chloroaniline-3-sulphonic acid, is obtained in a similar manner from 3-nitro-4-hydroxy-4′-chloroazobenzene-3′-sulphonic acid, $OH \cdot C_6H_3(NO_2) \cdot N:N \cdot C_6H_3 \cdot Cl \cdot SO_3H$.
F. M. G. M.

Preparation of 5-Chloro-6-amino-1-naphthol-3-sulphonic Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 258299). —When β-naphthylamine-5 : 7-disulphonic acid is treated with *p*-toluenesulphonyl chloride and the product subsequently chlorinated, it gives rise to 1-*chloro*-2-p-*toluenesulphonylaminonaphthalene*-5 : 7-*disulphonic acid*, a pale yellow, crystalline powder ; when this is fused at 150—180° with potassium hydroxide, it furnishes 5-*chloro*-6-p-*toluenesulphonylamino*-1-*naphthol*-3-*sulphonic acid*, a red, crystalline powder, which when stirred into fuming sulphuric acid yields 5-*chloro*-6-*amino*-1-*naphthol*-3-*sulphonic acid*. F. M. G. M.

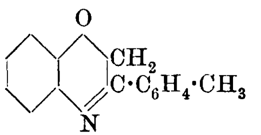
Preparation of Creosol (*p*-Hydroxytolyl 3-Methyl Ether). SACCHARIN-FABRIK AKTIENGESELLSCHAFT VORM. FAHLBERG, LIST & CO. (D.R.-P. 258105. Compare A., 1877, ii, 888; 1899, i, 346).—When homocatechol is treated with methyl sulphate, it furnishes a 70% yield of pure creosol together with 5—6% of homoveratrole.
F. M. G. M.

Desmotropy of Phenols in the Anthracene Series. ROLAND SCHOLL (*Ber.*, 1913, **46**, 1442).—A claim for priority against Meyer and Schlösser (this vol., i, 295). H. W.

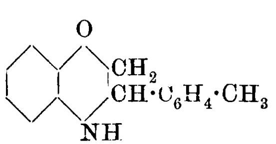
Certain *p*-Toluoylmethyl-, Phenyl-, Nitrophenyl-, Tolyl- and Naphthyl-ethers; 3-*p*-Tolyl-1 : 4-benzoxazine and 3-*p*-Tolylphenmorpholine and their Derivatives. FRANZ KUNCKELL [with KARL PULS] (*Ber. Deut. pharm. Ges.*, 1913, **23**, 269—278).—A series of ethers has been prepared by the action of *p*-tolyl chloromethyl ketone, $C_6H_4Me \cdot CO \cdot CH_2Cl$, on the sodium or potassium salts of phenols.

Phenyl-p-*toluoylmethyl ether*, $C_6H_4Me \cdot CO \cdot CH_2 \cdot OPh$, white needles, m. p. 73—75°, is prepared by boiling an alcoholic solution of *p*-tolyl chloromethyl ketone with an aqueous solution of potassium phenoxide. When dissolved in alcohol and treated with an excess of bromine water, it yields a monobromo-*derivative*, $C_{15}H_{13}O_2Br$, needles, m. p. 105—107°. The similarly prepared p-*nitrophenyl* p-*toluoylmethyl ether* forms pale yellow leaflets, m. p. 165—166°, and is transformed by

phenylhydrazine in acetic acid solution into a somewhat unstable *phenylhydrazone*, yellow needles, m. p. 167—168°. o-*Nitrophenyl* p-*toluoylmethyl ether* is best obtained by heating an intimate mixture of dry potassium *o*-nitrophenoxide with *p*-tolyl chloromethyl ketone at 70°, and crystallises in yellowish-white needles, m. p. 123—124°. p-*Chlorophenyl* p-*toluoylmethyl ether* forms a white, crystalline powder, m. p. 123—124°. Phenyl *p*-toluoylmethyl sulphide, m. p. 64°, is obtained by heating a mixture of sodium phenyl sulphide and *p*-tolyl chloromethyl ketone with light petroleum at 80° during several hours. m-*Tolyl* p-*toluoylmethyl ether*, white leaflets, m. p. 72°, and p-*tolyl* p-*toluoylmethyl ether*, needles, m. p. 101—102°, are similarly prepared. o-*Tolyl* p-*toluoylmethyl ether*, needles, has m. p. 82°. p-*Toluoylmethyl β-naphthyl ether*, prepared by boiling an alcoholic solution of *p*-tolyl chloromethyl ketone with a solution of *β*-naphthol in aqueous potassium hydroxide, forms colourless, rhombic crystals, m. p. 82—83°. The similarly obtained p-*toluoylmethyl a-naphthyl ether*, m. p. 99—101°, yields with bromine in acetic acid solution a *compound*, $C_{19}H_{15}O_2Br$, silky needles, m. p. 148—150°.



(I.)



(II.)

3-p-*Tolyl* 1 : 4-*benzoxazine* (formula I.), m. p. 90—92°, is obtained by the reduction of a cold alcoholic solution of *o*-nitrophenyl *p*-toluoylmethyl ether by stannous chloride and fuming hydrochloric acid. Its *hydrochloride* was analysed. When the same ether is reduced at a higher temperature by tin and hydrochloric acid, 3-p-*tolylphenmorpholine* (formula II.) is formed in white needles, m. p. 67—68°. It yields a *nitroso*-derivative, m. p. 101—102°. The *hydrochloride*, needles, m. p. 190—191°, and the *platinichloride*, m. p. 180—182°, were analysed.

H. W.

Syntheses in the Fatty Aromatic Series. IX. JULIUS VON BRAUN, A. GRABOWSKI, and G. KIRSCHBAUM (*Ber.*, 1913, **46**, 1266—1282. Compare A., 1912, i, 265 ; 1911, i, 830).—A systematic investigation of the effect of alterations in structure on the odour of the primary alcohols and aldehydes of the phenylethane and phenylpropane groups. It is found that the introduction of a methyl radicle into the benzene ring has very little effect, but that such substitution at the carbon atom adjacent to the carbinol or aldehyde group of phenylpropyl alcohol or phenylpropaldehyde causes a characteristic change in the odour; substitution of a methyl radicle into the corresponding position of the phenylethane derivatives or at the carbon atom adjacent to the benzene ring in the phenylpropane derivatives produces only a slight weakening of the odour of the parent substances.

m-Xylyl bromide, $C_6H_4Me\cdot CH_2Br$, was converted through the cyanide into tolylethylamine, the benzoyl derivative of which when fused with phosphorus pentachloride and then distilled under reduced

pressure, undergoes decomposition into benzonitrile and m-*tolylethyl chloride*, a colourless liquid of pleasant odour, b. p. 112°/23 mm.; this on heating with sodium acetate and acetic acid for fifteen hours yields the corresponding *acetate*, a liquid of fruity odour, b. p. 130°/18 mm., which is easily hydrolysed to β-m-*tolylethyl alcohol*,

$$C_6H_4Me\cdot CH_2\cdot CH_2\cdot OH,$$

a liquid, b. p. 123—125°/18 mm., D_4^{20} 1·001, of a pleasant odour, resembling that of phenylethyl alcohol.

γ-*m*-Tolylpropyl alcohol can be produced by a process similar to the last, but a more direct method is possible by starting with 6-methylquinoline or 8-methylquinoline; these can be reduced to the corresponding tetrahydroquinoline derivatives, which by the Schotten-Baumann reaction are converted into *benzoyl*-6-*methyltetrahydroquinoline*, m. p. 78°, and *benzoyl*-8-*methyltetrahydroquinoline*, needles, m. p. 100°, respectively. If these benzoyl compounds are caused to undergo scission by heating with phosphorus pentachloride (A., 1904, i, 918) they produce *benzo*-o-γ-*chloropropyl*-p-*toluidide*, m. p. 151°, and *benzo*-o-γ-*chloropropyl*-o-*toluidide*, m. p. 112°, which on cautious hydrolysis by hydrochloric acid in a sealed tube yield the hydrochlorides of o-γ-*chloropropyl*-p-*toluidine* (*hydrochloride*, m. p. 183°) and o-γ-*chloropropyl*-o-*toluidine* (*hydrochloride*, m. p. 172°; red *platinichloride*, m. p. 191°). Diazotisation of chloropropyl-*p*-toluidine hydrochloride, followed by treatment with copper powder, gives rise to 6-*chloro*-3-*methylphenylpropyl chloride*, $CH_2Cl\cdot[CH_2]_2\cdot C_6H_3MeCl$, b. p. 125°/9 mm., possessing an odour resembling that of orange rind. If chloropropyl-*p*-toluidine is diazotised in solution in sulphuric acid and the reaction product warmed, the resultant *chloropropyl*-p-*cresol* when heated with alkali loses hydrogen chloride with the formation of 6-*methylchroman*, $C_6H_3Me{<}\begin{matrix}CH_2\cdot CH_2\\ O\text{——}CH_2\end{matrix}$, a pale yellow liquid, b. p. 107°/12 mm., of peppermint odour, which gives a red coloration with concentrated sulphuric acid. Reduction of a diazotised solution of the chloropropyltoluidine hydrochloride by an alkaline solution of stannous chloride produces m-*tolylpropyl chloride*, b. p. 130°/14 mm., which can be converted through the *acetate*, b. p. 136°/10 mm., into γ-m-*tolylpropyl alcohol*, $C_6H_4Me\cdot[CH_2]_2\cdot CH_2\cdot OH$, b. p. 140°/14 mm., D_4^{20} 0·9609, which closely resembles phenylpropyl alcohol in odour.

The most satisfactory starting point for γ-phenyl-*n*-butyl alcohol is acetophenone, which by condensation with zinc and ethyl bromoacetate followed by dehydration is converted into β-phenylcrotonic acid; this can be reduced to β-phenyl-*n*-butyric acid, the *ethyl* ester, b. p. 118°/9 mm., of which can be reduced by sodium and alcohol, giving a 60% yield of γ-*phenyl*-n-*butyl alcohol*, $CHMePh\cdot CH_2\cdot CH_2\cdot OH$, b. p. 134°/16 mm., D_4^{20} 0·9834, which resembles phenylpropyl and phenylethyl alcohols in odour. When heated with hydrochloric acid, the alcohol yields the corresponding *chloride*, b. p. 114—116°/17 mm., which is remarkably resistant to the usual chemical agents; it gives no reaction with potassium acetate and acetic acid, and when treated in light petroleum with aluminium chloride is hardly affected, yielding only traces of a non-volatile hydrocarbon and of a hydrocarbon, b. p.

90—100°/10 mm., possibly methylhydrindene; even with sodium the reaction does not occur normally, as the product is *isobutylbenzene*, b. p. 174—175°, D_4^{20} 0·8625. γ-*Phenyl*-n-*butyl bromide*, b. p. 108—110°/8 mm., can be obtained in a similar manner from the phenylbutyl alcohol, and reacts normally with ethyl sodiomalonate and ethyl sodioacetoacetate as well as with magnesium; the product from its slow reaction with sodium is a mixture of approximately equal quantities of *iso*butylbenzene and *βη-diphenyloctane*, a colourless liquid, b. p. 192—193°/10 mm., D_4^{20} 0·9539, resembling glycerol in appearance. γ-Phenylpropyl bromide, on the other hand, gives with sodium a 75% yield of αζ-diphenylhexane.

γ-*Phenyl-β-methylpropyl alcohol*, $CH_2Ph\cdot CHMe\cdot CH_2\cdot OH$, is a rather viscous oil, b. p. 128—129°/16 mm., D_4^{20} 0·9826, with an odour recalling linalool. It is obtained in 65% yield by the reduction of ethyl β-phenyl-α-methylpropionate by sodium and alcohol; the corresponding *phenylmethylpropyl chloride*, b. p. 112—114°/17 mm., is even less reactive than γ-phenyl-*n*-butyl chloride, for whilst the latter reacts with sodium iodide, the former fails to do so. The *bromide*, b. p. 110°/9 mm., however, behaves in a less abnormal manner, reacting with ethyl sodiomalonate and ethyl sodioacetoacetate; with sodium it reacts slowly, producing *iso*butylbenzene together with *βε-dibenzylhexane*, a viscous oil, b. p. 186—188°/8 mm., D_4^{20} 0·9457.

β-Phenyl-*n*-propyl alcohol, $CHMePh\cdot CH_2\cdot OH$, can be obtained by the reduction of the corresponding aldehyde (hydratropaldehyde: Claisen, A., 1905, i, 286). An attempt to prepare it through α-phenylethyl bromide by the Grignard reaction miscarried, because the action of magnesium was merely synthetic, producing βγ-diphenylbutane, m. p. 121—122°. The chloride of the above alcohol was prepared by a series of changes, commencing with β-phenyl-*n*-butyric acid; this reacts with phosphorus pentachloride, producing the acid *chloride*, b. p. 114°/11 mm., which with ammonia in ethereal solution yields the *amide*, m. p. 98·5°; this amide can be converted by the usual process with hypobromite into *β-phenyl*-n-*propylamine*, b. p. 104°/21 mm.; yellow *platinichloride*, m. p. 229° (decomp.); yellow *picrate*, m. p. 180°; *benzoyl* derivative, m. p. 85°. The last-named substance when fused with phosphorus pentachloride, and the mixture distilled under reduced pressure, gives a distillate which on hydrolysis with hydrochloric acid yields *β-phenyl*-n-*propyl chloride*, b. p. 98—100°/22 mm. The same chloride is obtained from benzo-*o*-β-chloro*iso*propylanilide (the scission product of 3-methyldihydroindole: von Braun and Kirschbaum, A., 1912, i, 499) by cautious hydrolysis with hydrochloric acid and reduction of the diazo-compound of the resultant *o*-β-chloro*iso*propylaniline by alkaline stannous chloride solution. The yield of chloride in these two methods of preparation is not very satisfactory, and the product is very unreactive, being completely unaffected by the acetates of the alkali metals or of silver.

β-Phenyl-*n*-butaldehyde, $CHPhMe\cdot CH_2\cdot CHO$, was prepared by the "nitro" method, because in spite of its lack of reactivity, γ-phenyl-*n*-butyl chloride will undergo double decomposition with sodium iodide producing γ-*phenyl*-n-*butyl iodide*, a colourless liquid, b. p. 132°/14 mm.; this reacts in the usual manner with silver nitrite, and the reaction

mixture on distillation gives γ-*phenyl*-n-*butyl nitrite*, b. p. approx. 120°/12 mm., and α-*nitro*-γ-*phenyl*-n-*butane*, b. p. 138°/12 mm. The latter substance when treated in alcoholic solution with an equimolecular quantity of sodium hydroxide solution, and then with a solution of stannous chloride in hydrochloric acid, produces an oil which, after boiling with dilute sulphuric acid, yields β-*phenyl*-n-*butaldehyde*, b. p. 110°/9 mm.; *phenylhydrazone*, oily; the odour of the substance is sharp, and recalls that of phenylacetaldehyde.

D. F. T.

Cholesterol. XVI. Methyl *iso*Hexyl Ketone, a Degradation Product of Cholesterol. ADOLF WINDAUS and C. RESAU (*Ber.*, 1913, **46**, 1246—1248).—It has been observed by many workers that the oxidation of cholesterol by various methods is always accompanied by the formation of a substance of pleasant odour (compare Windaus, A., 1909, i, 920). The odoriferous substance has now been isolated by collecting the distillate from a boiling solution of cholesteryl acetate in acetic acid to which a solution of chromic acid was gradually added; acetic acid was removed from the distillate by sodium hydroxide solution, the liquid was again distilled, then dissolved in ether, and the acetone removed by shaking with water. Careful evaporation of the ether then gave a small residue of the pleasant smelling oil; *semicarbazone*, colourless, rectangular leaflets, m. p. 153—154°.

The composition, $C_9H_{19}ON_3$, of the semicarbazone suggested that the parent substance is an octanone, and a comparison of the m. p.'s of the semicarbazones indicated that the odoriferous substance was methyl *iso*hexyl ketone. For further confirmation, methyl *iso*hexyl ketone (Darzens, A., 1905, i, 172) was prepared (p-*nitrophenylhydrazone*, deep yellow crystals, m. p. 83°), and the identity of the semicarbazones was satisfactorily established. D. F. T.

Preparation of Alkali Salts of *m*-Hydroxyphenoxypropanesulphonic Acid. ALBERT WOLFF (D.R.-P. 258473).—*Sodium* γ-*chloro*-β-*hydroxypropane*-α-*sulphonate*, $CH_2Cl\cdot CH(OH)\cdot CH_2\cdot SO_3Na$, hard, colourless crystals, is obtained when a boiling aqueous solution of sodium sulphite (252 parts) in 500 parts of water is treated with 128 parts of α-dichlorohydrin.

Sodium β-*hydroxy*-γ-m-*hydroxyphenoxypropane*-α-*sulphonate*,

$$OH\cdot C_6H_4\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot SO_3Na,$$

a colourless, crystalline powder, can be prepared in 90% yield by heating a concentrated solution of catechol (110 parts) in 56 parts of sodium hydroxide with 196 parts of the foregoing sodium chlorohydroxypropanesulphonate during two hours under reflux in the presence of an indifferent gas such as hydrogen. F. M. G. M.

Aromatic Telluretine Compounds. I. KARL LEDERER (*Ber.*, 1913, **46**, 1358—1362).—Diphenyl telluride has been condensed with bromoacetic acid and its esters, and compounds analogous to dimethylthetine bromide (Brown and Letts, A., 1874, 980) and to phenylmethylselenetine bromide (Pope and Neville, T., 1902, **81**, 1553) have been

obtained. The corresponding purely aromatic derivatives of sulphur and selenium could not be prepared.

Diphenyl telluride and methyl bromoacetate were left together for two or three days and then precipitated with ether. The *methyl* ester of *diphenyltelluretine bromide*, $TePh_2Br\cdot CH_2\cdot CO_2Me$, formed stout prisms from hot water, m. p. 105—106°. It was transformed by silver chloride into the *chloride*, m. p. 115—116°, with which zinc, gold, mercuric and platinic chlorides formed *double* salts. The *chromate* and *dichromate* could not be recrystallised, but the *picrate*,

$$C_6H_3(NO_2)_3\cdot O\cdot TePh_2\cdot CH_2\cdot CO_2Me,$$

formed well-defined, yellow needles, m. p. 144—145°. The *ethyl* ester, m. p. 63—64°, from ethyl bromoacetate was resolved by boiling water into its components. *Diphenyltelluretine bromide*, $TePh_2Br\cdot CH_2\cdot CO_2H$, itself was obtained from bromoacetic acid as a very hygroscopic mass, which, on shaking with silver oxide, gave *diphenyltelluretine*,

$$OH\cdot TePh_2\cdot CH_2\cdot CO_2H,$$

in the form of needles, m. p. 117—118°. The esters were hydrolysed by, and gave the same compound with, silver oxide. J. C. W.

Preparation and Reactions of Acid Haloids. HERMANN STAUDINGER and E. ANTHES (*Ber.*, 1913, **46**, 1417—1426).—Acid chlorides can be converted into the corresponding bromides or iodides by the action of an excess of hydrogen bromide or hydrogen iodide, the reaction being interpreted according to the scheme:

$$R\cdot COCl + HI \rightleftharpoons R\cdot CClI\cdot OH \rightleftharpoons R\cdot COI + HCl.$$

The analogous reaction with hydrocyanic acid does not appear to be applicable to the production of nitriles.

Acetyl chloride was converted into almost pure acetyl bromide by the action of dry hydrogen bromide, the yield being 80%. Similarly, cooled acetyl chloride and hydrogen iodide gave a 70% yield of acetyl iodide, b. p. 105—108°. *Diphenylacetyl iodide*, pale yellow crystals, m. p. 46°, obtained from hydrogen iodide and diphenylacetyl chloride, was far more sensitive to the action of moisture than the latter substance, and, when heated at 150°, was decomposed with an almost quantitative elimination of carbon monoxide.

Benzoyl chloride was incompletely transformed into the bromide at the ordinary temperature; completely, however, at 100°. Benzoyl iodide was readily obtained in 95% yield from benzoyl chloride and hydrogen iodide. It had b. p. 109—109·5°/10 mm., and was colourless when pure, rapidly becoming yellow when preserved. The rate of decomposition of the benzoyl haloids by water has been investigated by shaking dilute ethereal solutions with water at 0° and titration of the acid formed. The iodide was found to be more readily decomposed than the bromide, and the latter more readily than the chloride. It was also noticed that elimination of the halogen acid was incomplete (compare Straus and Hüssy, A., 1909, i, 490). This was attributed to decomposition of the benzoyl haloid by ether, but no ethyl iodide and only traces of ethyl benzoate could be detected. When ether was replaced by toluene or xylene, sharp differences in the behaviour of the haloids could not be detected, probably owing to the slight solubility of water in the hydrocarbons. When heated in a sealed tube for twenty

hours at 190°, benzoyl iodide yielded iodine, benzoic acid, and black, asphalt-like products, but no carbon monoxide. At 250°, carbon monoxide was not liberated. At 500°, however, under 15—25 mm. pressure, benzoyl iodide yielded iodobenzene and iodine, whilst at 700° still more pronounced decomposition occurred. Benzoyl bromide was stable at 500°, but yielded bromobenzene at 700°, whilst decomposition of benzoyl chloride did not occur even at 700°.

Benzoyl iodide reacted vigorously with benzaldehyde with formation of *iodobenzyl benzoate*, $Ph\cdot CO_2\cdot CHIPh$. The product so obtained was contaminated with iodine and could not be purified owing to its extreme instability. It was obtained, however, in colourless crystals, m. p. about 60°, by mixing the reagents in light petroleum solution. Benzoyl bromide reacted slowly with benzaldehyde, bromobenzyl benzoate, m. p. 65°, being formed, whilst no compound was obtained from benzoyl chloride.

Benzoyl iodide was scarcely affected by treatment with dry hydrogen chloride for three hours, but, after fifteen hours, the presence of benzoyl chloride was ascertained.

Benzoyl iodide reacted slowly with mercury at the ordinary temperature. At 120—130° reaction was complete within two to three days. Benzil did not appear to be formed. The main products, particularly at the higher temperature, were brown resins and a *substance*, m. p. 40°, which has not yet been investigated. In benzene solution, reaction occurred more slowly. In ethereal solution a ready action was observed, the products of which were ethyl iodide and ethyl benzoate.

Hydrogen bromide did not react with carbonyl chloride even at 200°. Slight reaction was observed when hydrogen iodide was mixed with gaseous carbonyl chloride.

Hydrogen cyanide appeared to be without action on boiling acetyl chloride or on oxalyl chloride at 15—20°. H. W.

The Perkin Reaction. HANS MEYER and ROBERT BEER (*Monatsh.*, 1913, **34**, 649—658).—In spite of the earlier investigations, it is still not certain whether in the Perkin synthesis the reaction occurs between the aldehyde and the salt of the fatty acid, or whether the anhydride plays a primary part.

It is now demonstrated that the yield of unsaturated acid depends largely on the aldehyde used; with sodium acetate and acetic anhydride, *o*-iodobenzaldehyde, *o*-chlorobenzaldehyde, *o*-nitrobenzaldehyde, benzaldehyde and *p*-dimethylaminobenzaldehyde gave yields in decreasing order of magnitude; with potassium acetate and acetic anhydride the relative behaviour of the various aldehydes appears to be the same, but the yields are uniformly better.

A comparison of the yields obtained by using *o*-chlorobenzaldehyde with the acetates of various metals in the presence of acetic anhydride shows that the alkali metals give better results the higher the atomic weight; lead acetate gives results comparable with the acetates of the alkali metals; mercuric acetate is poorer, whilst the acetates of copper and of the alkaline earth metals produce very small yields of chlorocinnamic acid.

The presence of an acid anhydride is not indispensable: benzaldehyde heated for twenty-six hours with potassium acetate and acetic acid gives a 30% yield of cinnamic acid. The yields of unsaturated acid when *o*-chlorobenzaldehyde is heated with an acetate and acetic acid is usually somewhat smaller than when acetic anhydride is used, but rubidium and lead acetates gave actually slightly better yields with the acid than with the anhydride. Michael's view (A., 1901, i, 358) that the Perkin reaction occurs between aldehyde and acid anhydride is, therefore, untenable.

The rôle of the acetic acid in the immediately preceding experiments appears to be merely that of solvent, and it is found that a 40% yield of unsaturated acid can be obtained by heating together *o*-chlorobenzaldehyde and potassium acetate, without the addition of a third substance, to 240° for thirty-six hours. D. F. T.

The Halogen-Substituted Cinnamic Acids and their Behaviour in Ultra-violet Light. Richard Stoermer and Paul Heymann (*Ber.*, 1913, **46**, 1249—1266. Compare A., 1912, i, 974).—In reply to Liebermann (this vol., i, 265), the authors submit that the former's proof of the structure of *allo*-cinnamic acid is not above suspicion, and that the nature of his experiments renders his decision merely a probability. The action of sulphuric acid on *allo*-cinnamic acid yields only ordinary cinnamic acid, and even if fuming sulphuric acid is used, the main product under suitable conditions is ordinary cinnamic acid accompanied by a relatively very small quantity of truxone (compare Liebermann, A., 1898, i, 662). It is also already recognised that there are exceptions to Liebermann's method of deciding the constitution of these isomerides by physical properties.

The main portion of the paper consists of the results of an extension of the investigation of the behaviour of ethylenic stereoisomerides in ultra-violet light (Stoermer, A., 1911, i, 295; 1910, i, 114).

α-Chlorocinnamic acid (Sudborough and James, T., 1906, **89**, 107), m. p. 137° (*aniline* salt, needles, m. p. 137°), exposed in acetic acid solution to the ultra-violet rays from a mercury lamp for twenty-one days is converted to the extent of 21% into *allo*-α-chlorocinnamic acid, m. p. 111° (*aniline* salt, needles, m. p. 96°). In a similar manner in methyl alcoholic solution, α-chlorocinnamamide, m. p. 121°, is converted to the extent of 10% into the amide (m. p. 134°) of the *allo*-acid in ten days.

α-Bromocinnamic acid, m. p. 131° (*aniline* salt, needles, m. p. 132°), when exposed in acetic acid to ultra-violet rays for twenty-one days is converted to the extent of 10% into *allo*-α-bromocinnamic acid, m. p. 120° (*aniline* salt, scales, m. p. 102°). When a methyl alcoholic solution of the *allo*-acid was exposed to ultra-violet rays, 71% was converted into the more stable isomeride. Similarly, α-bromocinnamamide, leaflets, m. p. 117°, in methyl-alcoholic solution is converted into the *allo*-isomeride (needles, m. p. 129°; 24% in 240 hours); the latter substance under similar treatment is re-converted to the extent of 50% into the original amide.

β-Bromocinnamic acid, needles or leaflets, m. p. 135°, is readily pro-

duced by submitting the *allo*-isomeride (Erlenmeyer, A., 1896, i, 46) in chloroform solution containing a little bromine to the action of sunlight; the product is an equilibrium mixture. The action of ultra-violet rays on an acetic acid solution for thirty-five days converted 40% of the acid into the *allo*-isomeride, m. p. 159—160°. Ultra-violet illumination converted 75% of the *allo*-acid in ethyl acetate solution into the ordinary acid.

Of the two β-chlorocinnamic acids, m. p. 142° and 132° respectively, the latter from its similarity to the analogous bromo-compound must be the *allo*-isomeride (compare Michael and Pendleton, A., 1889, 1063). The acetic acid solution of the former (*trans*-) compound is converted to the extent of 40% in twenty-one days into the *allo*-isomeride; the *aniline* salt, like that of *allo*-β-bromocinnamic acid, is unstable. In contact with bromine in sunlight the *allo*-acid is slowly re-converted into the other form.

The authors discontinue the use of the term *allo* in connexion with the αβ-dihalogen-substituted cinnamic acids, because the compounds which from their power of indone formation must be the *cis*-isomerides are more stable than the *trans*-isomerides.

cis-αβ-Dichlorocinnamic acid, m. p. 121° (*aniline* salt, needles, m. p. 129°), when treated with cold sulphuric acid yields dichloroindone.

When a solution in acetic acid is submitted to ultra-violet rays for twenty-one days, 45% of the acid undergoes conversion into the hitherto unknown trans-*αβ-dichlorocinnamic acid*, rhombic tablets, m. p. 101°; *barium* salt, woolly needles; *aniline* salt, needles, m. p. 121°. The *trans*-acid is also obtained by the elimination of hydrogen chloride from the dichloride of α-chlorocinnamic acid by the action of potassium hydroxide solution; it is separated from the *cis*-isomeride simultaneously formed by the sparing solubility of the *potassium* salt of the *trans*-acid in alcohol. The action of sunlight on a chloroform solution of the *trans*-acid containing a little bromine causes a re-conversion into the *cis*-isomeride.

The action of bromine on phenylpropiolic acid solution in carbon disulphide in the absence of sunlight produces a mixture of *cis*-αβ-dibromocinnamic acid, yellow prisms, m. p. 100°, with the isomeric *trans*-acid, scales, m. p. 136°, in approximately the proportion 2 : 1; the two acids give *aniline* salts, needles, m. p. 126° and 128° respectively. In chloroform solution containing bromine, sunlight causes a partial change of the *trans*- into the *cis*-isomeride, but as the latter always predominates in the equilibrium mixture, it may be regarded as the more stable (compare Roser and Haselhoff, A., 1888, 1304). In ultra-violet light, the *cis*-acid, dissolved in acetic acid, is converted into the *trans*-acid to the extent of 40% in fourteen days. This *cis*-acid is converted by cold sulphuric acid into dibromoindone, but a much better method for the production of this substance is the action of aluminium chloride on the corresponding acid chloride in carbon disulphide solution at water-bath temperature; under these conditions a quantitative yield of dibromoindone, m. p. 123°, is obtained.

αβ-Di-iodocinnamic acid, m. p. 171° (Liebermann and Sachse, A., 1892, 470), decomposes when exposed in solution to ultra-violet rays; consequently no isomerisation could be detected; from the fact that the

known acid gives no indone formation with sulphuric acid, it is presumably of the *trans*-configuration.

Curves are given illustrating the course of the isomerisation of the acids, and the properties of the various acids are tabulated.

D. F. T.

The Constitution of Abietic Acid. PAUL LEVY (*Zeitsch. anorg. Chem.*, 1913, **81**, 145—155).—The evidence for the constitution of abietic acid is reviewed and a few new experiments described. Oxidation with nitric acid yields dinitropropane and *trans-cyclo*hexane-1 : 2-dicarboxylic acid. Abietic acid is related to retene and pinene, contains a *cyclo*hexane ring and an *iso*propyl group, and has its carboxyl group attached to a tertiary carbon atom. None of the formulæ hitherto proposed conforms to all these conditions, with the exception of that due to Easterfield and Bagley (T., 1904, **85**, 1241).

C. H. D.

Benzoylated Cyanohydrins and Amides from Aldehydes, and the Corresponding Hydroxy-acids. JULES ALOY and CHARLES RABAUT (*Bull. Soc. chim.*, 1913, [iv], **13**, 457—460. Compare A., 1912, i, 462).—The preparation of benzoylated cyanohydrins by the action of benzoyl chloride on a mixture of an aldehyde with aqueous potassium cyanide has been extended to the fatty and heterocyclic series.

Benzoylglycollonitrile [*Benzoyloxyacetonitrile*], $OBz\cdot CH_2\cdot CN$, from formaldehyde, forms well-defined, stable crystals, m. p. 26—27°, b. p. 275° or 165°/25 mm., which dissolve in concentrated hydrochloric acid or slightly warmed 60% sulphuric acid with the formation of *benzoyloxyacetamide*, $CO\cdot NH_2\cdot CH_2\cdot OBz$, in hard, lustrous crystals, m. p. 117—118°. Hydrolysis by hot dilute sodium hydroxide provides a convenient method for the preparation of glycollic acid, but when an insufficient quantity of very dilute alkali is employed and the reaction is arrested as soon as ammonia ceases to be liberated, benzoyloxyacetic acid, m. p. 79°, results. The *silver* salt was analysed. Alcoholic ammonia converts the nitrile into benzamide and the amide into benzamide and glycollamide. Sodium ethoxide causes no replacement by sodium in the $-CH_2$ group, but yields sodium cyanide and benzoate and ethyl benzoate, and in the case of benzoylmandelonitrile gives rise to benzoin.

Similarly, α-benzoyloxybutyronitrile is obtained from propaldehyde as an impure oil, which gives *α-benzoyloxybutyramide*, $OBz\cdot CHEt\cdot CO\cdot NH_2$, m. p. 92°, and finally sodium α-hydroxybutyrate on hydrolysis, whilst *α-benzoyloxy*iso*valeronitrile*, $CHMe_2\cdot CH(OBz)\cdot CN$, from *iso*butaldehyde, has m. p. 21—22°, and gives the *amide*, m. p. 98°, and then α-hydroxy*iso*valeric acid on hydrolysis. *Benzoyloxyfurylacetonitrile*,

$$C_4H_3O\cdot CH(OBz)\cdot CN,$$

from furfuraldehyde, has m.p. 47—48°, but hydrolysis led to discoloured, indefinite substances.

The reaction is being extended to the ketones, in which case prolonged agitation is necessary (compare Francis and Davis, T., 1909, **95**, 1403; 1910, **97**, 949).

J. C. W.

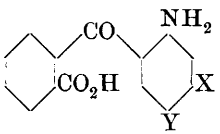
Racemisation of Tropic Acid and its Esters, together with a Theory of Racemisation, Substitution, and the Walden Inversion. JOHANNES GADAMER (*J. pr. Chem.*, 1913, [ii], **87**, 312—392).—This paper contains a full and detailed account of the author's theory, a short description of which has already appeared (A., 1912, i, 934; compare Frankland, Presidential Address, T., 1913, **103**, 722—725).

[With MAX KUNTZE.]—*Ethyl* l-*tropate*, prepared from ethyl iodide and silver *l*-tropate, has $[\alpha]_D^{12}$ $-47\cdot5°$ in alcoholic solution; the d-*ester* has $[\alpha]_D^{14}$ $+46\cdot6°$.

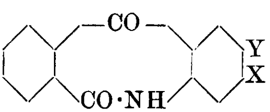
Experiments are also described to show that the conversion of hyoscyamine into atropine is due to ionisation at the asymmetric atom.

F. B.

Preparation of an Inner Anhydride (Lactam) of 2-Aminobenzoyl-*o*-benzoic Acid. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 258343).—When the 2-aminobenzoyl-*o*-benzoic acids of the general formula I (where X and Y may be hydrogen, methyl, a halogen or carboxylic group) are heated either alone with condensing agents or with solvents of high boiling point, they readily lose water and furnish inner anhydrides (lactams) of general formula II, and which are readily hydrolysed by alkali hydroxides to regenerate the parent substance.



(I.)



(II.)

When 2-*aminobenzoyl*-o-*benzoic acid*, rhombic crystals, m. p. 195° (with formation of the lactam), is heated at 200° with nitrobenzene it furnishes the corresponding *lactam*, m. p. 245°; the base accompanied by another isomeride is obtained by the nitration and subsequent reduction of benzoyl-*o*-benzoic acid and separation effected by means of the *calcium* salts.

2:5-*Diaminobenzoyl* o-*benzoic acid*, yellow needles, m. p. 265°, is obtained by heating 2-*amino*-5-*acetylaminobenzoyl*-o-*benzoic acid* (prepared by the nitration and subsequent reduction of 3-acetylaminobenzoyl-*o*-benzoic acid) with 30% sulphuric acid and subsequent decomposition of the *lactam* thus formed.

2-*Amino*-5-*acetylamino*-4-*carboxybenzoyl*-o-*benzoic acid*, yellow needles, m. p. 315°, is obtained by the oxidation (with potassium permanganate) of 2-*nitro*-5-*acetylamino*-4-*toluoyl*-o-*benzoic acid* and reduction of the so-obtained 2-*nitro*-5-*acetylamino*-4-*carboxybenzoyl*-o-*benzoic acid*, m. p. 247°; when heated with 30% sulphuric acid, the foregoing amino-acetylamino-base furnishes the *sulphate* of 2:5-*diamino*-4-*carboxybenzoyl*-o-*benzoic acid*, m. p. 340° (about), together with its *lactam*.

F. M. G. M.

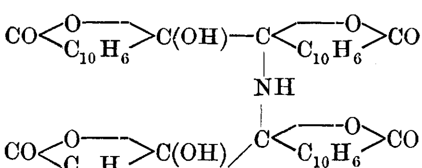
Reduction of the Anhydrides and Imides of Phthalic and Naphthalic Acids. ARNOLD REISSERT (*Ber.*, 1913, **46**, 1484—1491).—The reduction of phthalic anhydride by zinc dust and acetic acid is known to give a complex mixture, from which diphthalyl, hydro-

diphthalyl-lactonic acid and phthalide can be isolated (Wislicenus, A., 1885, 57), whilst reduction by distillation with zinc dust yields a mixture of zinc phthalate and diphthalyl.

It is now discovered that when phthalic anhydride is gradually introduced into an agitated suspension of zinc dust in a solution of calcium chloride in 40% alcohol at 20—22° about half is converted into phthalic acid and half into diphthalyl-lactonic acid, for which the author prefers the formula $CO<\substack{-O-\\C_6H_4}>CH\cdot CO\cdot C_6H_4\cdot CO_2H$.

No satisfactory method for the preparation of phthalide from phthalic anhydride could be discovered, but it was found that phthalimide can be reduced by stirring with a suspension of zinc dust in cold 2*N*-sodium hydroxide solution with the production of *hydroxyphthalimidine* (compare Graebe, A., 1885, 979), $C_6H_4<\substack{CH(OH)\\CO}>NH$, needles, m. p. 171—172°, which on boiling with acetic acid is converted into a *substance*, needles, m. p. 240—241°, of which the structure is probably $CO<\substack{C_6H_4\\NH}>CH—C(OH)<\substack{C_6H_4\\CO}>NH$. If after the reduction of phthalimide to hydroxyphthalimidine the reaction mixture containing excess of zinc is heated, a further reduction occurs and ammonia is liberated with the production of phthalide, $C_6H_4<\substack{CO\\CH_2}>O$, in almost theoretical yield.

If naphthalic anhydride is shaken with zinc dust and 2*N*-sodium hydroxide solution, a blue solution is obtained, which on addition of more alkali and further shaking becomes red; on neutralisation a reddish-yellow, crystalline *substance*, $C_{24}H_{12}O_5$, m. p. 213—215°, is precipitated, whilst the naphthalic acid produced simultaneously remains in solution. The coloured reduction product, which the author designates *deoxynaphthalic anhydride*, possibly of the formula $CO<\substack{O\\C_{10}H_6}>C\overset{}{\underset{\diagdown O\diagup}{—}}C<\substack{O\\C_{10}H_6}>CO$, gives an unstable blue colour with sodium carbonate solution and a stable red one with sodium hydroxide; on mixing intimately with concentrated ammonia solution the substance is converted into a *compound*, for which the annexed structure is suggested; this is a yellowish-red substance, which dissolves in alkali solutions with a bright blue or violet colour.



The reduction of naphthalimide by a similar process to that which was successful with phthalimide yielded only a pasty product.

D. F. T.

Action of Acylamino-acid Chlorides on the Sodium Compounds of the Esters of Malonic and Cyanoacetic Acids.

SIEGMUND GABRIEL (*Ber.*, 1913, **46**, 1319—1358).—A number of

phthaliminoacylmalonic esters of the series

$$C_8H_4O_2{:}N\cdot CXY\cdot CO\cdot CH(CO_2R)_2,$$

where X and Y = H or alkyl, have been prepared from acylamino-chlorides. It is found that the stability of the esters is enhanced when X and Y represent 1 or 2 alkyl groups, the non-substituted compounds having the character of strong acids and losing one $-CO_2R$ group on boiling with water (A., 1909, i, 491; 1911, i, 212). The presence of these groups is also a criterion for the pyrrolone condensation (A., 1911, i, 227), which also occurs when the malonic ester group is replaced by $-CH_2\cdot CN$, $-CH_2\cdot CO\cdot NH_2$, or by methyl, and when a benzoyl nucleus is substituted for the phthalyl group.

The same substituted phthaliminoacylmalonic esters are peculiar in their behaviour towards sodium alkyloxides, for the yellow sodium compound of the ester changes into the colourless neutral salt of a strong acid. Phenoxyacylmalonic esters underwent no such isomerism, whereas benzoylamino*iso*butyryl chloride condensed with methyl sodiomalonate to form a strongly acid compound with one methyl alcohol group less than the expected malonic ester. Benzoylmethylamino*iso*butyryl chloride, on the other hand, gave the malonic ester, from which it appears that an unsubstituted imino-group is necessary for the formation of the acidic compounds. These are shown to be derivatives of tetramic acid (Anschütz, A., 1912, i, 836), and their formation from methyl phthalimino*iso*butyrylmalonate, for example, presupposes the preliminary opening of the phthalyl ring and the addition of alcohol according to the scheme:

$$C_6H_4{<}{\scriptstyle CO \atop CO}{>}N\cdot CMe_2\cdot CO\cdot CH(CO_2Me)_2 + R\cdot OH$$
$$= CO_2R\cdot C_6H_4\cdot CO\cdot NH\cdot CMe_2\cdot CO\cdot CH(CO_2Me)_2$$
$$= CO_2R\cdot C_6H_4\cdot CO\cdot N{<}{\scriptstyle CO - CH\cdot CO_2Me \atop CMe_2\cdot CO} + CH_3\cdot OH.$$

This is supported by synthesis and by the fact that the methyl ethyl ester obtained from the methyl malonate and sodium ethoxide on the one hand, and from the ethyl malonate and sodium methoxide on the other, were isomeric. All these tetramic acid derivatives lose the ester group which is attached to the tetramic acid ring on hydrolysis with very dilute acids, and are decomposed by hydriodic acid into phthalic acid, alkyl iodide, carbon dioxide, and aminomethylbutanone.

[With JAMES COLMAN and KARL A. BÖTTCHER.]—For the preparation of ethyl phthalimino*iso*butyrylmalonate (A., 1911, i, 213), it is recommended to use enough ethyl sodiomalonate to form the *sodium* compound of the new ester. This forms light yellow needles, and gives a yellow, alkaline solution which is decomposed by carbon dioxide. The ethyl alcoholic solution or the solution of the free ester mixed with sodium ethoxide gradually becomes pale in the cold, quickly on warming, and on evaporation deposits the white, isomeric *sodium* salt, $C_{19}H_{20}O_7NNa$, which gives a neutral solution and is only decomposed by mineral acids, when *ethyl carbethoxybenzoyldimethyltetramcarboxylate* [2 : 4-*diketo*-1-*benzoyl*-5 : 5-*dimethylpyrrolidine*-o-3-*dicarboxylate*], $CO_2Et\cdot C_6H_4\cdot CO\cdot N{<}{\scriptstyle CO - CH\cdot CO_2Et \atop CMe_2\cdot CO}$, is formed as a crystalline

powder, m. p. 81°. It has a strongly acid reaction, gives an orange-red colour with ferric chloride, and yields the *tetramic acid*,

$$CO_2Et\cdot C_6H_4\cdot CO\cdot N<\begin{matrix}CO{-}{-}CH_2\\ CMe_2\cdot CO\end{matrix},$$

on hydrolysis with warm dilute hydrochloric acid as a white powder, m. p. 198—199°, which disengages carbon dioxide from barium carbonate, gives a red coloration with ferric chloride, and an *ammonium* salt, in slender, white needles. The acid gives with one molecule of bromine the *monobromide*,

$$CO_2Et\cdot C_6H_4\cdot CO\cdot N<\begin{matrix}CO{-}{-}CHBr\\ CMe_2\cdot CO\end{matrix},$$

m. p. 159—160°, from glacial acetic acid, which forms a hydrate with $1H_2O$ in rhombic needles, m. p. 121—122°, from dilute acetic acid, and yields phthalic acid and *bromoaminomethylbutanone hydrobromide*, $CH_2Br\cdot CO\cdot CMe_2\cdot NH_2,HBr$, in leaflets, m. p. 156°, on boiling with hydrobromic acid. This ketone reduces Fehling's solution and forms a *picrate*, which gives a turbid liquid at 135° becoming clear at 147°. Excess of bromine gives the *dibromide*, $C_{16}H_{15}O_5NBr_2$, m. p. 155°, which is neutral and can no longer become enolic. Chlorine yields the neutral *dichloride* in flat needles, m. p. 126—126·5°, from which the *hydrochloride* of *dichloroaminomethylbutanone*,

$$CHCl_2\cdot CO\cdot CMe_2\cdot NH_2,HCl,$$

m. p. 203°, was obtained. The *oxime*,

$$CO_2Et\cdot C_6H_4\cdot CO\cdot N<\begin{matrix}CO{-}{-}CH_2\\ CMe_2\cdot C{:}N\cdot OH\end{matrix},$$

forms microscopic crystals, m. p. 193°.

When the initial ethyl malonate is treated with sodium methoxide or when the sodium compound is left with methyl alcohol, the white, microcrystalline, neutral *sodium* salt, $C_{18}H_{18}O_7NNa$, is obtained, from which hydrochloric acid precipitates *ethyl carbomethoxybenzoyldimethyltetramcarboxylate* [*methyl ethyl* 2 : 4-*diketo*-1-*benzoyl*-5 : 5-*dimethylpyrrolidine*-o-3-*dicarboxylate*], $CO_2Me\cdot C_6H_4\cdot CO\cdot N<\begin{matrix}CO{-}{-}CH\cdot CO_2Et\\ CMe_2\cdot CO\end{matrix}$, which forms colourless needles, m. p. 133—134°, gives a *copper* and a *silver* salt, and, on hydrolysis, the *tetramic acid*, $C_{15}H_{15}O_5N$, in needles, m. p. 210—211°. The acid distils unchanged in a vacuum, yields an *ammonium* salt, an *oxime*, $C_{15}H_{16}O_5N_2$, in sparkling prisms, m. p. 210°, and a *hydrazone*, $C_{15}H_{17}O_4N_3$, in short prisms, m. p. 222—223°. The *methyl ether*, $CO_2Me\cdot C_6H_4\cdot CO\cdot N<\begin{matrix}CO{-}{-}CH\\ CMe_2\cdot C\cdot OMe\end{matrix}$, is obtained by the action of methyl alcohol and hydrogen chloride as a crystalline powder, m. p. 103—104°, which gives no colour with ferric chloride, is insoluble in alkalis, and yields a *bromo*-derivative, $C_{16}H_{16}O_5NBr$, in matted needles, m. p. 140°. The *acetyl* compound,

$$CO_2Me\cdot C_6H_4\cdot CO\cdot N<\begin{matrix}CO{-}{-}CH\\ CMe_2\cdot C\cdot OAc\end{matrix},$$

forms crystalline granules, m. p. 119—120°. The *monobromo*-derivative forms flat, rectangular prisms, m. p. 221°, which yield an *ammonium* salt and the above bromoaminomethylbutanone hydro-

bromide. The *dibromo*-derivative forms glistening needles, m. p. 193°, and the *dichloride*, m. p. 172—173°, yields the above dichloroaminomethylbutanone salt on hydrolysis.

*Methyl phthalimino*iso*butyrylmalonate*,

$$C_8H_4O_2\colon N\cdot CMe_2\cdot CO\cdot CH(CO_2Me)_2,$$

forms colourless, rhombohedral crystals, m. p. 91°, which give a dark cherry-red colour with ferric chloride. The *sodium* compound is yellow, reacts alkaline, and changes in methyl alcohol into the colourless, neutral *isomeride*, from which hydrochloric acid liberates *methyl carbomethoxybenzoyldimethyltetramcarboxylate* [2 : 4-*diketo*-1-*benzoyl*-5 : 5-*dimethylpyrrolidine*-o-3-*dicarboxylate*],

$$CO_2Me\cdot C_6H_4\cdot CO\cdot N\!<\!\begin{array}{l}CO\text{---}CH\cdot CO_2Me\\ CMe_2\cdot CH\end{array},$$

in short, thick columns, m. p. 155°, which may be distilled in a vacuum. It forms a *silver* salt, and gives the above tetramic acid, m. p. 210—211°, on hydrolysis. In order to synthesise the compound, α-amino*iso*butyric acid was condensed with the chloride of methyl hydrogen phthalate (Meyer, A., 1901, i, 750) to form *carbomethoxybenzoylamino*iso*butyric acid*, $CO_2Me\cdot C_6H_4\cdot CO\cdot NH\cdot CMe_2\cdot CO_2H$, in rhombic tablets, m. p. 168°. This was converted into the *chloride* by means of thionyl chloride, and then condensed with methyl sodiomalonate and the product identified with the expected ester, m. p. 155°. When the methyl ester, m. p. 91°, is allowed to react with sodium ethoxide, the neutral *sodium* salt of *methyl carbethoxybenzoyldimethyltetramcarboxylate*,

$$CO_2Et\cdot C_6H_4\cdot CO\cdot N\!<\!\begin{array}{l}CO\text{---}CH\cdot CO_2Me\\ CMe_2\cdot CO\end{array},$$

is formed as a granular powder, m. p. 99°, which gives a *copper* salt. In contrast to its isomeride, m. p. 133—134°, its tetramic acid derivative is the ethyl compound, m. p. 199°, and not the methyl, m. p. 210—211°.

The methyl ester, m. p. 91°, but not so the isomeride, m. p. 155°, condenses in presence of methyl sodiomalonate in boiling benzene to *methyl benzoylenedimethylpyrrolonecarboxylate*,

$$\begin{array}{l}C_6H_4\cdot C\colon C(CO_2Me)\\ CO\text{---}N\cdot CMe_2\end{array}\!>\!CO,$$

in yellow needles, m. p. 165° (compare the ethyl ester, A., 1911, i, 213). Similarly, phthaliminomethylbutanone (*ibid.*) gave benzoylenedimethylpyrrolone (A., 1911, i, 228). *Methyl phthalimino*iso*butyrate*, $C_8H_4O_2\colon N\cdot CMe_2\cdot CO_2Me$, prepared from the chloride in colourless, rhombic plates, m. p. 78°, combined with methyl alcohol when left with that liquid or when warmed with sodium methoxide solution, and gave the *methyl* ester of *methyl phthalamino*iso*butyrate*

$$CO_2Me\cdot C_6H_4\cdot CO\cdot NH\cdot CMe_2\cdot CO_2Me,$$

in delicate needles, m. p. 116—117°, thus behaving differently, as was expected, from the phthaliminoacetates and propionates, which give *iso*quinoline derivatives (A., 1900, i, 358). The methyl ester, m. p. 91°, may also be methylated by the action of methyl iodide on the sodium compound. *Methyl phthalimino*iso*butyrylmethylmalonate*,

$$C_8H_4O_2\colon N\cdot CMe_2\cdot CO\cdot CMe(CO_2Me)_2,$$

forms prisms, m. p. 121°, and on hydrolysis with hydrochloric acid yields *aminomethylpentanone hydrochloride*, $C_2H_5\cdot CO\cdot CMe_2\cdot NH_2,HCl$,

in rectangular tablets, m. p. 164°. The *hydriodide*, $C_6H_{13}ON,HI$, crystallises in needles, m. p. 141—142°, and gives a *picrate*, m. p. 145°. The *benzoyl* derivative forms silky needles, m. p. 118°, and the *phthalyl* compound crystallises in rhombic tablets, m. p. 70°, whilst the free *base*, $C_2H_5\cdot CO\cdot CMe_2\cdot NH_2$, is a colourless, mobile liquid, which, unlike aminomethylbutanone, but like amino*iso*butyrophenone (A., 1911, i, 212), distils without condensation, b. p. 157·5°/762 mm.

α-Phthalylalanyl chloride (A., 1908, i, 182) has also been condensed with ethyl sodiomalonate, forming a light yellow *sodium* compound, from which carbon dioxide separated *ethyl α-phthalylalanylmalonate*, $C_8H_4O_2{:}N\cdot CHMe\cdot CO\cdot CH(CO_2Et)_2$, in rhombic plates, m. p. 73—74°. Contrary to the above phthalimino*iso*butyrylmalonates, it did not form a tetramic or a pyrrolone derivative. When hydrolysed by means of fuming hydriodic acid, methyl α-aminoethyl ketone *hydriodide*, C_4H_9NO,HI, m. p. 89°, is formed (Künne, A., 1895, i, 685), but hydrobromic acid at 70° led to *α-phthaliminoethyl methyl ketone*, $C_8H_4O_2{:}N\cdot CHMe\cdot COMe$, which formed flat leaflets, m. p. 85—86°.

Phenoxyacetyl chloride was also condensed with methyl sodiomalonate, when the new *sodium* salt was obtained in silky, white needles, from which carbon dioxide separated *methyl phenoxyacetylmalonate*, $OPh\cdot CH_2\cdot CO\cdot CH(CO_2Me)_2$, as an oil.

Similarly, *phenoxy*iso*butyryl chloride*, $OPh\cdot CMe_2\cdot COCl$, a colourless oil, b. p. 112—113°/12·5 mm., yielded *ethyl α-phenoxy*iso*butyrylmalonate*, $OPh\cdot CMe_2\cdot CO\cdot CH(CO_2Et)_2$, in prisms, m. p. 69°. The chloride was obtained from ethyl phenoxy*iso*butyrate, b. p. 127°/12 mm. (compare Bischoff, A., 1900, i, 346), by the action of phosphorus pentachloride on the free acid, and yielded the *amide*, $OPh\cdot CMe_2\cdot CO\cdot NH_2$, in silky needles, m. p. 116°.

*Ethyl α-phthalimino*iso*butyrylcyanoacetate*,

$$C_8H_4O_2{:}N\cdot CMe_2\cdot CO\cdot CH(CN)\cdot CO_2Et,$$

was obtained by adding phthalimino*iso*butyryl chloride to ethyl sodiocyanoacetate suspended in benzene, and decomposing the new light yellow salt with hydrochloric acid. It forms flat leaflets, m. p. 111°, and has acidic properties, giving an *ammonium* salt,

$$C_{17}H_{15}N_2O_5,NH_4,H_2O,$$

and a *copper* salt. On hydrolysis with dilute hydrochloric acid it yields *α-phthalimino*iso*butyrylacetonitrile*, $C_8H_4O_2{:}N\cdot CMe_2\cdot CO\cdot CH_2\cdot CN$, in long needles, m. p. 154°. When left or warmed with dilute alkalis the substance loses water and forms *o-benzoylenecyanodimethylpyrrolone*, $\begin{array}{l}C_6H_4\cdot C{:}C(CN)\\ |\qquad\ \ |\\ CO{-}{-}N\cdot CMe_2{-}\end{array}\!\!>CO$ in yellow prisms, m. p. 273°, which are converted by hydrobromic acid into benzoylenedimethylpyrrolone (*loc. cit.*). The nitrile also dissolves in cold concentrated sulphuric acid with the formation of *phthalimino*iso*butyrylacetamide*,

$$C_8H_4O_2{:}N\cdot CMe_2\cdot CO\cdot CH_2\cdot CO\cdot NH_2,$$

in long, flat needles, m. p. 130°. This compound condenses very readily to *o-benzoylenedimethylpyrrolonecarbonamide*,

$$\begin{array}{l}C_6H_4\cdot C{:}C(CO\cdot NH_2)\\ |\qquad\ \ |\\ CO{-}{-}N\cdot CMe_2{-}{-}{-}{-}\end{array}\!\!>CO,$$

which forms long, yellow prisms, m. p. 217°. When warmed with

concentrated sulphuric acid, however, the nitrile takes up $2H_2O$ and forms the *phthaloylic acid* derivative of *amino*iso*butyrylacetamide* (o-*carboxybenzoylamino*iso*butyrylacetamide*),

$$CO_2H\cdot C_6H_4\cdot CO\cdot NH\cdot CMe_2\cdot CO\cdot CH_2\cdot CO\cdot NH_2,$$

as a crystalline powder, m. p. 171°, which merely dissolves and undergoes no condensation in alkalis.

Benzoylamino*iso*butyric acid (dimethylhippuric acid) was prepared by benzoylating amino*iso*butyric acid in acetone in presence of pyridine and then converted into the chloride (Mohr, A., 1910, i, 117). The latter was condensed with methyl sodiomalonate, when the expected ester was not obtained, but rather *methyl benzoyldimethyltetramcarboxylate* [2 : 4-*diketo*-1-*benzoyl*-5 : 5-*dimethylpyrrolidine*-3-*carboxylate*], $\begin{array}{l}\mathrm{NBz\cdot CO\cdot CH\cdot CO_2Me}\\ \mathrm{CMe_2 \text{——} CO}\end{array}$, which forms rhombic tablets or short prisms, m. p. 154—155°. The substance had an acid reaction, dissolved in ammonia, and gave a *copper* salt and an orange-red coloration with ferric chloride. Hydrolysis with hydrochloric or hydriodic acid gave the salts of aminomethylbutanone. The analogous *ethyl* ester, $C_{16}H_{17}O_5N$, forms short prisms, m. p. 111°. Condensation of the above chloride with ethyl cyanoacetate, however, followed a normal course, and led to *ethyl benzoylamino*iso*butyrylcyanoacetate*, $NHBz\cdot CMe_2\cdot CO\cdot CH(CN)\cdot CO_2Et$, which formed colourless rhombohedra, m. p. 165°. The compound forms salts with ammonia and silver, and gives a cherry-red coloration with ferric chloride. Hydrolysis with hydrochloric acid leads to *benzoylamino*iso*butyrylacetonitrile*, $NHBz\cdot CMe_2\cdot CO\cdot CH_2\cdot CN$, which forms long needles.

For the condensation of malonic esters with benzoylmethylamino*iso*butyryl chloride, methylamino*iso*butyric acid, prepared by a modification of Zelinsky and Stadnikoff's general method (A., 1906, i, 425), was benzoylated as above, the *benzoylmethylamino*iso*butyric acid*, $NMeBz\cdot CMe_2\cdot CO_2H$, short prisms, m. p. 183°, was treated with thionyl chloride, and the crude product left with methyl sodiomalonate. *Methyl benzoylmethylamino*iso*butyrylmalonate*,

$$NMeBz\cdot CMe_2\cdot CO\cdot CH(CO_2Me)_2,$$

forms colourless, short columns, m. p. 125°. It is gradually resolved into its components by boiling water, but is not only hydrolysed, but, furthermore, condensed by hydriodic acid to *phenyltrimethylpyrrolone*, $\begin{array}{l}\mathrm{CPh{:}CH\cdot CO}\\ \mathrm{NMe \text{——} CMe_2}\end{array}$. This base crystallises in hexagonal tablets, m. p. 100°, b. p. 346—347°/768 mm., and forms a soluble chloride, a sparingly soluble nitrate, iodide and picrate, m. p. 147°, and a platinichloride. J. C. W.

Condensation of Pyromellitic Anhydride with Benzene and with Toluene. II. Ernst Philippi (*Monatsh.*, 1913, **34**, 705—717. Compare A., 1911, i, 793; Mills and Mills, T., 1912, **101**, 2194).—It has not been found possible to produce substances analogous to anthranol in the dinaphthanthracene group by intramolecular elimination of water from reduced derivatives of dibenzoylbenzenecarboxylic acids.

In the condensation of dibenzoylbenzenedicarboxylic acids to diphthaloylbenzene by concentrated sulphuric acid, 2-*benzoylanthraquinone*-

3-*carboxylic acid*, m. p. 283—285°, is obtained as a by-product, but by allowing the reaction to proceed at a lower temperature for a shorter period this substance becomes the main product; the *sodium* and *potassium* salts are sparingly soluble. Reduction of the acid with ammoniacal zinc dust and copper sulphate solution gives a poor yield of 2-*benzylanthracene*-3-*carboxylic acid*, m. p. 235—237°, which can be further reduced by hydriodic acid and phosphorus to 1 : 5-*dibenzylbenzene*-2 : 4-*dicarboxylic acid*, which decomposes without melting. No dianthranol nor any other condensation product could be obtained by heating this substance with sulphuric acid.

Reduction of diphthaloylbenzene by distillation with zinc dust in an atmosphere of hydrogen under reduced pressure and also by alkaline hyposulphite yielded a sparingly soluble, reddish-brown, crystalline solid; this was unaltered by a temperature of 360°, and from the presence of two hydroxyl groups the structure is probably

$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_2<\genfrac{}{}{0pt}{}{C(OH)}{C(OH)}>C_6H_4.$$

The product of reduction of diphthaloylbenzene with hydriodic acid and phosphorus was exceedingly difficult to purify; it is an almost colourless *substance*, m. p. 210—215° (decomp.), the composition of which indicates a formula $C_{22}H_{20}$.

The condensation of pyromellitic anhydride with toluene by means of aluminium chloride proceeds in exactly the same way as with benzene; the reaction product is a mixture of two acids of the structure $C_6H_3Me{\cdot}CO{\cdot}C_6H_2(CO_2H)_2{\cdot}CO{\cdot}C_6H_3Me$, namely, 1 : 5-*di*-p-*toluoylbenzene*-2 : 4-*dicarboxylic acid* and 1 : 4-*di*-p-*toluoyl*-2 : 5-*benzenedicarboxylic acid*, which can be separated by fractional crystallisation from nitrobenzene; the former acid has m. p. 245—248°, whilst the latter and less soluble acid decomposes without melting. Reduction of the more soluble isomeride by zinc dust and copper in alkaline solution is exceedingly slow, and yields only the *lactone*,

$$O<\genfrac{}{}{0pt}{}{CH(C_6H_4Me)}{CO}>C_6H_2<\genfrac{}{}{0pt}{}{CH(C_6H_4Me)}{CO}>O,$$

a yellow solid which does not melt below 240°. The same lactone is also obtained when the reducing agent is a mixture of phosphorus and hydriodic acid, but in this case it is accompanied by 1 : 5-*di*-p-*tolylbenzene*-2 : 4-*dicarboxylic acid*, a yellow solid, m. p. near 238°.

D. F. T.

Hydrogenation of Santonin in Presence of Palladium Black. GUIDO BARGELLINI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 443—447).—The action of hydrogen on an alcoholic solution of santonin in the presence of palladium black yields a dihydrosantonin and a tetrahydrosantonin. The alcoholic solution of santonin containing palladium black is treated with hydrogen at 40—50 cm. pressure until the volume corresponding with the dihydro-compound has been absorbed (for 5 grams this takes fifteen to twenty minutes). The *dihydrosantonin*, $C_{15}H_{20}O_3$, so obtained, has m. p. 148—150°, $[\alpha]_D+23°$ (in 2·106% alcoholic solution), and gives with alcoholic potassium hydroxide a yellow solution having a green fluorescence. It yields a *semicarbazone*, $C_{16}H_{23}O_3N_3$, which forms microscopic needles, m. p. 238—239°.

When the hydrogenation is continued until a further equal amount of hydrogen has been absorbed, a *tetrahydrosantonin*, $C_{15}H_{22}O_3$, is obtained; it forms colourless laminæ, m. p. 154—155°, $[\alpha]_D + 61.5°$ (in 2·234% alcoholic solution). This substance does not become yellow when exposed to light, and is stable towards permanganate; it yields no coloration with potassium hydroxide. R. V. S.

Combination of Phenolcarboxylic Acids. III. FERDINAND MAUTHNER (*J. pr. Chem.*, 1913, [ii], **87**, 409—415).—A continuation of previous work (A., 1911, i, 725; 1912, i, 267).

Methyl p-3 : 5-*dimethoxybenzoyloxybenzoate*, prepared by shaking an ethereal solution of 3 : 5-dimethoxybenzoyl chloride with methyl *p*-hydroxybenzoate dissolved in aqueous sodium hydroxide, crystallises in colourless needles, m. p. 91—92°. *Methyl* m-3 : 5-*dimethoxybenzoyloxybenzoate*, from methyl *m*-hydroxybenzoate, has m. p. 66—67°.

Methyl m-3 : 5-*dimethoxybenzoyloxy*-p-*methoxybenzoate*, from 3 : 5-dimethoxybenzoyl chloride and methyl vanillate, has m. p. 89—90°.

Methyl 2-(3′ : 5′)-*dimethoxybenzoyloxy-3-naphthoate*, from methyl 2-hydroxy-3-naphthoate, has m. p. 119—120°.

3 : 4 : 5-Trimethoxybenzoyl chloride reacts with methyl *m*-hydroxybenzoate, yielding *methyl* m-3 : 4 : 5-*trimethoxybenzoyloxybenzoate*, m. p. 143—144°, and with methyl 2-hydroxy-3-naphthoate to form *methyl* 2-(3′ : 4′ : 5′)-*trimethoxybenzoyloxy-3-naphthoate*, m. p. 149—150°.

Methyl m-4-*methoxybenzoyloxybenzoate*, prepared from anisoyl chloride and methyl *m*-hydroxybenzoate, has m. p. 79—80°.

All the compounds described above crystallise in colourless needles.

The 3 : 4 : 5 : 2′ : 6′-pentamethyl ether of dimethyl gallate (A., 1911, i, 725) has m. p. 173—174°. F. B.

Tetra-alkylation of *cyclo*Hexanone and β-Methyl*cyclo*hexanone and Trialkylation of Menthone. ALBIN HALLER (*Compt. rend.*, 1913, **156**, 1199—1206. Compare A., 1908, i, 987; 1909, i, 108, 654; 1910, i, 219, 300; 1912, i, 269).—By the use of sodamide as condensing agent, all the hydrogen atoms attached to the two carbon atoms adjacent to the ketone group in the substituted or non-substituted *cyclo*hexanones can be substituted by alkyl groups, chiefly methyl and allyl, condensation of the *cyclo*hexanone on itself taking place to a certain extent at the same time. This latter condensation is increased if the methyl iodide is replaced by its higher homologues for substitution. The tetra-, penta-, and hexa-alkyl*cyclo*hexanones so obtained give neither oximes nor semicarbazones. The substitution is performed by dissolving the ketone (1 mol.) in anhydrous ether, or preferably toluene in some cases, adding the sodamide (1 mol.) in fine powder, and when all action has ceased adding the alkyl iodide in theoretical quantity. On the crude product obtained by treatment with water and then drying, this treatment is repeated two or three times. By this means the following compounds have been prepared:

1 : 1 : 3 : 3-*Tetramethyl*cyclo*hexan-2-one*, $CH_2<\begin{matrix}CH_2\cdot CMe_2\\ CH_2\cdot CMe_2\end{matrix}>CO$, b. p. 185—186°, $D^{17.5}$ 0·8936, n_D^{18} 1·447, which on reduction with sodium

and alcohol gives the corresponding *alcohol*, b. p. 195—197°/767 mm., D^{17} 0·9001, n_D^{17} 1·455, giving a *phenylurethane*, m. p. 97—98°.

Attempts to prepare the ethyl derivatives by similar methods gave a mixture of small quantities of mono- and di-ethyl derivatives and a large amount of other condensation products.

1 : 1 : 3 : 3 - *Tetra-allyl*cyclo*hexan-2-one*, b. p. 170—171°/18 mm., D^{17} 0·9490, n_D^{16} 1·4920, giving on reduction the secondary *alcohol*, b. p. 171—173°/15 mm., D^{15} 0·9523, n_D^{17} 1·4975, which gave no phenylurethane.

1 : 2 : 2 : 4 : 4-Pentamethyl*cyclo*hexan-3-one (compare A., 1905, i, 214, 602) was prepared in an active and inactive form. The active ketone had b. p. 201—202°/765 mm., 93—94°/23 mm., D^{20} 0·8979, $n_D^{17.5}$ 1·4515, $[\alpha]_D$ +24°0′, and gave the corresponding *alcohol*, b. p. 210—212°/767 mm., giving a *phenylurethane*, m. p. 105—106°. The inactive ketone had b. p. 202—203°/765 mm., D^{18} 0·8997, $n_D^{17.5}$ 1·4553, and gave the *alcohol*, m. p. 45°, b. p. 213—214°/767 mm., yielding a *phenylurethane*, m. p. 127°.

1-*Methyl*-2 : 2 : 4 : 4-*tetra-allyl*cyclo*hexan*-3-*one*, b. p. 165—169°/12 mm., D^{15} 0·954, $[\alpha]_D$ +36°17′, on reduction yields the corresponding *alcohol*, b. p. 187—189°/25 mm., D^{17} 0·9613, $n_D^{16.5}$ 1·5054, $[\alpha]_D$ −9°52′, which yields no phenylurethane.

The alkylation of the menthones in order to pass beyond the mono-alkyl stage had to be carried out in toluene as a solvent. The products so obtained were:

Dimethylmenthone, b. p. 108—109°/14 mm., which on reduction gave the *alcohol*, b. p. 245—247°, $[\alpha]_D$ + 3°23′, yielding a *phenylurethane*, m. p. 90—91°. Attempts to prepare trimethylmenthone were not successful.

Diallylmenthone has b. p. 146—147°/13 mm., $[\alpha]_D$ + 25°50′.

Triallylmenthone has b. p. 166—167°/14 mm., $[\alpha]_D$ + 6°40′. W. G.

Arylsulphonylacetones, Arylsulphonylacetophenones, and Cyanobenzylarylsulphones. JULIUS TRÖGER and O. BECK (*J. pr. Chem.*, 1913, [ii], **87**, 289—311. Compare this vol., i, 169).—A number of arylsulphonylacetophenones, $SO_2R\cdot CH_2\cdot COPh$, and arylsulphonylacetones, $SO_2R\cdot CH_2\cdot COMe$, have been prepared by the interaction of the sodium salts of arylsulphinic acids with ω-chloroacetophenone and chloroacetone respectively. They resemble the arylsulphonylacetonitriles described previously (A., 1905, i, 336, 870), in that they dissolve in aqueous alkali hydroxides, and are reprecipitated unchanged by mineral acids. The mobility of the methylene hydrogen atoms in the arylsulphonyl-ketones is, however, not so great as in the case of the arylsulphonylacetonitriles, since condensation products with amyl nitrite and aromatic aldehydes could not be obtained.

Attempts to prepare arylsulphonylacetophenones by the action of magnesium phenyl bromide on the corresponding arylsulphonylacetonitriles proved unsuccessful, the latter compounds being recovered from the reaction unchanged. Acetonitrile and phenylacetonitrile readily react with magnesium phenyl bromide, yielding acetophenone and deoxybenzoin respectively. In the case of chloroacetonitrile, which should give rise to ω-chloroacetophenone, no definite compound

could be isolated from the reaction product. A similar retarding influence of the arylsulphonyl group has been observed with the arylsulphonylacetophenones, which do not react with organo-magnesium compounds, whereas acetophenone readily reacts with magnesium phenyl bromide and magnesium methyl iodide, yielding diphenylmethylcarbinol and phenyldimethylcarbinol respectively.

o-*Methoxybenzenesulphonylacetone*, $OMe{\cdot}C_6H_4{\cdot}SO_2{\cdot}CH_2{\cdot}COMe$, prepared by heating sodium *o*-methoxybenzenesulphinate with chloroacetone in alcoholic solution, forms white, prismatic needles, m. p. 65°, and yields an *oxime*, m. p. 160·5°.

p-*Ethoxybenzenesulphonylacetophenone*, obtained from sodium *p*-ethoxybenzenesulphinate in a similar manner, crystallises in white needles, m. p. 67·5°; the *oxime* forms leaflets, m. p. 127°. The following compounds were prepared by heating ω-chloroacetophenone with the sodium salts of arylsulphinic acids in alcoholic solution: *benzenesulphonylacetophenone*, $SO_2Ph{\cdot}CH_2{\cdot}COPh$, which crystallises in white needles, m. p. 96°, and forms an *oxime*, m. p. 134°, a *semicarbazone*, m. p. 194·5°, and a *phenylhydrazone*, yellow needles, m. p. 170°; p-*chlorobenzenesulphonylacetophenone*, white needles, m. p. 132—133° (*oxime*, m. p. 131—132°); *a-naphthalenesulphonylacetophenone* forms white needles, m. p. 89°, and yields an *oxime*, m. p. 173°, and a *phenylhydrazone*, yellow, prismatic columns, m. p. 191—192°; p-*toluenesulphonylacetophenone*, m. p. 110° (*semicarbazone*, m. p. 208·5°); o-*methoxybenzenesulphonylacetophenone* forms stout, prismatic crystals, m. p. 79°, and yields a *phenylhydrazone*, crystallising in yellow prisms, which become yellowish-red at 165°, m. p. 167·5°; p-*ethoxybenzenesulphonylacetophenone*, white, prismatic needles, m. p. 130° (*oxime*, m. p. 150°).

ω-Benzenesulphonyl-p-*toluonitrile*, $SO_2Ph{\cdot}CH_2{\cdot}C_6H_4{\cdot}CN$, obtained by the interaction of ω-chloro-*p*-toluonitrile and sodium benzenesulphinate in alcoholic solution, crystallises in white needles, m. p. 204·5°. The following sulphones were prepared in a similar manner: ω-p-*chlorobenzenesulphonyl*-p-*toluonitrile*, m. p. 148·5°; ω-p-*toluenesulphonyl*-p-*toluonitrile*, prismatic needles, m. p. 211°; *ω-a-naphthalenesulphonyl*-p-*toluonitrile*, m. p. 162·5°; o-*methoxybenzenesulphonyl*-p-*toluonitrile*, m. p. 121°; ω-p-*ethoxybenzenesulphonyl*-p-*toluonitrile*, m. p. 164°. The above-mentioned sulphones differ from the arylsulphonyl-ketones and nitriles in being insoluble in aqueous alkali hydroxides. F. B.

The Friedel-Crafts Reaction. VI. GUSTAV HELLER (*Ber.*, 1913, **46**, 1497—1504. Compare A., 1912, i, 357, 358; etc.).—It has already been shown (A., 1912, i, 358; 1908, i, 994) that, whereas, *o*- and *p*-chlorotoluenes react normally with phthalic anhydride in the presence of aluminium chloride, the three bromotoluenes behave anomalously, yielding the same *o*-bromotoluoylbenzoic acid. The behaviour of the chloro- and bromo-toluenes with benzoyl chloride and aluminium chloride has therefore now been investigated.

[With LEOPOLD BUB.]—Benzoyl chloride was introduced into a well cooled mixture of *o*-chlorotoluene and aluminium chloride, and the mixture subsequently warmed; the product was a *phenyl chlorotolyl ketone*, $C_6H_3MeCl{\cdot}COPh$, colourless leaflets, m. p. 82—83°, which

was oxidised by chromium trioxide in acetic acid solution to a *chlorobenzophenonecarboxylic acid*, leaflets, m. p. indistinct at 187°. In a similar manner *p*-chlorotoluene gave rise to an isomeric *phenyl chlorotolyl ketone*, m. p. 35—36°, by the oxidation of which no characteristic acid could be obtained.

p-Bromotoluene, as also the *m*-isomeride, again exhibit anomalous behaviour, producing under similar conditions to the above only uncrystallisable oils, which from their inconstant b. p. must be mixtures caused probably by a wandering of the substituent groups during the reaction. On the other hand, *o*-bromotoluene gave an oily product which partly crystallised to a yellow solid, m. p. 173°, a *phenyl hydroxytolyl ketone*, $OH\cdot C_6H_3Me\cdot COPh$; this is the first case of the replacement of bromine by hydroxyl in a Friedel-Crafts reaction, and as the primary reaction occurred in the absence of water, the hydroxy-compound must have been produced from an intermediate substance during the subsequent treatment.

The interaction of phenol, aluminium chloride, and benzoyl chloride yielded a mixture of 4-hydroxydiphenyl-ketone and phenyl benzoate. *o*-Cresol gave the same phenyl hydroxytolyl ketone (*acetyl* derivative, needles, m. p. 68—69°) as was obtained in the above reaction with *o*-bromotoluene. *m*-Cresol produced a yellow oil, from which could be separated two isomeric *phenyl hydroxytolyl ketones*, yellow crystals, m. p. 63°, and colourless needles, m. p. 129° (compare Bartolotti, A., 1901, i, 36), respectively, and *m*-tolyl benzoate. The product obtained with *p*-cresol was exclusively *p*-tolyl benzoate.

It has already been shown that phthalic anhydride condenses with *β*-chloronaphthalene in the presence of aluminium chloride with the formation of an acid, which by dehydration gives a ketone (Heller and Grünthal, A., 1912, i, 357). Oxidation of the ketone by a mixture of potassium permanganate and nitric acid yielded anthraquinone-2 : 3-dicarboxylic acid; the ketone must therefore be of the structure 2-chloro-6 : 7-phthaloylnaphthalene, $C_6H_4<^{CO}_{CO}>C_{10}H_5Cl$, and the acid must be an *o*-*β*-chloronaphthoylbenzoic acid, $C_{10}H_6Cl\cdot CO\cdot C_6H_4\cdot CO_2H$.

D. F. T.

The Condensation of 2 : 5-Dimethoxybenzoyl Chloride with Phenolic Ethers.

FERDINAND MAUTHNER (*J. pr. Chem.*, 1913, [ii], **87**, 403—409).—An account of the preparation of a number of methoxybenzophenones from 2 : 5-dimethoxybenzoyl chloride and phenolic ethers by means of the Friedel-Crafts reaction.

2 : 5-Dimethoxybenzoic acid is best prepared by methylating *o*-resorcylic acid with methyl sulphate and aqueous sodium hydroxide at the ordinary temperature; the chloride has b. p. 157—158°/16 mm., m. p. 35—36° (compare Kostanecki and Lampe, A., 1908, i, 442); the *amide* and *anilide* crystallise in lustrous, silky needles, m. p. 148—149° and 124—125° respectively.

3 : 5 : 4′-*Trimethoxybenzophenone*, prepared from the chloride and anisole in carbon disulphide solution in the presence of aluminium chloride, forms colourless needles, m. p. 97—98°.

3 : 5 : 3′ : 4′-*Tetramethoxybenzophenone*, obtained from veratrole in a similar manner, crystallises in colourless needles, m. p. 114—115°.

3 : 5 : 2′ : 4′-*Tetramethoxybenzophenone*, from resorcinol dimethyl ether, forms needles, m. p. 73—74°.

2′-*Hydroxy*-3 : 5 : 3′ : 4′-*tetramethoxybenzophenone*, prepared from pyrogallol trimethyl ether, forms light yellow crystals, m. p. 123—124°.

3 : 5 : 2′ : 4′ : 6′-*Pentamethoxybenzophenone*, from phloroglucinol trimethyl ether, crystallises in small needles, m. p. 132—133°. F. B.

Benzilbenzoin. ALFRED BENRATH (*J. pr. Chem.*, 1913, [ii], **87**, 416—422).—Klinger's benzilbenzoin (A., 1886, 888) is produced by the photochemical reduction of benzil in solutions of aldehydes and aromatic hydrocarbons (compare Benrath, A., 1906, i, 535). When heated alone or in solution it decomposes into benzoin and benzil. Owing to this decomposition it has no definite m. p.; it begins to soften at 86°, and is completely fused at a temperature dependent on the rate of heating, the highest recorded temperature being 143°. A mixture of benzil and benzoin in equimolecular proportions shows the same m. p. interval as benzilbenzoin, and hence the latter compound must have the formula COPh·COPh,COPh·CHPh·OH.

The fusion curve of mixtures of benzoin and benzil is recorded; it shows a eutectic point at 86°. F. B.

Preparation of Derivatives of *p*-Benzoquinone. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 257834).—When *p*-benzoquinone, its homologues, or halogen derivatives are boiled with naphthylaminesulphonic acids in the presence of sodium acetate they yield compounds which, after further condensation with zinc chloride (or concentrated sulphuric acid), dye wood or silk in reddish-violet to blue shades.

The tinctorial properties of the *disulphonaphthylaminodichlorobenzoquinones* thus obtained from chloroanil with β-naphthylamine-5- and -8-sulphonic acids are tabulated in the original. F. M. G. M.

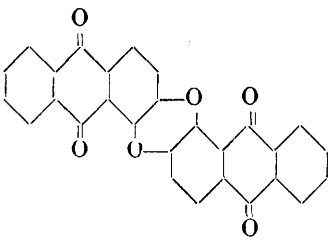
Preparation of a Derivative of Anthraquinone. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 258439).—When 1-aminoanthraquinone (10 parts) dissolved in 500 parts of cooled 60% sulphuric acid is slowly treated with sodium chlorate (2 parts) dissolved in 40 parts of the same solvent, a blue coloration is rapidly developed, followed by the separation of a deep blue precipitate which can be purified by boiling with alcohol and crystallisation from nitrobenzene.

This *compound* is not apparently obtained when other oxidising agents are employed; it gives a colourless "vat" with alkaline hyposulphite, and on further reduction with stannous chloride furnishes leucoquinizarin. F. M. G. M.

Behaviour of Dibenzoyl-1 : 5-dibenzylaminoanthraquinone with Alkaline Sodium Hyposulphite. CHRISTIAN SEER (*Monatsh.*, 1913, **34**, 579).—A correction; dibenzoyl-1 : 5-dibenzylaminoanthraquinone is not reduced by alkaline hyposulphite as previously stated (A., 1912, i, 571). D. F. T.

Preparation of Di- and Tri-anthrimides of the β-Anthraquinone Series. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 257811).—It is found that dianthrimide can be prepared by heating together β-aminoanthraquinone (22·3 parts), β-chloroanthraquinone (24·2 parts), and potassium carbonate (7 parts) at 300°, whilst trianthrimide, a brown powder, is obtained in a similar manner from 2 : 6-diaminoanthraquinone (1 mol.) and β-chloroanthraquinone (2 mols.) or from β-aminoanthraquinone and 2 : 7-dichloroanthraquinone.

F. M. G. M.



[Preparation of an Anthraquinone Derivative.] R. WEDEKIND & Co. (D.R.-P. 257832).—The *compound* (annexed formula) is obtained by the condensation of 1-chloro-2-hydroxyanthraquinone; it crystallises from nitrobenzene, does not melt at 300°, and furnishes cotton dyes.

F. M. G. M.

Attempts to Prepare a 3 : 4 : 3′ : 4′-Tetrahydroxy-1 : 1′-dianthraquinonyl. CHRISTIAN SEER and KARL EHRENREICH (*Monatsh.*, 1913, **34**, 631—648).—An unsuccessful endeavour to prepare a tetrahydroxyanthraquinonyl with the hydroxyl groups disposed in the same positions as in alizarin (compare Scholl and Seer, A., 1911, i, 453).

4-Aminoalizarin proved useless as a starting point, as it was found impossible to convert this through the diazo-compound into 4-iodoalizarin.

Alizarin dimethyl ether (1 : 2-dimethoxyanthraquinone) can be nitrated at 0° by potassium nitrate and sulphuric acid, or by nitric acid (D 1·51), with the formation of 4-*nitro*-1 : 2-*dimethoxyanthraquinone*, deep yellow, prismatic needles, which give a red solution in sulphuric acid. This substance when suspended in aqueous ammonium sulphide at 100° is reduced to 4-*amino*-1 : 2-*dimethoxyanthraquinone*, deep red needles, m. p. 182—185°, the hydrochloride of which, after diazotisation in acetic acid and treatment with aqueous potassium iodide solution, is converted into 4-*iodo*-1 : 2-*dimethoxyanthraquinone*, yellowish-brown, prismatic needles, m. p. 172—174°. The position of the iodo-group in this, and therefore of the nitro-group in the earlier substance, is proved by its red solution in sulphuric acid changing to a deep green (due to the formation of 3 : 4 : 3′ : 4′-tetramethoxy-μ-benzodianthrone, $CO<\begin{matrix}C_6H(OMe)_2\\C_6H_4\end{matrix}>C{=}C<\begin{matrix}C_6H(OMe)_2\\C_6H_4\end{matrix}>CO$; compare Scholl and Mansfeld, A., 1910, i, 494) when treated with copper powder. Attempts to achieve the desired aim of the research by heating the iodo-compound with aluminium chloride at 150—160° eliminated only two methoxy-groups with the formation of 4 : 4′-*dihydroxy*-3 : 3′-*dimethoxy*-1 : 1′-*dianthraquinonyl*,

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H(OH)(OMe){-}C_6H(OH)(OMe)<\begin{matrix}CO\\CO\end{matrix}>C_6H_4,$$

microscopic, orange-red prisms, which sublimes above 320°; it dissolves in alkali to a bluish-violet colour, which changes to red on addition of sodium hyposulphite.

Another attempt to achieve the object of the investigation was made by Scholl and Seer's method with phthalic anhydride (*loc. cit.*). For this purpose veratrole was nitrated to 4-nitro-1 : 2-dimethoxybenzene, and this was reduced by tin and hydrochloric acid. Reduction at water-bath temperature produced, however, a halogen-substituted amino-compound, 2(?)-*chloro*-4 : 5-*dimethoxyaniline*, colourless needles, m. p. 72—73°; *hydrochloride*, needles, which slowly decompose above 150°; this was converted by diazotisation and potassium iodide into 2(?)-*chloro*-1-*iodo*-4 : 5-*dimethoxybenzene*, colourless needles, m. p. 69—70°, which, on heating with copper powder at 270—280° in an atmosphere of carbon dioxide, was converted into 6(?) : 6′(?)-*dichloro*-3 : 4 : 3′ : 4′-*tetramethoxydiphenyl*, colourless needles, m. p. 160—161°, soluble in sulphuric acid to a green solution. The successful reduction of nitrodimethoxybenzene to 4 : 5-dimethoxyaniline could be effected by the gradual addition of tin to the suspension of the solid in hydrochloric acid, and the product could then be converted into 1-iodo-4 : 5-dimethoxybenzene, but it was found that this substance can be more conveniently obtained by the action of iodine and mercuric oxide on an alcoholic solution of veratrole at the ordinary temperature. When heated with copper powder at 260°, the iodo-compound is converted into 3 : 4 : 3′ : 4′-*tetramethoxydiphenyl*, colourless, silky needles, m. p. 130—132°, the solution of which in sulphuric acid passes slowly from golden-yellow to emerald-green. It was not found possible to prepare from the last substance a tetrahydroxydianthraquinonyl of the desired structure; heating with phthalic anhydride and aluminium chloride yielded a complex, deep blue mixture in which the desired substance was probably present. D. F. T

Camphor and Phenols. I. Compounds of Camphor with Quinol, Resorcinol, and Catechol. N. N. Efremov (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 348—362).—Thermal and micrographic examination of mixtures of camphor with the three dihydroxybenzenes demonstrates the existence of the three isomeric compounds,

$$C_6H_4(OH)_2,C_{10}H_{16}O,$$

melting without decomposition at 29·0° (ortho) and 11·5° (meta) respectively. The compound with quinol also melts without decomposing, but it does not correspond with a maximum on the melting-point curve.

The dihydroxybenzenes form with camphor solid solutions containing for resorcinol, 20·0%, for catechol, 15%, and for quinol, 37·5% by weight of camphor.

The eutectic mixtures formed by camphor with the dihydroxybenzenes are viscous liquids prone to supercooling, and crystallise slowly only at −15° to −20° in spherolites having a fine granular structure. In each case the eutectic mixture contains 66·6 mols.% of camphor and has a characteristic yellow colour. T. H. P.

The Constitution of "Terpineol-35°-glycuronic Acid." Juho Hämäläinen (*Biochem. Zeitsch.*, 1913, **50**, 220—222).—The conjugation

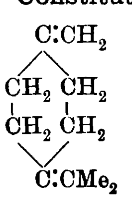
of the terpineol with glycuronic acid takes place with the scission of water. The author has administered the alcohol to rabbits, and succeeded in insolating the acid from the urine in the form of the anhydrous sodium salt, $C_{16}H_{25}O_7Na$. The urine was first precipitated with normal and then with basic lead acetate. The precipitate from the latter contained the lead salt of the glycuronate; from this the barium salt was obtained, and was crystallised from a water–alcohol–ether mixture. By treatment of this with the theoretical amount of sodium sulphate, a crystalline hydrated sodium salt was prepared.

S. B. S.

Essential Oil of Crithmum maritimum (Linn.) from Sardinia. LUIGI FRANCESCONI and E. SERNAGIOTTO (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 231—237, 312—317).—The oil of this plant from Sardinia differs from that from a French source described by Delépine, A., 1909, i, 642; 1910, i, 401).—Details are given of the properties of various fractions of the oil and of the yield from different parts of the plant. The chemical investigation of the oil shows that the only constituents common to both are dillapiole and *p*-cymene. The *d*-pinene, dipentene, and thymol methyl ether of the French oil are not present in the other, which contains, however, *β*-phellandrene and a new terpene, to which the name *crithmene* is applied. There is also a white *substance* crystallising in leaflets, m. p. 63°, which has the properties of a paraffin.

Crithmene yields an *a-nitrosochloride*, which crystallises in laminæ, m. p. 101—102°, and a *β-nitrosochloride*, $C_{10}H_{16}ONCl$, which forms quadratic plates, m. p. 103—104°; both are optically inactive. The *tetrabromide* is oily. The *nitrolpiperides* prepared from the nitrosochlorides have m. p. 138°. The compound with *benzylamine* has m. p. 103—104°. When the nitrosochloride is decomposed with alcoholic potassium hydroxide and distilled in steam, a white, micro-crystalline *substance*, m. p. 131°, is left; it contains nitrogen, and when heated with hydrochloric acid does not reduce Fehling's solution. When the decomposition of the nitrosochloride is effected under somewhat different conditions, a yellow, stable, crystalline *substance*, m. p. 53—54°, is obtained. The fractions of the oil, b. p. 178—179°, gave a crystalline *nitrosite*, m. p. 89—90°. The new terpene yields a dihydrochloride, m. p. 52°, identical with that of terpinene. R. V. S.

Constitutional Formula of Crithmene. III. LUIGI FRANCESCONI and E. SERNAGIOTTO (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 382—386. Compare preceding abstract).—After reviewing the various formulæ possible for this substance, the authors believe it to be $\Delta^{1,7-4,8}$-p-*menthadiene* (annexed formula).



This constitution accords with the physical and chemical properties of the substance. R. V. S.

Depolymerisation and Transformation of Caoutchouc. G. STAFFORD WHITBY (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 190—193. Compare this vol., i, 575).—It has been found that certain samples of

caoutchouc undergo a form of degenerative change in which the caoutchouc is converted into resin. During this process the original "tackiness" of the caoutchouc disappears, and the samples assume a smooth, polished appearance and become brittle. The extent to which the transformation occurs may be seen by the fact that a sample of such caoutchouc, which gave 9·9% of resin six weeks after collection, was found to contain 78% at the end of sixteen weeks.

The transformation is accompanied by increase in weight as a result of oxidation. A sample containing 19% of resin was found to have increased in weight to the extent of 4·38% at the end of three weeks. When kept in an air-bath at 100°, the increase in weight during the same period was 1·63%. The change goes on therefore at 100°, but at a slower rate. It is shown that the degenerative process has no connexion with the action of light, and that it is probably due to abnormal conditions, the origin of which must be sought for in the living plant. In this connexion, the function of the latex in the plant is obviously of primary importance, and in the later part of the paper the author puts forward the view that the latex represents a reserve supply of food which is rendered available by the action of an oxydase, and that the degenerative change of the extracted latex bears some relation to this oxidation process. H. M. D.

Chemistry of Caoutchouc. III. Additive Compounds of Caoutchouc with Halogen Hydracids and Halogens. FRIEDRICH W. HINRICHSEN, HERMANN QUENSELL and ERICH KINDSCHER (*Ber.*, 1913, **46**, 1283—1287).—Attempts have been made to obtain non-colloidal derivatives from caoutchouc, but without success. Cold benzene or chloroform solutions of pure Para caoutchouc have been saturated with hydrogen chloride, bromide or iodide, but the substances obtained on dilution with light petroleum still showed the Brownian movement when viewed in benzene solution under the ultra-microscope. The analyses were somewhat low for the *dihydrochloride*, $C_{10}H_{16},2HCl$, a white powder, and the *dihydrobromide*, a white powder, which still retained bromine after boiling with alcoholic potassium hydroxide, whilst the *hydriodide*, $C_{10}H_{16},HI$, was a colourless, sticky substance.

Chlorine in cold chloroform gave rise to substitution as well as addition, a white *powder*, which after repeated precipitation from alcohol gave numbers approximating to the formula $C_{10}H_{14}Cl_6$ (compare Gladstone and Hibbert, T., 1888, **53**, 679). The bromination of caoutchouc in ice-cold chloroform is practically independent of the amount of bromine used or of the time, and leads to the tetrabromide. The application of the process to the estimation of caoutchouc will be published later. J. C. W.

Chemistry of Caoutchouc. IV. Action of Iodine on Caoutchouc. FRIEDRICH W. HINRICHSEN and RICHARD KEMPF (*Ber.*, 1913, **46**, 1287—1291).—Weber (A., 1900, i, 354) described a compound, $C_{20}H_{32}I_6$, which he obtained by the action of iodine on caoutchouc in cold chloroform. Such a great absorption of iodine could not be obtained in the present experiments, but it is found that

the process is a photochemical reaction, and, as such, is almost independent of temperature. Small portions of a 1% solution of iodine were quickly rendered colourless in sunlight on addition to a 1% solution of caoutchouc in carbon disulphide, when the end-point corresponded with the absorption of one atom of iodine by two molecules of hydrocarbon. A specific action of short-waved light could not be determined, but the volume of air over the liquid seemed to be of importance. On filtering the bleached and somewhat evaporated solution into light petroleum, a white *powder* was obtained which approximated to the formula $C_{20}H_{27}O_7I$. It gave up iodine when kept, but in an iodine atmosphere in the dark it rapidly absorbed the halogen, and after three weeks had increased in weight by 170%. The glistening black *product* approximated therefore to $C_{20}H_{27}O_7I_8$. J. C. W.

Chemistry of Caoutchouc. V. Treatment of Caoutchouc with Sulphur Chloride and Sulphur. FRIEDRICH W. HINRICHSEN and ERICH KINDSCHER (*Ber.*, 1913, **46**, 1291—1297. Compare A., 1910, i, 330).—The cold vulcanisation of caoutchouc was studied by mixing a constant weight of caoutchouc in dry benzene with varying amounts of sulphur chloride and, after some time, measuring the excess of reagent. The end-product was found to agree with the formula $(C_{10}H_{16})_2S_2Cl_2$. The action of sulphur was first studied in naphthalene solution, but now systematic experiments have been carried out at 170° in cumene. The product is repeatedly extracted with acetone, when the resulting hard, brown powder is found to contain a proportion of sulphur which approaches to 32% more and more as the initial concentration of sulphur and the time of heating are increased. This corresponds with $C_{10}H_{16}S_2$ (compare Spence and Young, A., 1912, i, 706), and since the substance does not absorb bromine it is regarded as a definite compound. If the uncombined sulphur is extracted by alcoholic sodium hydroxide, however, the product contains less than 26% of sulphur. J. C. W.

Vulcanisation of Caoutchouc. II. GUSTAV BERNSTEIN (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 193—196. Compare A., 1912, i, 1006).—The "depolymerisation" of caoutchouc under the influence of a rise of temperature, mechanical treatment, and ultra-violet light has been investigated by measurements of the viscosity of xylene solutions of the caoutchouc. Samples of caoutchouc which in xylene solution show widely different viscosities are found to give the same value for the viscosity when subjected to the depolymerising action of heat, light or mechanical treatment until the viscosity has become constant. This result would seem to show that the state of aggregation which is finally attained is independent of the special characteristics of the original caoutchouc.

From measurements of the viscosity of xylene solutions of Hevea Plantation caoutchouc which was heated for five hours at temperatures between 30° and 100°, it has been found that rapid depolymerisation begins at 60—70°. This temperature was found to vary somewhat when caoutchoucs from other sources were examined in the same way.

If sulphur is mixed with the caoutchouc before exposure to ultra-violet light, it is found that vulcanisation takes place as a result of the light treatment. Vulcanisation also occurs when a xylene solution containing caoutchouc and sulphur is exposed to the short-waved rays. H. M. D.

Synthetic β-Glucosides of the Terpene Alcohols. JUHO HÄMÄLÄINEN (*Biochem. Zeitsch.*, 1913, **50**, 209—219).—By the method already described (this vol., i, 497), the following substances were prepared. *Sabinol-tetra-acetyl*-d-*glucoside*, $C_{24}H_{34}O_{16}$, long, glistening needles, m. p. 121° (corr.). *Sabinol-glucoside*, $C_{16}H_{26}O_6,H_2O$, m. p. 65—68° (corr.), $[\alpha]_D^{20}$ of anhydrous substance $-33·60°$. This glucoside is hydrolysed by emulsin. d-*Camphenilol-tetra-acetyl*-d-*glucoside*, $C_{23}H_{34}O_{10}$, long, glistening needles, m. p. 128·5—130° (corr.). d-*Camphenilol*-d-*glucoside*, $C_{15}H_{26}O_6,H_2O$, m. p. 95—98° (corr.), $[\alpha]_D^{20}$ of anhydrous substance $-25·47°$. This is slowly hydrolysed by emulsin. l-*Fenchyl-tetra-acetyl*-d-*glucoside*, $C_{24}H_{36}O_{10}$, m. p. 119—121·5° (corr.). l-*Fenchyl*-d-*glucoside*, $C_{16}H_{28}O_6$, with $[\alpha]_D^{20}$ $-36·57°$. The substance with water of crystallisation has m. p. 124—127° (corr.), m. p. of anhydrous glucoside 130—132·5° (corr.), sinters at 122°. It is slowly hydrolysed by emulsin. r-*Borneol-tetra-acetyl*-d-*glucoside*, $C_{24}H_{30}O_{10}$, m. p. 119·5—122·5° (corr.). r-*Borneol*-d-*glucoside*, $C_{16}H_{28}O_6$, with $[\alpha]_D^{20}$ $-32·99°$, m. p. of substance with water of crystallisation 133—134·5° (corr.), and of anhydrous substance 143—144·5° (corr.), sinters at 132°. It is very slowly hydrolysed by emulsin. l-*Borneol-tetra-acetyl*-d-*glucoside*, $C_{24}H_{36}O_{10}$, m. p 124° (corr.). l-*Borneol*-d-*glucoside*, $C_{16}H_{28}O_6,H_2O$, m. p. 132·5—133·5° (corr.). The anhydrous substance has m. p. 138—141° (corr.), and $[\alpha]_D^{20}$ $-60·12°$. It is fairly readily hydrolysed by emulsin. S. B. S.

Helleborein. ERNST SIEBURG (*Arch. Pharm.*, 1913, **251**, 154—183. Compare Thaeter, A., 1898, i, 39).—Helleborein is shown to belong to the group of saponins. On hydrolysis it yields acetic acid, dextrose, arabinose, and two sapogenins called "acid" and "neutral" helleboretin respectively, which are closely related and probably contain a terpene-like nucleus. As the result of pharmacological experiments, the author suggests that helleborein is not a suitable substitute for digitalin in medicine.

Helleborein (Merck), $(C_{21}H_{34}O_{10})_x$, $[\alpha]_D^{22}$ $-2·8°$, is amorphous; it furnishes an *acetyl* derivative, $(C_{21}H_{29}O_{10}Ac_5)_3$, m. p. 129—130°, which separates from alcohol in yellow scales, and on treatment with baryta yields a *product*, which is helleborein less one acetyl group (see below), and forms a pale yellow powder. *Benzoylhelleborein*, $(C_{21}H_{29}O_{10}Bz_5)_3$, m. p. 142°, is a snow-white, amorphous substance. When boiled with baryta solution, helleborein loses one molecule of acetic acid, and the latter acid is also formed when the glucoside is treated with bromine water. On hydrolysis, by boiling with dilute sulphuric acid, 1 mol. of acetic acid and 2 mols. each of dextrose and arabinose are formed. The other products of hydrolysis are *acid helleboretin* and *neutral helleboretin*. The former has the formula $C_{21}H_{36}O_7$, and appears to be a lactone, since it does not decompose carbonates and is not completely

soluble in alkali hydroxide solutions. Its behaviour on treatment with melted potassium hydroxide or nitric acid, and on distillation with zinc dust is recorded. Neutral helleboretin, $C_{15}H_{24}O_3$, is a greenish-black mass. The deacetylated helleborein referred to above does not produce hæmolysis, and is not poisonous to rabbits. T. A. H.

Structure of the Natural Saponins. ANNE W. VAN DER HAAR (*Arch. Pharm.*, 1913, **251**, 217—222. Compare A., 1912, i, 885).—The method of investigation previously described (*loc. cit.*) has been applied to guaiacum-saponin, saponin and sapotoxin from Levantine saponaria root, senegin and digitonin, and it is shown that all five of these saponins give the characteristic colour reaction with sulphuric acid. Further, the sapogenins obtained from them by acid hydrolysis, on distillation with zinc dust, yield products which can be separated by steam distillation into terpene-like oils and non-volatile products. The terpene-like oils give a violet coloration with acetic acid and sulphuric acid, whilst the non-volatile substances give the blue (phytosterol) reaction with this reagent. In the case of the products from the sapogenin derived from senegin, these colour reactions are, however, reversed. T. A. H.

Strophanthic Acid, a Saponin from the Seeds of Strophanthus Gratus. ERNST SIEBURG (*Ber. Deut. pharm. Ges.*, 1913, **23**, 278—290).—The different varieties of *Strophanthus* do not contain more than 0·2% of strophanthic acid.

The mother liquors obtained in the manufacture of *g*-strophanthin formed the starting material for the isolation of the acid. They were neutralised, diluted with water, freed from fat, and acidified with hydrochloric acid. The crude precipitated acid was repeatedly washed with water, and then precipitated with basic acid acetate; the precipitate was washed with water, and extracted with boiling 80% alcohol; the extract was diluted with water and shaken with *iso*butyl alcohol; from its solution in the latter medium, *g*-strophanthic acid was precipitated by addition of ether as a white, amorphous, voluminous mass, which was acid towards litmus, and readily dissolved in aqueous alkali carbonate and hydrogen carbonate solutions.

g-Strophanthic acid is precipitated from its aqueous solution by phosphotungstic, phosphomolybdic, and picric acids, but not by tannin. It has only feeble reducing action towards the ordinary reagents. It does not contain a methoxy-group. It yield precipitates with the salts of many heavy metals, such as copper, lead, zinc, ferrous and ferric iron, and barium, but the products do not appear to be definite chemical individuals. The solubility of the free acid appears to depend somewhat on the age of the specimens. Ultimate analysis, titration with sodium hydroxide, and analysis of the *silver* and *lithium* salts lead to the formula $C_{21}H_{34}O_{10}$ for the acid, but determination of molecular weight in glacial acetic acid solution indicates the formula $(C_{21}H_{34}O_{10})_4$.

When hydrolysed with 3% aqueous sulphuric acid, and subsequently with 4% alcoholic hydrochloric acid, strophanthic acid yields dextrose and *strophanthigenin*, $(C_{12}H_{18}O_2)_2,3\frac{1}{2}H_2O$, white needles, m. p. about

294°. The latter is faintly acidic in solution, but does not dissolve even in concentrated alkali. With bromine in glacial acetic acid solution, it yields an uncrystallisable *product*, $C_{12}H_{18}Br_2O_2$. Oxidation with potassium permanganate converts it into a crystalline *acid*, which has not been further investigated.

The following colour reactions are shown by *g*-strophanthic acid, and generally with greater readiness by *g*-strophanthigenin, but are not given by *k*-strophanthin, *g*-strophanthin, or *g*-strophanthidin: (1) a trace of substance gives an immediate yellowish-red coloration, with concentrated sulphuric acid, which gradually changes to an eosine-red with greenish fluorescence; (2) if a dilute solution of the substance in alcohol is mixed with an alcoholic solution of benzaldehyde and evaporated, the residue gives an immediate bright red coloration with sulphuric acid; (3) if a trace of the substance is dissolved in acetic anhydride and concentrated sulphuric acid cautiously added, a red ring is formed which rapidly becomes violet, then blue, and finally green; (4) a saturated alcoholic solution of dextrose or arabinose yields with a trace of substance and concentrated sulphuric acid a red ring which quickly turns to violet; with furfuraldehyde, under like conditions, a blue to green colour is developed; (5) if rhamnose is used, as in (4), a permanent, deep cherry-red colour is formed; (6) a solution of the substance in a mixture of nine parts trichloroacetic acid and one part concentrated hydrochloric acid gradually develops a pale violet colour, which becomes more intense and slightly fluorescent. H. W.

Thiophen Analogues of Triphenylethyl. MOSES GOMBERG and R. L. JICKLING (*J. Amer. Chem. Soc.*, 1913, **35**, 446—447).—Attempts have been made to prepare analogues of triphenylmethyl containing other than exclusively aromatic groups.

Thienyldiphenylcarbinyl chloride has m. p. 81°; when a solution in benzene is treated with molecular silver, it becomes dark red, and an unsaturated hydrocarbon is produced which absorbs oxygen with formation of the peroxide $(C_4SH_3{\cdot}CPh_2)O_2$.

Dithienylphenylcarbinol, m. p. 90°, has been prepared by the Grignard synthesis from ethyl benzoate and thienyl chloride. E. G.

1 : 4-Dithiens. TREAT B. JOHNSON, ROBERT C. MORAN, and EDWARD F. KOHMANN (*J. Amer. Chem. Soc.*, 1913, **35**, 447—452).—Johnson and Moran (A., 1912, i, 913) have found that when 2-benzoylmethylthiol-4-methyl-1 : 6-dihydro-6-pyrimidone is hydrolysed with concentrated hydrochloric acid, it yields 4-methyluracil together with a crystalline compound containing sulphur. A study of the latter compound has shown that it has the structure $S<\begin{matrix}CPh{:}CH\\CH{:}CPh\end{matrix}>S$, and it has therefore been designated 2 : 5-diphenyl-1 : 4-dithien. Both this substance and the corresponding 2 : 5-ditolyl compound are yellow, but dissolve in concentrated sulphuric acid to form beautiful purple solutions. Characteristic colorations are also produced by strong nitric acid and by solution of bromine in glacial acetic acid. In this respect the dithiens resemble Fries and Volk's thianthren compounds (A., 1909, i, 406). 1 : 4-Dithien, the parent substance of the compounds now

described, has been obtained by Levi and termed by him biophen (A., 1891, 551).

2 : 5-*Diphenyl*-1 : 4-*dithien*, m. p. 118—119°, crystallises in yellow prisms and is exceedingly stable.

2-p-*Toluoylmethylthiol*-4-*methyl*-1 : 6-*dihydro*-6-*pyrimidone*,

$$NH<\begin{matrix}C(S\cdot CH_2\cdot CO\cdot C_6H_4Me):N \\ CO\text{————————}CH\end{matrix}>CMe,$$

m. p. 194—195°, obtained by the action of *p*-chloroacetyltoluene on the sodium salt of 2-thio-4-methyluracil, forms colourless, prismatic crystals. On hydrolysis with 20% hydrochloric acid, it yields 2 : 5-*di-tolyl*-1 : 4-*dithien*, m. p. 137—138°, which crystallises in yellow needles.

E. G.

The Hellebore Group. III. Alkaloids of Delphinium Ajacis.

OSKAR KELLER and O. VÖLKER (*Arch. Pharm.*, 1913, **251**, 207—216. Compare A., 1910, ii, 887, 888).—This plant yields two new alkaloids, which are characterised.

The alkaloids were isolated from an alcoholic extract of the seeds. *Ajacine*, $C_{15}H_{21}O_4N,H_2O$, m. p. 142—143°, crystallises in colourless needles from dilute alcohol, is alkaline in reaction, and yields salts which are readily soluble and difficult to crystallise. The *hydrochloride*, $B_2,HCl,2H_2O$, m. p. 93°, is amorphous, as is also the *aurichloride*, $B_2,HAuCl_4$, and the *platinichloride*, B_4,H_2PtCl_6. The alkaloid absorbs bromine, contains 3 methoxyl groups, is not esterified by benzoyl chloride or acetic anhydride, does not react with methyl iodide or methyl sulphate, and is not affected by nitrous acid. On oxidation, it furnished a product smelling of butyric or valeric acid, and on distillation with zinc dust yielded a substance having an odour of benzaldehyde. On treatment with cyanogen bromide, it furnished a crystalline *compound*, m. p. 132—133°.

Ajaconine, m. p. 162—163°, forms colourless, glancing prisms, but concordant results could not be obtained on combustion, and crystalline salts could not be prepared. It contains no methoxyl groups. With methyl iodide, a crystalline *methiodide*, m. p. 121°, slender needles, was obtained, which appears to have the formula $C_{18}H_{31}O_2N,HI,H_2O$, whence the formula $C_{17}H_{29}O_2N$ is assigned provisionally to the parent base. The latter may be a secondary base, since it reacts with nitrous acid, forming a substance which gives Liebermann's reaction. Ajaconine also yields an amorphous *dibenzoyl* derivative, from which an amorphous *aurichloride* was prepared.

The behaviour of both alkaloids with the usual precipitants and reagents is described. The seeds also contain other alkaloids, which are amorphous.

T. A. H.

Comparative Solubility of Morphine and Narcotine in Pure or Aqueous Acetone and in Distilled Water.

GABRIEL GUÉRIN (*J. Pharm. Chim.*, 1913, [vii], 7, 438).—One litre of pure anhydrous acetone dissolves at 15°, 1·28 grams of morphine and 41·96 grams of narcotine. In a mixture of equal volumes of acetone and water at 15°, the solubilities are morphine 1·32 grams, and narcotine 0·70 gram

per litre. In distilled water at 15°, the solubilities are morphine, 0·288 gram, and narcotine, 0·10 gram per litre. W. P. S.

*apo*Morphine. I. Supposed Formation of *apo*Morphine on Heating or Keeping Morphine Solutions. MORITZ FEINBERG (*Zeitsch. physiol. Chem.*, 1913, **84**, 363—378).—*apo*Morphine is not formed either on prolonged boiling of morphine, morphine hydrochloride, or liquids containing morphine, such as pantopone, or on keeping such solutions with or without the addition of a nutrient substance. The separations occasionally observed from such solutions are due to traces of the sparingly soluble morphine base. Preparations of *apo*morphine obtained in commerce had the theoretical proportion of chlorine, and agreed as to their optical activity. They are therefore to be regarded as pure. E. F. A.

The Polymorphism of Codeine, Thebaine, and Narcotine; a New Type of Spherolites. PAUL GAUBERT (*Compt. rend.*, 1913, **156**, 1161—1163).—Codeine, thebaine and narcotine, and other alkaloids derived from opium, exhibit the phenomenon of superfusion, become solid without crystallisation, and can be kept in this vitreous state for several months. They are all polymorphic, codeine having five crystalline forms, narcotine three, and thebaine two, varying in stability with the temperature, and they also all present curious spherolitic formations at different temperatures. W. G.

The Structure of Ratanhine. GUIDO GOLDSCHMIEDT (*Monatsh.*, 1913, **34**, 659—664. Compare this vol., i, 71).—The estimation of methyl attached to nitrogen in ratanhine indicates the presence of a methylamino-group in this substance, and it is therefore possible that ratanhine is α-methylamino-β-p-hydroxyphenylpropionic acid (methyltyrosine). The m. p. is so indefinite that it is of little use as a comparison with the synthetical substance of this structure (Johnson and Nicolet, A., 1912, i, 585), but the action of iodine on alkaline solutions of ratanhine and of the synthetic substance produces apparently the same di-iodo-compound from each. The probability of the above structure for ratanhine is strongly confirmed by the close resemblance of the base, which is obtained by scission of carbon dioxide, with β-p-hydroxyphenylethylmethylamine (Walpole, T., 1910, **97**, 945); the free bases, together with the hydrochlorides and platinichlorides, exhibit a close agreement in m. p. It is therefore to be accepted that ratanhine, which is also known by the names surinamine (Blau, A., 1909, i, 51), geoffroyine, angeline, and andirine, is α-methylamino-β-p-hydroxyphenylpropionic acid,

$OH\cdot C_6H_4\cdot CH_2\cdot CH(NHMe)\cdot CO_2H$. D. F. T.

Synthesis of 2:3:4-Trimethylpyrrole and of 2:3:4-Trimethyl-5-ethylpyrrole (Isomeric Phyllopyrroles). HANS FISCHER and AMANDUS HAHN (*Zeitsch. physiol. Chem.*, 1913, **84**, 254—261).—Fischer and Krollpfeiffer (this vol., i, 93) have described the formation of the phthalide of a trimethylpyrrole by treating tetramethylpyrrole with phthalic anhydride. Potassium hydroxide

converts this phthalide into the corresponding acid, which after prolonged treatment with glacial acetic acid and hydrogen iodide loses the phthalic acid residue and forms 2 : 3 : 4-trimethylpyrrole, described by Piloty and Hirsch (A., 1912, i, 925). This alkylpyrrole has marked crystallising properties; it forms a crystalline picrate and an azo-dye, and is oxidised by nitrous acid to an oxime, which is converted into dimethylmaleinimide on hydrolysis.

Heating with sodium ethoxide converts the trimethylpyrrole into the isomeric phyllopyrrole, which does not crystallise.

Tetramethylpyrrole is produced when the above phthalide is heated with sodium methoxide.

On heating indigotin with sodium methoxide in sealed tubes at 230°, the C:C-junction is broken, and dimethylindole is formed as well as a second unknown compound, which crystallises well and forms a picrate, m. p. 176—177°.

3 : 4 : 5-Trimethylpyrrole crystallises in prisms, m. p. 37—38°, becoming red when exposed to the air. The picrate has m. p. 147—148°. E. F. A.

Complex Acetatoferri-bases Containing Pyridine. RUDOLF F. WEINLAND and CHR. BECK (*Zeitsch. anorg. Chem.*, 1913, **80**, 402—447. Compare A., 1910, i, 296, 635).—When pyridine (5 mols.) is added to a solution of hydrated ferric chloride (1 mol.) in glacial acetic acid (5 mols.), heat is developed and a dark green mass is obtained on cooling. When this is dissolved in chloroform and precipitated with benzene, yellowish-green crystals are obtained. Digestion with absolute alcohol converts this salt, with loss of water, into a brown, octahedral salt, and an exactly similar salt is obtained from ferric bromide. The original chloride yields a yellowish-green iodide with concentrated aqueous potassium iodide, the chlorine being completely eliminated, whilst the chloride is regenerated from the acetate and lithium chloride. These reactions point to the formulæ: $\left[Fe_4 \begin{matrix}(OAc)_6\\ 3Py\\ (OH)_2\end{matrix}\right]Cl_4$ and $\left[Fe_4 \begin{matrix}(OAc)_6\\ 3Py\\ O\end{matrix}\right]Cl_4$ for the green and brown salts respectively. The original crude product is a chloride-acetate, containing more pyridine. The brown solutions of these salts in water slowly decompose, forming a gelatinous precipitate. Benzene does not precipitate a pure tetrabromide from chloroform solution, but a mixed salt containing more pyridine. Removal of water gives a salt corresponding exactly with the chloride.

A solution of ferric acetate and lithium iodide in glacial acetic acid yields an iodide-acetate, composed of two mixed salts. Digestion with absolute alcohol yields a red, octahedral periodide-acetate,

$$\left[Fe_4 \begin{matrix}(OAc)_6\\ 4Py\\ O\end{matrix}\right]\begin{matrix}I_2{\cdot}I_2\\ (OAc)_2\end{matrix}.$$

The iodide obtained from the chloride is a mixed salt. Nitrate-acetates have also been obtained.

Ferric acetate, pyridine, and glacial acetic acid yield a compound,

$\left[Fe_4 \begin{matrix} (OAc)_6 \\ 3Py \\ OH \end{matrix} \right](OAc)_5$. Dissolving in chloroform and precipitating with benzene gives a bright copper-red salt,

$$\left[Fe_3 \begin{matrix} (OAc)_5 \\ Py \\ (OH)_2 \end{matrix} \right](OAc)_2,H_2O.$$

Solutions of ferric chloride in at least 15 mols. glacial acetic acid yield after a time with 2 mols. of pyridine, garnet-red prisms, which contain more chlorine than the previous salts, and appear to contain a complex anion, $\left[Fe \begin{matrix} Cl_5 \\ H_2O \end{matrix} \right]$, which is already known. The salt is acid and is only stable in presence of an excess of acetic acid. It has the constitution $\left[Fe_4 \begin{matrix} (OAc)_6 \\ 5Py \end{matrix} \right] \begin{matrix} (OAc)_2,CH_3\cdot CO_2H \\ \left[Fe \begin{matrix} Cl_5 \\ H_2O \end{matrix} \right]_2 \end{matrix}$ $,12H_2O$. It yields a periodide with concentrated aqueous potassium iodide,

$$\left[Fe_4 \begin{matrix} (OAc)_6 \\ 5Py \\ OH \end{matrix} \right] \begin{matrix} I_3,I_3 \\ (OAc)_2 \end{matrix}.$$

The iron atoms in the complex cations are regarded as linked together through the acetyl groups by means of subsidiary valencies. The pyridine in these compounds, like the ammonia in the complex chromiacetates, can pass in and out of the cation without, as in metal-ammines, affecting the negative groups. C. H. D.

Pyridine Derivatives. ERNST SCHMIDT (*Arch. Pharm.*, 1913, **251**, 183—207).—In continuation of work already described (A., 1905, i, 23), attempts have been made to prepare formocholine (trimethylhydroxymethylammonium hydroxide), and in default of this its pyridine analogue, by new methods which will give larger yields. The products obtained in these unsuccessful attempts are described.

Prescott and Baer (A., 1897, i, 95) have shown that by the interaction of methylene iodide and pyridine, methylenedipyridyl iodide, $CH_2(C_5H_5NI)_2$, is formed, and a further study of this reaction under various conditions shows that this is practically the sole product. It forms yellow leaflets, m. p. 220° (decomp.), but after decolorisation by animal charcoal forms colourless tablets, m. p. 222—223°, containing $1H_2O$ from water. The *chloride*,

$$CH_2(C_5H_5NCl)_2,H_2O,$$

is similar, but remains unmelted at 260°. The *platinichloride* forms yellow needles from alcohol, and does not melt at 260°. The *picrate* forms long, yellow needles, m. p. 230°, and the *mercurichloride*, $CH_2(C_5H_5NCl)_2,4HgCl_2$, long, glancing needles, m. p. 230°; the mother liquor from the preparation of the latter salt deposits on evaporation a second *mercurichloride*, m. p. 124—126°, containing 1 mol. $HgCl_2$.

Attempts to demethylate pyridylformocholine methyl ether (A., 1901, i, 443) by L. KRAUSS furnished only pyridine.

Re-examination of Prescott and Baer's work (*loc. cit.*) on the interaction of ethylene bromide and pyridine shows that in addition

to ethylenedipyridyl bromide some bromoethylpyridyl bromide (*platinichloride*, $[C_5H_5NCl\cdot C_2H_4Br]_2,PtCl_4$, long needles, m. p. 220°) is formed. In isolating the substance, the mother liquors were treated with platinic chloride, and in this way the following double *platinichlorides* and *aurichlorides* with pyridine were obtained.

(1). $[C_5H_5N,HCl]_2,PtCl_4+[C_5H_5NCl\cdot C_2H_4Cl]_2,PtCl_4$, reddish-yellow leaflets, m. p. 195°; $C_5H_5N,HAuCl_4+C_5H_5NCl\cdot C_2H_4Cl,AuCl_3$, glancing needles, m. p. 142—143°.

(2). $[C_5H_5N,HCl]_2,PtCl_4+C_5H_5NCl\cdot C_2H_4Cl,PtCl_4$, yellowish-brown, nodular crystals, m. p. 180—181°; the corresponding *aurichloride* formed leaflets, m. p. 155°.

Ethylenedipyridyl chloride, $C_2H_4[C_5H_5NCl]_2$, obtained by treating the bromide with silver chloride in water or by the direct action of ethylene chloride on pyridine, crystallises in leaflets or tablets, both forms containing alcohol of crystallisation, and does not melt at 260°. The *aurichloride*, $B,2AuCl_3$, forms small, leafy crystals from dilute alcohol. The *picrate*, m. p. 246°, forms yellow leaflets. *Chloroethylpyridyl chloride* is a hygroscopic, syrupy mass; the *platinichloride*, m. p. 218° (decomp.), forms needles, and the *aurichloride*, m. p. 135—136°, needles or leaflets, from water.

[With A. SEEBERG.]—On heating bromoethylpyridyl bromide with silver nitrate in aqueous solution, pyridinecholine is produced. This yields an aurichloride, m. p. 117°, crystallising in broad needles or leaflets, a platinichloride, m. p. 179°, forming reddish-yellow tablets, and a *mercurichloride*, m. p. 188—189°, as a colourless, crystalline powder (compare Roithner, A., 1895, i, 319, and Litterscheid, A., 1902, i, 308).

When silver oxide is used the product is pyridineneurine, which yields an aurichloride, m. p. 178°, crystallising in long, yellow needles, and a platinichloride, m. p. 193° (decomp.), forming small tablets.

T. A. H.

Kynurenic Acid. (Miss) ANNIE HOMER (*Proc. Physiol. Soc.*, 1913, xviii; *J. Physiol.*, **46**).—The kynurenic acid of dog's urine is 2-hydroxyquinoline-4-carboxylic acid. It has m. p. 288—289°; this is a higher figure than that given by previous workers. W. D. H.

The Ten Stereoisomeric Tetrahydroquinaldinomethylenecamphors. WILLIAM J. POPE and JOHN READ (*Proc. Camb. Phil. Soc.*, 1913, **17**, [2], 204).—The two enantiomorphously related tetrahydroquinaldines condense readily with the two similarly related oxymethylenecamphors, yielding products of the constitution

$$C_{10}H_{12}N\cdot CH:C<\begin{matrix}C_8H_{14}\\|\\CO\end{matrix}.$$

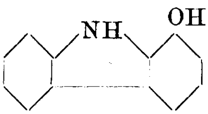
Since each component of the condensation can be obtained in a dextro- and a lævo-rotatory form, four simple optically active condensation products can be obtained, represented by the configurations: (1) *d-D*, (2) *l-L*, (3) *d-L*, (4) *l-D* (*d-* and *l-* represent the configurations of the tetrahydroquinaldine residue, and *D-* and *L-* those of the oxymethylenecamphor nucleus). From these the two racemic compounds (5) [*d-D*, *l-L*] and (6) [*d-L*, *l-D*] can be prepared, whilst in the present

instance the following two pairs of partly racemic compounds are also obtainable: (7) [*d*-*D*, *d*-*L*], (8) [*l*-*L*, *l*-*D*], (9) [*d*-*D*, *l*-*D*], and (10) [*l*-*L*, *d*-*L*].

It would be anticipated that no resolution of externally compensated tetrahydroquinaldine into its optically active components would be possible with the aid of *d*- or *l*-oxymethylenecamphor. It is shown, however, that on treating externally compensated tetrahydroquinaldine with less than one-half an equivalent of *d*-oxymethylenecamphor, a resolution can be effected because the *l*-base condenses more rapidly than the *d*-isomeride with *d*-oxymethylenecamphor; under these conditions the condensation yields about 80% of the partly racemic compound (9) and 20% of the optically active substance (4), from which *l*-tetrahydroquinaldine may be separated. H. W.

Preparation of Hydroxycarbazole. Farbenfabriken vorm. Friedrich Bayer & Co. (D.R.-P. 258298. Compare A., 1907, i, 1074; T., 1911, **99**, 103).—*Carbazoletrisulphonic acid* is obtained when carbazole (3 parts) dissolved in concentrated sulphuric acid (10 parts) is gently warmed with 3 parts of fuming sulphuric acid (20% SO_3).

Potassium carbazoletrisulphonate forms colourless crystals, and when fused with potassium hydroxide (3 parts), first at 190—200° and subsequently at 220—230°, furnishes the crystalline *potassium hydroxycarbazoledisulphonate*.



1-*Hydroxycarbazole* (annexed formula), colourless leaflets, m. p. 163°, is obtained when the foregoing potassium hydroxycarbazole disulphonate is heated with 5% sulphuric acid during five hours at 180°, and is not identical with the hydroxycarbazole (m. p. 255—256°) prepared by Ruff and Stein (A., 1901, i, 620). F. M. G. M.

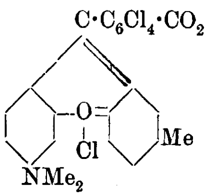
Action of Formic Acid on Triphenylmethane Dyes. Alfred Guyot and A. Kovache (*Compt. rend.*, 1913, **156**, 1324—1327. Compare A., 1912, i, 186, 972).—Hexamethyl-violet and malachite-green are only very slightly reduced by pure formic acid. The addition of sodium formate, however, causes rapid reduction with the evolution of carbon dioxide, which takes place in two stages, the second requiring the presence of a large amount of formate. The hexamethyl-violet is first reduced like the simple triarylcarbinols (*loc. cit.*), and gives hexamethyltriaminotriphenylmethane, which then undergoes further reduction to dimethylaniline and tetramethyl-*p*-diaminodiphenylmethane, with the evolution of a second molecule of carbon dioxide. This reduction is quantitative, whereas with malachite-green the reduction, whilst proceding similarly, is never quantitative in the second stage. The authors consider that this action of formic acid establishes evident relationship and a complete continuity between the dyes proper and the carbinols deprived of all auxochrome; between these two groups there only exists a difference in reactional aptitude, which can be attributed to the more or less pronounced basicity of the molecules, and which shows itself in the varying ease with which reduction takes place from one member to another. W. G.

Tetrachlororhodamines. MARCEL BLOCH (*Bull. Soc. ind. Mulhouse,* 1913, **83**, 81—84).—When an equimolecular mixture of *m*-dimethylaminophenol and tetrachlorophthalic anhydride is heated at 165°, *tetramethyltetrachlororhodamine phthalate* is obtained, which, by the successive action of sodium hydroxide and hydrochloric acid, is converted into the corresponding *hydrochloride,* green crystals, from which the free *base* is obtained by addition of sodium hydroxide. The latter dyes cotton, wool, and silk in reddish-violet shades exhibiting, in the case of the latter fibre, a magnificent fluorescence. The colours are stable towards light and alkalis. Attempts to esterify the rhodamine were unsuccessful, probably owing to the presence of electronegative atoms in the ortho-position to the carboxyl group.

When *m*-dimethylaminophenol is heated with tetrachlorophthalic anhydride in xylene solution, o-4-*dimethylamino*-2-*hydroxybenzoyltetrachlorobenzoic acid,* $NMe_2\cdot C_6H_3(OH)\cdot CO\cdot C_6Cl_4\cdot CO_2H$, is formed together with a *substance,* separating from glacial acetic acid in yellow needles, which probably has the formula $C_6Cl_4(CO\cdot O\cdot C_6H_4\cdot NMe_2)_2$.

By the condensation of tetrachlorophthalic anhydride with *m*- or *p*-phenylenediamine or their alkylated derivatives in glacial acetic acid solution, a series of yellow *compounds* has been prepared which yield colourless salts with hydrochloric acid. Results of analyses are in agreement with the general formula:

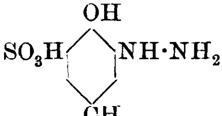
$$CO{<}^{C_6Cl_4}_{-O-}{>}C{:}N\cdot C_6H_4\cdot NR_2$$



Tetrachloroaporhodamine (annexed formula) is formed by the condensation of 4-dimethylamino-2-hydroxy-*o*-benzoyltetrachlorobenzoic acid with *p*-cresol in the presence of concentrated sulphuric acid, whilst with resorcinol or pyrogallol the same acid yields substituted rhodols.

H. W.

[Preparation of Hydroxyphenylhydrazinesulphonic Acids and their Condensation Products.] FARBWERK MÜHLHEIM VORM. A. LEONHARDT & Co. (D.R.-P. 258017).—When the *o*-hydroxyphenylhydrazines are condensed with *o*-diketones they give rise to dyes, and the preparation of the following substituted hydrazines by diazotisation and reduction of the corresponding bases is described: 4-*hydroxy*-m-*tolylhydrazine*-5-*sulphonic acid* (I); 2-*hydroxy*-1-*naphthylhydrazine*-4-*sulphonic acid* (II), and its *tolylsulphonyl* ester (III); 3-*nitro*-2-*hydroxyphenylhydrazine*-5-*sulphonic acid* (IV), and 5-*nitro*-4-*hydroxy*-m-*tolylhydrazine* (V), whilst the tinctorial properties of the *compounds* obtained by condensing them with camphorquinone, phenanthraquinone, and other *o*-diketones are tabulated in the original.



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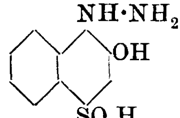

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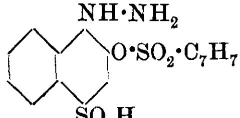

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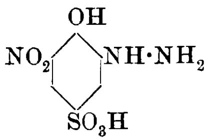
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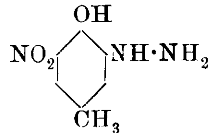
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F. M. G. M.

Hydrazones of Hydroxy-aldehydes and -ketones; Alkali-insoluble Naphthols. HENRY A. TORREY and CARL M. BREWSTER (*J. Amer. Chem. Soc.*, 1913, **35**, 426—444).—Torrey and Kipper (A., 1907, i, 325; 1908, i, 460) have shown that the insolubility of certain phenols in aqueous alkali hydroxides depends (1) on the hydroxyl group being in the ortho-position to a large side-chain, and (2) on the other substituting groups in the benzene nucleus to which the hydroxyl group is attached. In the present paper an account is given of certain naphthol derivatives which are insoluble in alkali hydroxide solutions. The naphthalene group, $\begin{array}{l}\mathrm{C{:}C-}\\ |\\ \mathrm{C{:}C-}\end{array}$, is more effective in producing insolubility than any other group yet studied. There does not seem to be any marked difference between the derivatives of 1-hydroxy-β-naphthyl methyl ketone (2-acetyl-1-naphthol) and naphthaldehyde; the phenylhydrazones, *p*-bromophenylhydrazones, phenylbenzylhydrazones, α- or β-naphthylhydrazones, and the benzidine compounds of both substances show the same insolubility.

The following compounds of 1-hydroxy-β-naphthyl methyl ketone are described. The α-*naphthylhydrazone*, $OH{\cdot}C_{10}H_6{\cdot}CMe{:}N{\cdot}NH{\cdot}C_{10}H_7$, m. p. 179—180°, insoluble in boiling aqueous sodium hydroxide; the β-*naphthylhydrazone*, m. p. 174—176°, insoluble in warm 10% sodium hydroxide; the *phenylbenzylhydrazone*, m. p. 130—132°, insoluble in boiling 10% sodium hydroxide; the *azine*, which decomposes at a high temperature and is insoluble in warm 10% sodium hydroxide, and its *acetate*, m. p. 169—170°; the *benzidine* compound,

$$C_{12}H_8(N{:}CMe{\cdot}C_{10}H_6{\cdot}OH)_2,$$

decomposing at 210°, and insoluble in boiling 10% and 30% sodium hydroxide; the *semicarbazone*, m. p. 245—250°, easily soluble in cold aqueous sodium hydroxide; the β-*naphthylimide*,

$$OH{\cdot}C_{10}H_6{\cdot}CMe{:}N{\cdot}C_{10}H_7,$$

m. p. 161—162°, insoluble in boiling 10% sodium hydroxide; and the p-*aminophenol* compound, $OH{\cdot}C_{10}H_6{\cdot}CMe{:}N{\cdot}C_6H_4{\cdot}OH$, which decomposes at 210—220° and is easily soluble in cold aqueous sodium hydroxide.

1:5-*Diphenyl*-3-α-*naphtholpyrazoline*, $OH{\cdot}C_{10}H_6{\cdot}C_3H_3N_2Ph_2$, m. p. 189° (decomp.), prepared by the action of phenylhydrazine on 2-benzylideneacetyl-1-naphthol (Kostanecki, A., 1898, i, 373), is insoluble in boiling 10% and 30% aqueous sodium hydroxide.

Bromo-1-hydroxy-β-naphthyl methyl ketone, $OH{\cdot}C_{10}H_5Br{\cdot}COMe$, has been described in an earlier paper (Torrey and Brewster, A., 1910, i, 48). The *acetyl* derivative, m. p. 95—96°, is insoluble in cold sodium hydroxide solution, but gradually decomposes on warming; the

a-naphthylhydrazone, m. p. 175—176° (decomp.), is insoluble in boiling 10% sodium hydroxide; the *β-naphthylhydrazone*, m. p. 184—186° (decomp.), and *phenylbenzylhydrazone*, m. p. 125—126°, are insoluble in warm 10% sodium hydroxide; the *oxime*, m. p. 189—190° (decomp.), yields with sodium hydroxide a green, slightly soluble salt; the *semicarbazone* and *azine* decompose at a high temperature; the former dissolves readily in dilute alkali hydroxide, whilst the latter is insoluble in boiling 10% sodium hydroxide.

The following compounds of 4-nitro-1-hydroxy-β-naphthyl methyl ketone are described. The *phenylhydrazone*, m. p. 222—223° (decomp.), imparts a red colour to cold 10% sodium hydroxide, and gradually dissolves on heating; it is insoluble in a 30% solution, however, and is decomposed when boiled with this reagent. The *a-naphthylhydrazone* decomposes at a high temperature, is insoluble in cold aqueous sodium hydroxide, but on warming renders the solution yellow. The *β-naphthylhydrazone* decomposes at 240°; it is insoluble in cold sodium hydroxide, but decomposes when heated with the solution. 4-*Nitro*-1-*acetoxy-β-naphthyl methyl ketone phenylhydrazone acetate*,

$$OAc \cdot C_{10}H_5(NO_2) \cdot CMe{:}N \cdot NAcPh,$$

has m. p. 197—198°.

β-Hydroxynaphthaldehydephenylhydrazone is insoluble in cold aqueous sodium hydroxide, and decomposes slightly when the solution is heated. The p-*bromophenylhydrazone*, m. p. 194—195° (decomp.), the *phenylbenzylhydrazone*, m.p. 152—153°, and the benzidine *compound*, $C_{18}H_8(N \cdot CH \cdot C_{10}H_6 \cdot OH)_2$, are insoluble in boiling 10% sodium hydroxide. The *semicarbazone*, m. p. above 240° (decomp.), is readily soluble in cold 10% sodium hydroxide. The *phenylhydrazone* of the *acetyl* derivative, $OAc \cdot C_{10}H_6 \cdot CH{:}N \cdot NHPh$, m. p. 164—165°, slowly decomposes when heated with sodium hydroxide solution. The *azine acetate*, $OAc \cdot C_{10}H_6 \cdot CH{:}N_2{:}CH \cdot C_{10}H_6 \cdot OH$, has m. p. 183—185°. β-Hydroxynaphthaldehyde yields two oximes, one of m. p. 148—150° (Horlacher, *Diss.*, 1899), and the other, m. p. 158—160°.

Bromo-1-*hydroxy-β-naphthyl dibromophenylethyl ketone* (*benzylidene*-2-*acetyl*-1-*naphthol tribromide*), $OH \cdot C_{10}H_5Br \cdot CO \cdot CHBr \cdot CHPhBr$, m. p. 199°, is slightly soluble in boiling 10% sodium hydroxide, but insoluble in a boiling 30% solution.

4-*Bromo*-1-*hydroxynaphthyl furfurylidenemethyl ketone*,

$$OH \cdot C_{10}H_5Br \cdot CO \cdot CH{:}CH \cdot C_4H_4O,$$

m. p. 154—155°, and the corresponding *piperonylidene* compound, decomposing at 209—214°, are insoluble in boiling 30% sodium hydroxide. The p-*nitrobenzylidene* compound, m. p. 194—195°, is slightly soluble in 10% sodium hydroxide, but insoluble in a 30% solution.

o-Hydroxyacetophenonephenylhydrazone is readily soluble in dilute sodium hydroxide. o-*Acetoxybenzaldehydephenylbenzylhydrazone* has m. p. 137—139°. Benzidine bis-salicylaldehyde is insoluble in cold 10% sodium hydroxide, whilst the corresponding azine is readily soluble.

5-*Bromo*-2-*acetoxybenzaldehydeacetylphenylhydrazone*,

$$OAc \cdot C_6H_3Br \cdot CH \cdot N{:}NAcPh,$$

has m. p. 135—136°. 5-*Bromosalicylaldehydeazine*, m. p. 305—307° (decomp.), is readily soluble in cold 10% sodium hydroxide. E. G.

The Optically Active Semicarbazone and Benzoylphenylhydrazone of *cyclo*Hexanone-4-carboxylic Acid. WILLIAM H. MILLS and (Miss) ALICE M. BAIN (*Proc. Camb. Phil. Soc.*, 1913, **17**, 203).—The *semicarbazone* of *cyclo*hexanone-4-carboxylic acid can be obtained in an optically active form by crystallising its *morphine* salt from dilute alcohol, the highest value obtained for the molecular rotation in alkaline solution being $[M]_D + 38{\cdot}8°$. The *benzoylphenylhydrazone* of the acid can similarly be obtained in an optically active form by crystallisation of its *quinine* salt from aqueous alcohol, the highest value found for the molecular rotation in alkaline solution being $[M]_D + 238{\cdot}6°$.

These optically active compounds agree so closely in their behaviour with the optically active oxime of this acid previously described by the authors (T., 1910, **97**, 1866) that there can be little doubt that the optical activity is due to similar causes in the three cases. The observations, accordingly, lend great support to the view that stereoisomerism in the sense of the Hantzsch-Werner hypothesis exists in the case of semicarbazones and phenylhydrazones. H. W.

Synthesis of Hydroxypyrrole and Pyrroline Derivatives from Ethyl Aminocrotonate. ERICH BENARY and BOLESLAV SILBERMANN (*Ber.*, 1913, **46**, 1363—1375).—As might be expected, ethyl β-amino-α-chloroacetylcrotonate (A., 1909, i, 888) readily yields pyrrole derivatives when deprived of the elements of hydrogen chloride. The product $NH{<}\begin{matrix}CMe:C\cdot CO_2Et\\ CH{=}C\cdot OH\end{matrix}$ (I.) gives a coloration with ferric chloride which is considered to be characteristic of a hydroxypyrrole, but in some cases it reacts in the tautomeric ketonic form $NH{<}\begin{matrix}CMe:C\cdot CO_2Et\\ CH_2{-}CO\end{matrix}$ (II.), and yields, *e.g.*, a dipyrroline derivative,

$$CO_2Et\cdot C{<}\begin{matrix}CO\\ CMe\cdot NH\end{matrix}{>}C:C{<}\begin{matrix}CO\\ NH\cdot CMe\end{matrix}{>}C\cdot CO_2Et \text{ (III.)},$$

on oxidation and an indoxylpyrroline, $CO_2Et\cdot C{<}\begin{matrix}CO\\ CMe\cdot NH\end{matrix}{>}C:C{<}\begin{matrix}CO\\ NH\end{matrix}{>}C_6H_4$ (IV.), on condensation with isatin.

The ester (I.) could not be hydrolysed, but it condenses in cold concentrated hydrochloric acid to form two bi-molecular compounds which can be easily transformed into one another, and to which the formulæ $CO_2Et\cdot C{<}\begin{matrix}C(OH)\\ CMe\cdot NH\end{matrix}{>}C\cdot C{<}\begin{matrix}C(CO_2Et)\\ CH\cdot NH{-}\end{matrix}{>}CMe$ (V.) and

$$CO_2Et\cdot C{<}\begin{matrix}C(OH)_2\\ CMe\cdot NH\end{matrix}{>}C:C{<}\begin{matrix}C(CO_2Et)\\ CH_2\cdot NH{-}\end{matrix}{>}CMe \text{ (VI.)}$$

are assigned.

Like other pyrrole derivatives with a free α-position, the ester couples with phenyldiazonium chloride and forms the compound

$$CO_2Et\cdot C{<}\begin{matrix}C(OH)\\ CMe\cdot NH\end{matrix}{>}C\cdot N:NPh \text{ (VII).}$$

With nitrous acid it yields the oximino-compound,

$$CO_2Et\cdot C{<}\begin{matrix}CO\\ CMe\cdot NH\end{matrix}{>}C:N\cdot OH \text{ (VIII.)},$$

which exists in two forms, but with sodium nitrite and glacial acetic acid it gives a nitroimine, $CO_2Et\cdot C\!\!<\!\!\begin{smallmatrix}\text{——CO——}\\ \text{CMe}\cdot\text{NH}\end{smallmatrix}\!\!>\!\!C{:}N\cdot NO_2$ (IX.) (compare Scholl, A., 1905, i, 181 ; 1906, i, 767), which behaves in water as a nitroiminic acid, analogous to nitroic acid (Hantzsch and Kissel, A., 1900, i, 89). The acidity is not due to the hydrogen atom of the imino-group, since this may be replaced by methyl without affecting that property.

The methylated nitroimine (X.) is slowly hydrolysed by cold alkali, when the nitroamide of acetoneoxalic acid (XI.) is formed with elimination of methylamine, alcohol, and carbon dioxide :

$$CO_2Et\cdot C\!\!<\!\!\begin{smallmatrix}\text{——CO——}\\ \text{CMe}\cdot\text{NMe}\end{smallmatrix}\!\!>\!\!C{:}N\cdot NO_2 \text{ (X.)} \longrightarrow CH_3\cdot CO\cdot CH_2\cdot CO\cdot CO\cdot NH\cdot NO_2 \text{ (XI.)}.$$

Ethyl 4-hydroxy-2-methylpyrrole-3-carboxylate (I.) is prepared by the addition of ethyl β-amino-α-chloroacetylcrotonate to alcoholic potassium hydroxide. It forms faintly yellow leaflets which decompose at 215°, reduces ammoniacal silver oxide, gives the pyrrole reaction, and produces a brown coloration in alcohol or a red precipitate in water with ferric chloride. It gives a dark red solution in cold concentrated hydrochloric acid which becomes green in time, and contains a mixture which on fractionation from alcohol deposits the *hydrate* of *ethyl 3-keto-5 : 5'-dimethyl-2 : 3'-dipyrroline-4 : 4'-dicarboxylate* (VI.) in reddish-brown needles, which are purified by conversion into the unstable, greenish additive compound with hydrochloric acid and leaving in vacuum. It gives no coloration with ferric chloride, and decomposes at 180°. The alcohol mother liquors contain *ethyl 3-hydroxy-5 : 5'-dimethyl-2 : 3'-dipyrrole-4 : 4'-dicarboxylate* (I.), which is precipitated by water, or obtained from the foregoing compound by the action of water, in the form of almost colourless leaflets which decompose at 157·5°, and give the above compound with hydrochloric acid and a transient green colour with ferric chloride.

The indigoid *ethyl bis-2-methylpyrroline-3-carboxylate* (III.) is obtained in brick-red, microscopic needles, decomp. 220—225°, which give a dark red potassium salt with alcoholic potassium hydroxide. The leuco-compound is grey, but is rapidly oxidised in the air. The *ethyl 2-indoxylpyrrolinecarboxylate* (IV.) is a dark red powder, decomp. 220—225°. *Ethyl 5-benzeneazo-4-hydroxy-2-methylpyrrole-3-carboxylate* (VII.) forms brownish-yellow needles, decomp. 225—226°, which give a red colour with ferric chloride in alcohol.

On treating the ester (I.) with sodium nitrite and dilute hydrochloric acid, the α-form of *ethyl 5-oximino-4-keto-2-methylpyrroline-3-carboxylate* (VIII.) is obtained. It is purified by means of its potassium salt, and then forms light yellow needles, decomp. 175°. When a few drops of hydrochloric acid are added to the warm alcoholic solution, the β-form crystallises in olive-green leaflets. *Ethyl 5-nitroimino-4-keto-2-methylpyrroline-3-carboxylate* (IX) forms shining yellow, flat needles with $1H_2O$, which dissolve in dilute alkalis, give precipitates with silver and lead salts, and respond to the Liebermann and Thiele-Lachman reactions. Both the hydrate

and the anhydrous compound give a brown *additive* compound, $C_8H_9O_5N_3,NH_3$, with ammonia.

Ethyl β-methylamino-α-chloroacetylcrotonate,

$$NHMe\cdot CMe\colon C(CO\cdot CH_2Cl)\cdot CO_2Et,$$

from ethyl methylaminocrotonate and chloroacetyl chloride in presence of pyridine in ether, forms long, white needles, m. p. 50·5—51°. With alkali it yields *ethyl 4-hydroxy-1 : 2-dimethylpyrrole-3-carboxylate* as a very hygroscopic mass, which, with nitrous acid, gives the analogous iso*nitroso*-compound, $C_9H_{12}O_4N_2$, in lemon-yellow needles, decomp. 162·5°, which are hydrolysed by cold sodium hydroxide to the *acid*, $C_7H_8O_4N_2$, colourless needles, decomp. 154—155°. The *nitroimino*-compound (X) is formed by the action of sodium nitrite and glacial acetic acid in orange needles with $1H_2O$, decomp. 200°, which give a brown *additive* compound with ammonia, and dissolve in sodium carbonate solution. The addition of dilute hydrochloric acid after eighteen hours to the red solution in sodium hydroxide precipitates *acetylpyruvonitroamide* (XI.) in colourless needles, decomp. 258°, which reduce ammoniacal silver oxide, and give a red coloration with ferric chloride. With phenylhydrazine it forms an indole *compound*, $C_{17}H_{15}O_3N_5$, in brick-red, soft needles, decomp. 244°, ammonia being eliminated. J. C. W.

Syntheses in the Group of the Indogenides. André Wahl and P. Bagard (*Compt. rend.*, 1913, **156**, 1382—1385).—Condensation of oxindole with cyclic aldehydes and isatin or its chloride in acetic acid solution yields, respectively, *iso*indogenides, *iso*indigotin, and indirubin (compare A., 1909, i, 330, 735). This reaction has now been extended, firstly by modifying the conditions of the reaction, and secondly by using substituted isatins.

Oxindole and isatins condense in alcoholic solution under the influence of sodium ethoxide, giving colourless products, constitutions of which have not yet been determined.

In concentrated sulphuric acid the condensation is accompanied by sulphonation, yielding *iso*indigotindisulphonic acid, which is isolated in the form of its *sodium* salt, $C_{16}H_8N_2O_2(SO_3Na)_2,2H_2O$, crystallising in brown leaflets, which become anhydrous at 100°. It is an acid colour, dyeing wool reddish-orange. Other salts have been prepared, namely: the *calcium* salt, red needles, crystallising with $5H_2O$; the *barium* salt, an amorphous, red powder; the *silver* salt, red needles, crystallising with $2H_2O$; the *nickel* salt, reddish-brown crystals, containing $5H_2O$. By decomposing the barium salt with the calculated quantity of sulphuric acid, the free *acid*, "*iso*indigo-carmine," is obtained, which is very soluble in alcohol and water, and yields an equally soluble *ammonium* salt on the addition of ammonia.

If oxindole is condensed with substituted derivatives of isatin in acetic acid solution, unsymmetrically-substituted derivatives of *iso*-indigotin are obtained, thus:

$$C_6H_4{<}^{CH_2}_{NH}{>}CO + CO{<}^{CO-}_{NH}{>}C_6H_3X =$$

$$H_2O + NH{<}^{C_6H_4}_{-CO-}{>}C\colon C{<}^{C_6H_3X}_{-CO-}{>}NH.$$

By this means *bromo*iso*indigotin*, *dibromo*iso*indigotin*, *methyl*iso*indigotin*, and *nitro*iso*indigotin*, all crystalline compounds, have been prepared.

By the interaction of substituted isatin chlorides and oxindole in benzene solution, substituted indirubins of the type

$$NH<\begin{matrix}C_6H_4\\ -CO-\end{matrix}>C:C<\begin{matrix}CO-\\ NH\end{matrix}>C_6H_3X$$

are obtained, isomeric with those prepared by Baeyer's condensation with indoxyl and isatins (compare A., 1911, i, 164, 577). These new indirubins, thus obtained, have a violet colour and dissolve in sodium hyposulphite, giving yellow dye liquors. The mono-substituted derivatives are only slightly fixed on the fibre. Nitroindirubin dyes a violet-black, due to the reduction of the nitro-group by the hyposulphite.

W. G.

The Condensation of *para*Quinones with Reduced Heterocyclic Nitrogen Compounds. JULIUS SCHMIDT and AUGUST SIGWART (*Ber.*, 1913, **46**, 1491—1497. Compare Möhlau and Redlich, A., 1912, i, 129).—The observation that hexahydrocarbazole when mixed with *p*-benzoquinone in alcoholic solution yields a violet-red liquid from which brown crystals, m. p. 199—200°, soon separate (A., 1912, i, 616) has now been followed up. The product has the composition $C_6H_2O_2(C_{12}H_{14}N)_2$, that is, bishexahydrocarbazyl-*p*-benzoquinone, analogous to the dianilino-*p*-benzoquinones (Zincke, A., 1883, 1117) and to diethyldianilino-*p*-benzoquinone (Fischer and Schrader, A., 1910, i, 270). Carbazole and dihydro- and tetrahydro-carbazole do not form such compounds, probably on account of their feebler basic character.

Piperidine and *p*-benzoquinone mixed in cold alcoholic solution give a brownish-violet coloration, followed by a deposit of brownish-violet needles with a steel-blue lustre, m. p. 172°; the substance is *dipiperidyl*-p-*benzoquinone*, $C_5NH_{10}\cdot C<\begin{matrix}CH\cdot CO\\ CO\cdot CH\end{matrix}>C\cdot C_5NH_{10}$.

The condensation product of *p*-benzoquinone with tetrahydroquinoline has already been described (Möhlau and Redlich, *loc. cit.*); 1-methyltetrahydroquinoline and 9-methylhexahydrocarbazole gave no condensation products, the crystalline deposit obtained in each case consisting of quinol. Pyrrole reacted with *p*-benzoquinone in alcoholic solution, but the dark crystalline powder, m. p. above 360°, was abnormal in composition, equimolecular quantities of the two substances apparently having entered into reaction. Coniine gave a deep coloration, but no solid product. Pyridine, quinoline, and *iso*quinoline caused only depositions of a nitrogen-free solid, which probably is some polymerisation product of quinone or quinhydrone.

Toluquinone gives rise to condensation products of small crystallising power, for although the expected colorations were obtained with piperidine and hexahydrocarbazole, no crystalline deposits could be obtained; tetrahydroquinoline gives a crystalline compound with toluquinone, but this has already been described (Möhlau and Redlich, *loc. cit.*). Naphthaquinone with hexahydrocarbazole, piperidine, and

tetrahydroquinoline gave deep red alcoholic solutions, but the deposit in each case consisted merely of naphthaquinhydrone.

Tetrachloro-*p*-benzoquinone (chloranil) behaves like *p*-benzoquinone with piperidine, producing *dipiperidyldichloro*-p *benzoquinone*,

$$C_5NH_{10}\cdot C{<}{\substack{CCl\cdot CO\\ CO\cdot CCl}}{>}C\cdot C_5NH_{10},$$

lustrous, bluish-black needles, m. p. 143—144°. D. F. T.

Action of *iso*Quinoline on 1 : 3-Dichloro-4 : 6-dinitrobenzene. THEODOR ZINCKE and G. WEISSPFENNING (*Annalen*, 1913, **397**, 255—273).—*iso*Quinoline and 1 : 3-dichloro-4 : 6-dinitrobenzene react in warm ether to form, after fourteen to fifteen days, *dinitrophenyldi*iso*quinolinium dichloride*, $C_9H_7NCl\cdot C{<}{\substack{C(NO_2)=\!=\!=CH\\ CH\cdot C(C_9H_7NCl)}}{>}C\cdot NO_2$, and an orange-red, crystalline *ψ-base*, $C_{15}H_{10}O_5N_3Cl$, m. p. 168° (decomp.), blackening at about 100°.

In its behaviour, dinitrophenyldi*iso*quinolinium dichloride resembles partly dinitrophenyldipyridinium dichloride (A., 1910, i, 585), partly 2-*op*-dinitrophenyl*iso*quinolinium chloride (this vol., i, 389). From it an orange-yellow *dichromate*, yellow *picrate*, m. p. 225°, and *platinichloride*, m. p. 250°, can be prepared. By treating its aqueous solution with sodium carbonate or ammonia, a *ψ-base* is obtained, a brownish-red powder, which is regarded as a dicarbinol base,

$$\begin{matrix} C_6H_4\cdot CH(OH) \\ | \qquad\qquad | \\ CH=\!=\!=CH \end{matrix}{>}N\cdot C_6H_2(NO_2)_2\cdot N{<}\begin{matrix} CH(OH)\cdot C_6H_4 \\ | \qquad\qquad | \\ CH=\!=\!=CH \end{matrix}.$$

This ψ-base regenerates salts of dinitrophenyldi*iso*quinolinium by treatment with acids, is converted into the yellow betaine (see below) by boiling dilute acetic acid, reacts with warm alcohols to form *carbinyl ethers*, $\begin{matrix} C_6H_4\cdot CH(OR) \\ | \qquad\qquad | \\ CH=\!=\!=CH \end{matrix}{>}N\cdot C_6H_2(NO_2)_2\cdot N{<}\begin{matrix} CH(OR)\cdot C_6H_4 \\ | \qquad\qquad | \\ CH=\!=\!=CH \end{matrix}$ (*methyl ether*, decomp. 180—190°, long, red needles; *ethyl ether*, m. p. 172°, red needles), and forms a *dihydrazide*,

$$C_6H_2(NO_2)_2(NH\cdot CH{:}CH\cdot C_6H_4\cdot CH{:}N\cdot NHPh)_2,$$

almost black crystals, by warming with alcoholic phenylhydrazine. In methyl alcoholic solution the ψ-base is converted by nitric acid, D 1·4, into the very characteristic *dinitrophenyldi*iso*quinolinium dinitrate*, $C_6H_2(NO_2)_2(C_9H_7N\cdot NO_3)_2,H_2O$, decomp. 140—150°, colourless needles.

By long keeping with 10% sodium nitrite, dinitrophenyldi*iso*quinolinium dichloride is converted into the *betaine*,

$$C_6H_2(NO_2)_2{<}\begin{matrix} O \\ | \\ C_9NH_7 \end{matrix},$$

yellow needles. The constitution of the latter, which is also obtained by treating the ψ-base with boiling 25—30% acetic acid, is proved by the formation of the substance from *iso*quinoline and 3-chloro-4 : 6-dinitrophenol at 100°. The betaine forms salts (*chloride*, colourless needles, *platinichloride*, *nitrate*) which are hydrolysed by an excess of water. A corresponding *thiobetaine*, $C_6H_2(NO_2)_2{<}\begin{matrix} S \\ | \\ C_9NH_7 \end{matrix}$, dark

crimson powder, is obtained by treating alcoholic dinitrophenyldi*iso*quinolinium dinitrate with hydrogen sulphide; it forms a very unstable *chloride* and *platinichloride*.

The ψ-base, $C_{15}H_{10}O_5N_3Cl$, behaves similarly to the ψ-base obtained from 2-*op*-dinitrophenyl*iso*quinolinium chloride (*loc. cit.*), and proves to be a chloro-derivative thereof. It has the constitution

$$\begin{matrix} C_6H_4\cdot CH(OH) \\ | \qquad\qquad \\ CH{=\!=\!=}CH \end{matrix}\!\!>N\cdot C_6H_2Cl(NO_2)_2,$$

forms a *chloride*, $\begin{matrix} C_6H_4\cdot CH \\ | \qquad \\ CH{=}CH \end{matrix}\!\!\geqslant NCl\cdot C_6H_2Cl(NO_2)_2$, colourless needles, *platinichloride*, and *nitrate*, and yields ethers by treatment with alcohols in chloroform; the *methyl ether*, m. p. 164—165° (decomp.), dark red needles, and *ethyl ether*, m. p. 156—157°, red leaflets, are described. By boiling with alcohol and aniline, the ψ-base is converted into 2-phenyl*iso*quinolinium chloride and 3-chloro-4:6-dinitroaniline, the latter being changed to 2:4-dinitro-5-aminodiphenylamine by the excess of aniline.

By warming with water, the ψ-base is transformed into an *isomeride*, $C_{15}H_{10}O_5N_3Cl$, m. p. 168° (decomp.), dark violet-red leaflets, which forms salts with acids very slowly, and does not yield ethers or a hydrazide. On the contrary the ψ-base is converted by boiling alcoholic phenylhydrazine into the *hydrazide*,

$$NHPh\cdot N\!:\!CH\cdot C_6H_4\cdot CH\!:\!CH\cdot NH\cdot C_6H_2Cl(NO_2)_2,$$

m. p. 155° (decomp.), blackish-red needles. C. S.

Preparation of 5:5-Dialkylbarbituric Acids Containing an Unsaturated Hydrocarbon Residue Attached to Nitrogen.

EMANUEL MERCK (D.R.-P. 258058. Compare A., 1899, i, 16; 1904, i, 380).—5:5-*Diethyl*-1-*allylbarbituric acid*, m. p. 77°, is obtained by heating monoallylcarbamide (20 parts) with diethylmalonyl chloride (40 parts) during fifty hours at 100—120°, whilst the latter compound with diallylcarbamide (sinapoline) furnishes 5:5-*diethyl*-1:3-*diallylbarbituric* acid, b. p. 153—157°/9 mm. F. M. G. M.

Pyrimidines. LXII. Syntheses of Pyrimidines Related Structurally to Pyrimidine-Nucleosides.

TREAT B. JOHNSON and LEWIS H. CHERNOFF (*J. Amer. Chem. Soc.*, 1913, **35**, 585—597; *J. Biol. Chem.*, 1913, **14**, 307—320).—This work was undertaken with the object of establishing the constitution of the nucleosides. The simplest nucleoside of thymine, namely, 4-hydroxymethyl-5-methyltetrahydropyrimid-2:6-dione, has been synthesised in the following manner.

When thiocarbamide is condensed with ethyl γ-ethoxy-α-methylacetoacetate (Johnson, this vol., i, 588) in presence of sodium ethoxide, 2-*thio*-4-*ethoxymethyl*-5-*methyltetrahydropyrimid*-2:6-*dione*,

$$NH\!<\!\begin{matrix} CS{-}NH \\ CO\cdot CMe \end{matrix}\!\!\geqslant C\cdot CH_2\cdot OEt,$$

m. p. 191—192°, is obtained, which crystallises in hexagonal tablets. On boiling this substance with chloroacetic acid and water, it is converted into 4-*ethoxymethyl*-5-*methyltetrahydropyrimid*-2:6-*dione*,

$$NH\!<\!\begin{matrix} CO{-}NH \\ CO\cdot CMe \end{matrix}\!\!\geqslant C\cdot CH_2\cdot OEt,$$

m. p. 220°, which forms arborescent crystals, and when heated with concentrated hydrochloric acid at 125—130° in a sealed tube yields 4-*chloromethyl*-5-*methyltetrahydropyrimid*-2 : 6-*dione*,

$$\mathrm{NH}<\begin{matrix}\mathrm{CO{-}NH}\\ \mathrm{CO\cdot CMe}\end{matrix}>\mathrm{C\cdot CH_2Cl},$$

m. p. 243°, which crystallises in plates. By the action of silver acetate on this chloro-compound, the *acetyl* derivative,

$$\mathrm{NH}<\begin{matrix}\mathrm{CO{-}NH}\\ \mathrm{CO\cdot CMe}\end{matrix}>\mathrm{C\cdot CH_2\cdot OAc},$$

m. p. 260—261° (decomp.), is produced, which is hydrolysed by barium hydroxide with formation of 4-*hydroxymethyl*-5-*methyltetrahydropyrimid*-2 : 6-*di-one*, $\mathrm{NH}<\begin{matrix}\mathrm{CO{-}NH}\\ \mathrm{CO\cdot CMe}\end{matrix}>\mathrm{C\cdot CH_2\cdot OH}$, m. p. 224—225° (decomp.), which crystallises in needles. An attempt to convert this simple nucleoside into thymine and formaldehyde by hydrolysis with 10% sulphuric acid was not successful, but on heating it with hydriodic acid and amorphous phosphorus it was converted into 4 : 5-dimethyltetrahydropyrimid-2 : 6-dione (4 : 5-dimethyluracil). E. G.

Abnormal Solubility of Colloidal Uric Acid. LEOPOLD LICHTWITZ (*Zeitsch. physiol. Chem.*, 1913, **84**, 416—418).—Polemical. Schade and Boden (this vol., i, 404) have regarded a supersaturated uric acid solution as a colloid gel. Their views are now criticised. The passage from the aggregate of molecules in drops to the amorphous solid phase, and from this to the crystalline form, takes place with very varying velocity, and the amorphous form can remain stable for a considerable time; it is therefore unnecessary to regard it as a colloid. E. F. A.

Purines. IX. 6 : 8-Dihydroxy-2-thiopurine and 6-Hydroxy-2 : 8-dithiopurine. The Desulphurisation of Thiopurines. A New Method of Preparing Xanthine. CARL O. JOHNS and ALBERT G. HOGAN (*J. Biol. Chem.*, 1913, **14**, 299—306).—6 : 8-*Dihydroxy-2-thiopurine* is easily prepared in quantity by heating a mixture of 4 : 5-diamino-6-hydroxy-2-thiopyrimidine with carbamide.

6-*Hydroxy*-2 : 8-*dithiopurine* is obtained by heating a mixture of 4 : 5-diamino-6-hydroxy-2-thiopyrimidine and thiocarbamide.

Hypoxanthine-2-thiolacetic acid and 6 : 8-dihydroxypurine-2-thiolacetic acid can be boiled with water for hours without undergoing notable decomposition. When boiled with 20% hydrochloric acid they are hydrolysed to xanthine and uric acid respectively. 6-Hydroxypurine-2 : 8-dithiolacetic acid is more stable, and it is not desulphurised by boiling for several hours with 20% hydrochloric acid, although a small quantity of a dihydroxypurine monothiolacetic acid is obtained.

6 : 8-*Dihydroxy-2-thiopurine*, $\begin{matrix}\mathrm{NH{-}CO\cdot C\cdot NH}\\ |\qquad\quad \| \\ \mathrm{CS\cdot NH\cdot C\cdot NH}\end{matrix}>\mathrm{CO}$, forms minute needles, which do not melt at 310°; they give a brilliant murexide reaction. The corresponding 6 : 8-*dihydroxypurine-2-thiolacetic acid* has decomp. 225°.

Hypoxanthine-2-thiolacetic acid, $\begin{matrix}\mathrm{NH\cdot CO\cdot C\cdot NH}\\ |\qquad\quad \| \\ \mathrm{CO_2H\cdot CH_2\cdot S\cdot C{=}N{-}C{-}N}\end{matrix}>\mathrm{CH}$,

prepared by the action of monochloroacetic acid on thiohypoxanthine, decomposes at 240°, forming a violet-coloured substance. It is decomposed quantitatively on boiling with 20% hydrochloric acid into xanthine. This forms the most convenient procedure of preparing pure xanthine in quantity; it is not necessary to isolate the intermediate thiolacetic acid. E. F. A.

Considerations and Experiments on the Constitution of the Azoxy-compounds. I. and II. ANGELO ANGELI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 201—213, 282—293).—A summary and discussion of the work of the author with various collaborators published in recent years. R. V. S.

Polyazoxy-compounds. ANGELO ANGELI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 356—360).—The paper deals with the action of hydrogen peroxide in acetic acid solution on bisbenzeneazobenzene (Mills, T., 1895, **67**, 929) and on the new *compound*,

$$NPh{:}N\cdot C_6H_4\cdot NO{:}N\cdot C_6H_4\cdot N{:}NPh.$$

This substance is prepared by the action of sodium ethoxide on *p*-nitroazobenzene; it crystallises in red laminæ, m. p. about 215°.

Bisbenzeneazobenzene, when treated with hydrogen peroxide and glacial acetic acid, yields *bisbenzeneazoxybenzene*, $C_6H_4(N_2O\cdot Ph)_2$, which forms lustrous, yellow laminæ, m. p. 155°. It yields a *dibromo*-derivative, $C_{18}H_{12}O_2N_4Br_2$, which forms yellow crystals, m. p. about 200°. The azoxy-compound has, therefore, probably the formula

$$Ph\cdot NO{:}N\cdot C_6H_4\cdot NO{:}NPh.$$

On treatment with concentrated sulphuric acid for one hour on the water-bath, it yields a product from which a substance, $C_{18}H_{14}ON_4$, can be extracted with benzene; it forms yellowish-green leaflets, m. p. 185° (yielding a red liquid), and is probably the p-*hydroxyazo*-compound, $Ph\cdot N_2\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot OH$.

Azoxybisazoxybenzene, $Ph\cdot N_2O\cdot C_6H_4\cdot N_2O\cdot C_6H_4\cdot N_2O\cdot Ph$, is obtained from the corresponding triazo-derivative above mentioned; it forms lustrous, golden-yellow crystals, m. p. 230°. It yields a *dibromide*,

$$C_{24}H_{16}O_3N_6Br_2,$$

which is a yellow, microcrystalline powder, decomposing about 265°, and in consequence the structural formula of the azoxy-compound is probably $Ph\cdot N{:}NO\cdot C_6H_4\cdot NO{:}N\cdot C_6H_4\cdot NO{:}N\cdot Ph$. The triazoxy-compound also suffers Wallach's re-arrangement, for on warming with sulphuric acid an intense blue coloration is obtained. R. V. S.

The Relation between the Metallic Salts and the Soluble Carbonates and its Bearing on the Precipitation of Protein. W. NEVILL HEARD (*J. Physiol.*, 1913, **46**, 104—129).—Since thorough dialysis removes all precipitation of emulsoid protein by salts of the heavy metals, precipitation must be associated with some removable constituent. The experiment of adding salts to such dialysed solutions shows that the production of a substance with a very low solubility product is the necessary condition in causing precipitation. The only salt in the dialysate which is capable of producing this result is a hydrogen carbonate, except in the case of silver. The reaction of the metals with emulsoid protein closely follows the reaction of these

metals with soluble hydrogen carbonates, and the conclusion is therefore drawn that the process depends on this reaction. Probably the precipitation with hydrogen carbonates and carbonates acts mainly by the removal of the hydroxyl ions freed by the hydrolysis of these salts. But the results with silver nitrate and sodium chloride suggest that there are other factors. W. D. H.

The Soluble Metallic Compounds of Sulphurised Proteins, with Special Reference to Copper. ROBERT UHL (*Zeitsch. physiol. Chem.*, 1913, **84**, 478—496).—The preparation is described of sulphur-protein compounds from various proteins by means of carbon disulphide. It is analogous to the preparation of dithiocarbamates from aliphatic amines. These substances are converted by salts of the heavy metals in presence of alkali into metal-sulphur-protein compounds which are soluble in water, and in which the sulphur is united to the metal. The compounds with copper, silver, and mercury have a high content of metal, are resistant to alkali, are not precipitated by protein solutions, are resistant to proteolytic enzymes, and do not diffuse through an animal membrane. Sulphur-peptone given subcutaneously or intravenously is relatively non-toxic. Its copper compound is also relatively non-poisonous, and produces no local reaction; the animal resists doses of copper five times greater than when given in any other way. It is deposited in most of the organs except the brain and heart; most appears in the liver, and is then secreted into the bile. It has but little effect on blood pressure, and inhibits diuresis. It is bactericidal to staphylococci, but has no action on anthrax or trypanosomes.

W. D. H.

Method of Preparing Ash-free Caseinogen and Casein LUCIUS L. VAN SLYKE and ALFRED W. BOSWORTH (*J. Biol. Chem.*, 1913, **14**, 203—206).—The ash-free proteins were prepared by alternate precipitation with dilute acid and solution in dilute ammonia several times, the last portion of calcium being removed by ammonium oxalate; after this the protein is precipitated with dilute acid and purified by treatment with water, alcohol and ether, being finally dried over sulphuric acid under reduced pressure. Elementary analyses are given of both proteins; the figures are very similar. W. D. H.

Preparation and Composition of Basic Calcium Caseinogenate and Caseinate. LUCIUS L. VAN SLYKE and ALFRED W. BOSWORTH (*J. Biol. Chem.*, 1913, **14**, 207—209).—Basic calcium caseinogenate and caseinate were prepared by treating the ash-free protein with calcium carbonate, or by dissolving the protein in lime-water and neutralising with hydrochloric acid. In the first reaction, the amount of carbon dioxide displaced by the protein was estimated, and also the amount of calcium in the resulting product. In the second method the calcium was also estimated. The compound contains 1·78% of calcium.

W. D. H.

Preparation and Composition of Unsaturated or Acid Caseinogenates and Caseinates. LUCIUS L. VAN SLYKE and ALFRED W. BOSWORTH (*J. Biol. Chem.*, 1913, **14**, 211—225).—These were prepared

by dissolving the ash-free protein in $N/50$-sodium, potassium or ammonium hydroxide, and careful neutralisation with hydrochloric acid. The caseinates contain twice the amount of the basic element present in the caseinogenates. Such compounds are monobasic. With calcium, strontium, and barium, monobasic and dibasic compounds were obtained; in the caseinates twice the amount of base combines with the protein molecule as combines in the caseinogenates. W. D. H.

Valency of Molecules, and Molecular Weights of Caseinogen and Casein. LUCIUS L. VAN SLYKE and ALFRED W. BOSWORTH (*J. Biol. Chem.*, 1913, **14**, 227—230).—From the study of the caseinogenates and caseinates, the molecular weight of caseinogen is given as 8888, and of casein as 4444. The valency of the protein molecule in basic caseinogenates is 8, in basic caseinates, 4. W. D. H.

Composition and Properties of the Brine-soluble Compound in Cheese. LUCIUS L. VAN SLYKE and ALFRED W. BOSWORTH (*J. Biol. Chem.*, 1913, **14**, 231—236).—The protein in cheese which dissolves in warm 5% solution of sodium chloride is mono-calcium caseinate, formed from calcium caseinate by removal of part of its calcium by lactic acid produced from lactose in the process of cheese-making. W. D. H.

Formation of Porphyrin. II. Porphyrinogen and its Relation to the Blood Pigment and its Derivatives. HANS FISCHER, ERICH BARTHOLOMÄUS, and HEINRICH RÖSE (*Zeitsch. physiol. Chem.*, 1913, **84**, 262—287. Compare this vol., i, 409).—Porphyrinogen, the first crystalline, colourless reduction product of the blood pigment, is obtained by the action at the ordinary temperature of glacial acetic acid and hydrogen iodide, in presence of phosphonium iodide, on hæmin, mesoporphyrin or hæmatoporphyrin. It is also obtained from the last two substances by reducing in alkaline solution with sodium amalgam, or with zinc dust and iron. Porphyrinogen is readily reconverted into mesoporphyrin by means of sodium methoxide, methyl alcoholic potassium hydroxide, alkaline potassium ferricyanide, or by exposure to atmospheric oxidation in neutral or alkaline solution.

Sodium methoxide splits off phyllopyrrole from porphyrinogen. The complete reduction is similar to that of hæmin. On oxidation, methyl ethylmaleinimide and hæmatic acid are obtained. When administered to animals, porphyrinogen has a sensibilising action, whereas mesoporphyrin has no action.

Use is made of the sparingly soluble sodium salt for the purification of mesoporphyrin. On total reduction of mesoporphyrin, phyllopyrrole is obtained with other products. E. F. A.

Behaviour of the True Nucleic Acids to Dyes. II. R. FEULGEN (*Zeitsch. physiol. Chem.*, 1913, **84**, 309—328. Compare A., 1912, i, 926). —Nucleic acid gives precipitates with basic dyes, but none with acid dyes. It is necessary to add the solution of sodium nucleate to the dye, otherwise the formation of colloidal gels prevents precipitation.

Nucleic acid and tetramethyldiaminotriphenylcarbinol give a

precipitate having the composition of a tetrabasic salt,

$$C_{43}H_{57}O_{34}N_{15}P_4,4(C_{23}H_{25}N_2),9H_2O.$$

Treatment with alcohol extracts the dye, leaving a more or less colourless residue. It is considered that an ethyl ether of the dye and nucleic acid are formed.

The compound with hexamethyl-*p*-rosaniline is also tetrabasic, namely, $C_{43}H_{57}O_{34}N_{15}P_4,4(C_{25}H_{30}N_3),9H_2O$. It forms a remarkable jelly during the preparation, which can be drawn out into very long threads. It is remarkable in being entirely soluble in methyl alcohol. Some decomposition takes place in alcoholic solution, part of the dye being eliminated.

The substances are considered to be chemical rather than adsorption compounds, and the whole of the phosphorus is shown to be fixed as nucleic acid.

Crystal-violet is a very suitable precipitant for nucleic acid, and may be used to purify it.

Methylene-blue gives a precipitate with nucleic acid, which is readily filtered and washed. It is entirely indifferent towards all solvents, and in no case could the dye be eliminated. E. F. A.

Preparation of an Iron Derivative of Iodoparanucleic Acid. KNOLL & Co. (D.R.-P. 258297. Compare A., 1909, i, 275).—When the iron derivative of paranucleic acid (Salkowski, A., 1901, i, 242, 434) is dissolved in 8% hydrochloric acid, and treated at 50° with a solution of iodine in potassium iodide, it furnishes the *iron* derivative of *iodoparanucleic acid,* a reddish-brown powder which has therapeutic properties and contains: iodine = 8%, iron = 13%, phosphorus = 2%, and nitrogen = 12%.

It can also be prepared from iodocaseinogen, pepsin, and a solution of iron alum; or by the action of iodine on paranuclein in the presence of iron alum. F. M. G. M.

Action of Quinones on Wool and Other Protein Substances. WASSILI W. SCHARVIN (*Zeitsch. angew. Chem.*, 1913, **26**, 254).—Wool is dyed reddish-brown when acted on by the vapour or solutions of *p*-benzoquinone. Derivatives of *p*-benzoquinone act in a similar manner, the rate of reaction and colour depending on the compound employed; anthaquinone and phenanthraquinone are without action on wool.

Silk, leather, casein, egg-albumin, gelatin, etc., are dyed similarly by *p*-benzoquinone and its derivatives.

The conclusion is drawn that the quinone reacts with the amino-groups in the protein, and in the case of chloro-derivatives it is found that part of the chlorine is eliminated as hydrogen chloride, although chlorine can also be detected in wool dyed with dichlorobenzoquinones. W. H. G.

Preparation of Fibrinogen by Dialysis Against Sucrose Syrup. MAURICE PIETTRE and ANTONY VILA (*Compt. rend.*, 1913, **156**, 1182—1185).—The plasma is demineralised by dialysis against a syrup of sucrose followed by dialysis against distilled water. The

plasma, placed in a collodion bag, is first immersed in the sugar syrup for eight to ten hours, then removed, and the bag and contents placed in distilled water until the contents of the bag have returned to their original volume. By this means practically the whole of the mineral substances are removed, and the fibrinogen is deposited during the second operation, thus being isolated in the minimum of time with the use of but little liquid. W. G.

β-Glutokyrine Sulphate. MAX SIEGFRIED (*Zeitsch. physiol. Chem.*, 1913, **84**, 288—299).—By the action of silver salts and barium hydroxide on glutokyrine a simplification of the glutokyrine molecule is brought about (compare Levene and Birchard, this vol., i, 109). There is no evidence that the silver and barium hydroxide treatment leads to a separation of the constituents of a mixture of kyrines. The quotient CO_2/N becomes smaller after treatment, but there is no increase in the nitrogen measured by Sörensen's formaldehyde method, indicating that no peptide linkings have been destroyed. On hydrolysis of the various fractions obtained during the treatment, arginine and lysine were obtained. E. F. A.

The Rate of Destruction of Pepsin by the Direct Electric Current. W. E. BURGE (*Amer. J. Physiol.*, 1913, **32**, 41—43).—The digestive activity of a solution of pepsin is decreased (as is that of ptyalin) by the passage through it of a direct electric current at a uniform rate per unit of current. W. D. H.

A New Method of Isolating Trypsin. HENRY LEOPOLD HOLZBERG (*J. Biol. Chem.*, 1913, **14**, 335—339).—The addition of safranine to aqueous solutions of Grübler's or Fairchild's trypsin, or to aqueous extracts of the pancreas causes a precipitate which is strongly proteolytic. The precipitate contains safranine, and is sparingly soluble in water. Removal of the safranine, or an increase in water solubility has not yet been accomplished. The precipitates produced by alcohol, or by a mixture of alcohol and ether in the mother liquor are practically devoid of proteolytic activity. W. D. H.

The Enzymes of the Pancreas. II. The Action of Calcium Salts in the Generation of Trypsin from Trypsinogen. JOHN MELLANBY and V. J. WOOLLEY (*J. Physiol.*, 1913, **46**, 159—172).—Salts of barium and strontium activate pancreatic juice as effectively as salts of calcium. On the addition of these salts to the juice the carbonate is precipitated, and the inhibiting alkali (sodium carbonate) is thus removed; the enterokinase (which is always present in the juice, although in variable amounts) is then allowed to act and convert trypsinogen into trypsin. W. D. H.

Action of Ammonia on Invertase. IV. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1913, **84**, 408—416. Compare this vol., i, 113, 541).—Invertase takes up rather more dry ammonia than diastase. Some of the ammonia is not removed in a vacuum, and nitrogen determinations indicate that part has combined with some constituent

of the enzyme. The treatment does not affect the activity of the enzyme, but after the removal of the ammonia in a vacuum the activity is less, indicating that some such chemical process as the formation of an anhydride is concerned. The conclusion is drawn that the presence of free carboxyl groups is necessary for the enzyme activity. The mere addition of ammonia to form ammonium salts and aldehyde additive compounds has no effect on the specific activity. There is thus a difference in the active chemical groups in diastase and invertase as already indicated in the experiments (*loc. cit.*) with anhydrous hydrogen chloride. E. F. A.

Synthetical Properties of Emulsin. VERNON K. KRIEBLE (*Biochem. Bull.*, 1913, **2**, 227).—An emulsin which produced *l*-mandelonitrile from amygdalin, two years later produced the *d*-variety. This is explained by the supposition that the fresh emulsin contains two enzymes, one of which synthesises the *d*-nitrile from benzaldehyde and hydrocyanic acid, whilst the other, which is less stable, synthesises the *l*-nitrile. Fresh emulsin from sweet almonds produces the *l*-, and from bitter almonds the *d*-nitrile. W. D. H.

The Biochemical Synthesis of β-Methylglucoside in a Neutral Liquid, not Participating in the Reaction. ÉMILE BOURQUELOT and ÉM. VERDON (*Compt. rend.*, 1913, **156**, 1264—1266; *J. Pharm. Chim.*, 1913, [vii], **7**, 482—486).—Emulsin, although insoluble in acetone, will bring about the synthesis of β-methylglucoside by its action on a solution of dextrose and methyl alcohol in acetone containing 20% of water. This synthesis in acetone solution is as complete as in alcoholic solution, but is somewhat slower at first. Thus the ferment is capable of synthesising and hydrolysing glucosides in a neutral liquid, such as acetone, in which it is completely insoluble (compare A., 1912, i, 593). W. G.

The Enzymes of the Character of Emulsin. LEOPOLD ROSENTHALER (*Biochem. Zeitsch.*, 1913, **50**, 486—496).—Adopting Euler's suggestion as to nomenclature, the enzyme which brings about the hydroxynitrile synthesis is termed the *oxynitrilese*, whereas that which causes the scission of the former substance is called the *oxynitrilase*. The conclusion is drawn that oxynitrilese is not identical with δ-emulsin (amygdalase + prunase), because (1) a preparation which has been heated for some time at 40° can still cause the synthesis of an optically active nitrile, whereas it does not lead to the decomposition of amygdalin. (2) A preparation which has been treated successively with acid and then with alkali (to neutralise the acid) behaves in a similar way. (3) Filtrates from the precipitates produced by copper sulphate, by saturation with magnesium sulphate or half-saturation with ammonium sulphate, produce no synthetic action, although they exert the degrading action. The experiments on which these conclusions are founded did not, however, always yield concordant results. The conclusion is also drawn that oxynitrilase and oxynitrilese are different. The grounds are (1) that the latter is more rapidly inactivated by the action of benzaldehyde cyanohydrin.

(2) In several fruits of Umbelliferæ, only the oxynitrilase is present. (3) Preparations can be artifically obtained which contain only the oxynitrilese. S. B. S.

Reversible Enzyme Action. Hydrolysis and Synthesis of Fats by a Lipase. UGO LOMBROSO (*Chem. Zentr.*, 1913, i, 1043—1044; from *Arch. Farmacol. sperim.*, 1912, **14**, 429—459).—Pancreatic secretion and intestinal juice were used as sources of lipase. At 37° hydrolysis of fats sets in immediately and continues until 80% has been changed. Synthesis is slow, requiring thirty to forty hours before it can be detected, and the amount is extremely small. The addition of bile had not the slightest effect on the synthetic process, but it accelerates the hydrolytic changes. Prolonged heating at 40° damages the hydrolytic enzyme, but does not affect the synthetic. Glycerol lessens the destructive influence of heat, but oleic acid has no such influence. The synthetic enzyme in the pancreas is not favoured by prolonged contact with either glycerol or oleic acid before these are mixed. Pancreatic juice preparations which contain the synthetic enzyme have only feeble lipoclastic properties. The addition of fats retards the synthetic changes, but does not stop them. Intestinal secretions which are active hydrolytically have no synthetic activity.
E. F. A.

Enzyme Action. V. Action of Neutral Salts on the Activity of Castor Bean Lipase. K. GEORGE FALK (*J. Amer. Chem. Soc.*, 1913, **35**, 601—616. Compare Falk and Nelson, A., 1912, i, 522, 593; Falk and Hamlin, this vol., i, 303; Falk, this vol., i, 433).—An account is given of experiments to determine the influence of neutral salts on the activity of a castor bean lipase preparation towards ethyl butyrate. In all cases, the change in the activity was found to be a continuous function of the concentration of the added salt. The activities, as compared with those of pure aqueous solutions, were decreased by the uni-univalent salts, by the chlorides and nitrates of barium and calcium (except for dilute solutions) and magnesium, by sodium oxalate, and by dilute solutions of sodium sulphate. The activities were increased by dilute solutions of the chlorides of barium and calcium, by concentrated solutions of sodium sulphate, by magnesium sulphate, and by manganous chloride and sulphate. Potassium sulphate solutions did not affect the activity.

The retarding action is probably due to coagulation of the enzyme by the salts, the ions of which produce their individual specific effects in each case. The accelerating action cannot be so easily explained, except perhaps for cases in which an increased formation of active lipase may be assumed (compare Falk and Hamlin, *loc. cit.*). E. G.

Enzyme Action. VI. Specificity of Lipase Action. K. GEORGE FALK (*J. Amer. Chem. Soc.*, 1913, **35**, 616—624).—An account is given of the effect of methyl and ethyl alcohols, acetone, glycerol, and dextrose on the activity of a preparation of lipase from the castor bean. Solutions of the alcohols and acetone exerted an inhibiting action on the hydrolysis of ethyl butyrate, the effect increasing with the con-

centration, but solutions of glycerol and dextrose did not produce any inhibiting effect except perhaps in concentrated solutions. It is considered probable that the simpler esters exert a specific inhibiting action on the activity of lipase similar to that exerted by the simpler alcohols, and that higher esters exert a smaller inhibiting action like that exerted by glycerol. This view is in harmony with the results obtained on testing the activity of castor bean lipase with solutions of methyl and ethyl acetates, ethyl butyrate, and glyceryl triacetate. In the light of these results, glyceryl triacetate is regarded as the most suitable ester for testing lipolytic activity. E. G.

Enzyme Action. VII. Further Study of the Hydrolytic Action of Amino-acids on Esters. MARSTON LOVELL HAMLIN (*J. Amer. Chem. Soc.*, 1913, **35**, 624—632).—In continuation of the study of the hydrolytic action of certain amino-acids on esters (Falk and Nelson, A., 1912, i, 593) it has been found that glycine, glutamic acid, and aspartic acid exert a varying action on methyl and ethyl acetates, glyceryl triacetate, phenyl acetate, ethyl butyrate, and ethyl and phenyl benzoates. If these esters are arranged in the order of decreasing amounts of hydrolysis, the order varies with the hydrolytic agent used, namely, water, glycine, or glutamic or aspartic acid, and this indicates that the action is selective. Solutions containing both glycine and acetic acid exert a smaller hydrolytic action on methyl acetate and ethyl butyrate than do solutions of acetic acid alone.

E. G.

Preparation of Thrombokinase from Fibrin. H. L. F. BUSWELL (*Proc. Physiol. Soc.*, 1913, iii; *J. Physiol.*, **46**).—Distilled water extracts thrombokinase from washed fibrin, but not thrombin.

W. D. H.

Glyoxylase. HENRY D. DAKIN and HAROLD W. DUDLEY (*J. Biol. Chem.*, 1913, **14**, 423—431).—The catalyst, *glyoxylase*, studied converts methylglyoxal into lactic acid, and phenylglyoxal into mandelic acid. Evidence is presented that the agent is an enzyme; it is contained in aqueous extracts of muscle, liver, blood corpuscles, yeast cells, and the tissues of the oyster, but not in serum, potatoes, or cultures of the *B. bulgaricus*. The acids yielded are mixtures of the lævo- and inactive forms. It is possible that more than one enzyme is concerned.

W. D. H.

Compounds of Carboxyarylarsinic Acids with Amino-acids Derived from Proteins. Hippuroarsinic Acid. LOUIS HUGOUNENQ and ALBERT MOREL (*J. Pharm. Chim.*, 1913, [vii], **7**, 383—389).—Hippuroarsinic acid and arsenohippuric acid have been prepared, and their physiological actions compared with those of benzarsinic acid and arsenobenzoic acid.

Dichloroarsinobenzoyl chloride (Fourneau and Ochslin, A., 1912, i, 928) reacts with glycine in presence of *N*-sodium hydroxide solution to give a liquid from which, on addition of hydrochloric acid, hippur-

arsine oxide is precipitated along with some benzarsine oxide. This precipitate on solution in sodium hydroxide solution is oxidised by hydrogen peroxide to a mixture of benzarsinic and hippuroarsinic acids, and the former is precipitated completely on adding hydrochloric acid in excess. The filtrate is made alkaline and concentrated under reduced pressure. On adding alcohol there separate *trisodium hivpurarsinate*, $Na_2AsO_3\cdot C_6H_4\cdot CO\cdot NH\cdot CH_2\cdot CO_2Na,4H_2O$, which crystallises from alcohol in needles, and on treatment with alcohol and hydrochloric acid furnishes crystalline *hippurarsinic acid*,

$$H_2AsO_3\cdot C_6H_4\cdot CO\cdot NH\cdot CH_2\cdot CO_2H,$$

which is very soluble in water, but like the analogous substances decomposes when its aqueous solution is boiled with calcium or barium chloride or magnesia mixture. On reduction by Ehrlich and Bertheim's method, it yields *arsenohippuric acid*,

$$CO_2H\cdot CH_2\cdot NH\cdot CO\cdot C_6H_4\cdot As\colon As\cdot C_6H_4\cdot CO\cdot NH\cdot CH_2\cdot CO_2H,$$

a yellow powder, soluble in solutions of alkali carbonates or phosphates, forming unstable solutions, which deposit highly toxic arsine oxides, but gives solutions in alkali hydroxides, which are stable in the absence of air, and have a toxicity similar to those of solutions of arsenobenzoic acid. T. A. H.

Physiological Chemistry.

Calorimetrical Experiments on Warm-blooded Animals. ARCHIBALD V. HILL and (Miss) A. M. HILL (*J. Physiol.*, 1913, **46**, 81—103).—An automatic self-registering respiration calorimeter for small, warm-blooded animals is described; by its use it is possible to estimate within 2% the total heat liberated. In fasting rats at 15°, the heat production per gram is constant if the animals are more than one-third the size of the full-grown animal; for smaller specimens the figure rises rapidly, and may reach 70% greater than for grown animals. If the body surface is S, and the weight W, then in rats, $S = 10 \times W^{2/3}$. The rate of heat production to S during inanition is not constant, being 140 cal. per sq. cm. for small animals, 99 for medium-sized, and 110 for large animals. Any assumption that heat production is determined by heat loss is therefore unjustifiable. The high value in small animals is probably not due to their smallness, but to their youth, and consequently high chemical activity. Rats fed on biscuit at 15° give out 13% more heat than when fasting. If this is due to Rubner's specific dynamic value of foodstuffs, it suggests that the animals, even when fasting, give out more heat than is necessary to keep them warm. If the animals are kept in the calorimeter in groups, the heat production is lessened, because contact prevents heat loss, and especially as company promotes sleep and rest; they certainly grow faster.

W. D. H.

Oxygen Capacity of the Blood Pigment. WILHELM MANCHOT (*Zeitsch. physiol. Chem.*, 1913, **84**, 306—308).—Polemical. A reply to Burn (this vol., i, 306) and to Butterfield (A., 1912, ii, 820).
E. F. A.

The Phosphorus-content of the Blood of Normal and Parathyroidectomised Dogs. ISIDOR GREENWALD (*J. Biol. Chem.*, 1913, **14**, 369—379).—After removal of the parathyroid glands, the total phosphorus of the blood and serum is increased, even at a time when the tremors are slight. The increase may be as much as 160 mg. of phosphorus per kilo. of blood. The greater part of this increase is in the fraction which is insoluble in the usual lipoid solvents, but is soluble in a mixture of dilute hydrochloric or acetic and picric acids. W. D. H.

Formation of Lactic Acid from Dextrose, Glyceraldehyde, and Dihydroxyacetone in the Blood of the Ox and Pig. ADAM LOEB (*Biochem. Zeitsch.*, 1913, **50**, 450—456).—The red corpuscles of the ox and pig, which do not cause glycolysis of either the blood-sugar or added sugar, and only produce a small amount of lactic acid, nevertheless show either as high (pig) or even a higher (ox) capacity for producing lactic acid from glyceraldehyde than the blood of the dog, which has considerable glycolytic action. The red corpuscles of the pig have, furthermore, a considerably greater capacity than those of either the dog or ox of converting dihydroxyacetone into lactic acid. S. B. S.

The Formation of Lactic Acid from Carbohydrates in Laked Blood. WALTER GRIESBACH (*Biochem. Zeitsch.*, 1913, **50**, 457—466).—From the blood of the ox and dog, cell-free blood solutions can be obtained, which, while they do not act on dextrose, can convert *dl*-glyceraldehyde and dihydroxyacetone into lactic acid as vigorously as the intact corpuscles. A mixture of racemic and *l*-acids is thereby produced, as is the case when the intact corpuscles are employed. The conclusion is drawn that the degradation of sugar into lactic acid takes place in two phases, and by two ferments; in the one phase the conversion of the dextrose into glyceraldehyde takes place, and this action is only possible when the cells are intact; in the second phase, the aldehyde is converted into lactic acid, and for this process the intact cell is not necessary.
S. B. S.

The Estimation of the So-called "Residual Reduction" of the Blood. PAUL MAYER (*Biochem. Zeitsch.*, 1913, **50**, 362—368).—By "residual reduction" is meant the reduction of Fehling's solution after the sugar in the blood has been removed by fermentation with yeast. It is now shown that pure dextrose solutions (0·1%), after treatment with various races of pure yeasts, also show a "residual reduction," after removal of proteins, etc., by colloidal iron hydroxide. This is due to substances derived from the yeast itself, and the concentrated solutions, after treatment, show reactions for amino-acids and, in most cases, also for purine substances.
S. B. S.

The Formaldehyde Titration of Proteins. II. FRIEDRICH OBERMAYER and ROBERT WILLHEIM (*Biochem. Zeitsch.*, 1913, **50**, 369—385. Compare A., 1912, ii, 399).—It is possible, by Sörensen's method, to estimate the reactive amino-groups in a protein, and the ratio of this reactive amino-nitrogen to the total nitrogen is designated the "amino-index." In euglobulin the mean value (21·5) of the index is higher than that of albumin (about 12). In mammals the value for pseudoglobulin is about the same as that for euglobulin, but in birds it does not differ very much from that of albumin (the mean value is about 15). By means of the determination of this index it is possible to show that the various protein fractions of serum are not homogeneous substances. It is also possible to demonstrate differences in the sera of different species, and the fraction salted out by 25—30% ammonium sulphate has a higher "amino-index" in the case of a hen (28·5—32·5) than in the case of an ox (19—21·5). The serum of the horse is similar to that of the ox, and the serum of the goose is similar to that of the hen; it is therefore possible that the "amino-index" of a definite fraction may be characteristic for definite classes of animals.

S. B. S.

The Specificity of Immunity Reactions, and their Explanation as Colloidal Chemical Phenomena. KURT LANDSTEINER (*Biochem. Zeitsch*, 1913, **50**, 176—184).—The author does not regard the contention of Michaelis and Davidsohn (this vol., i, 121), that certain immunity reactions are not of colloidal chemical character, as justified. The view was arrived at on the ground that certain precipitin reactions are independent to a large extent of the hydrogen ion concentrations. Attention is especially called to the fact that serum, blood corpuscles, etc., of different species exert the maximum action in the presence of different hydrogen ion concentrations. This point is illustrated by the adsorption of ricinus agglutin, by the different strengths of acid or alkali which hæmolyse the corpuscles, by the differences in the agglutination of stromata, and the differences in the precipitability of the sera precipitating reagents.

S. B. S.

The Coagulation of the Blood. The Significance of Various Physico-chemical Processes in the Action of Thrombin. M. LANDSBERG (*Biochem. Zeitsch.*, 1913, **50**, 245—272).—The temperature curve of reaction velocity of blood coagulation is the result of at least two concurrent processes. The main process is the reaction between the thrombin and fibrinogen, and is apparently of a chemical character. The other reaction, which is antagonistic to the first, is an inhibition of the thrombin action due to its adsorption by the proteins of the serum. Both processes are accelerated by increase of temperature, which exerts therefore a twofold influence on the clot formation. The temperature curve depends to a large extent on the conditions of the experiment. In such combinations, in which the adsorption process is reduced to a minimum, the clotting reaction resembles a fermentative process with an optimal temperature of 35—40°. In the combination,

magnesium sulphate plasma + Schmidt's thrombin, which is particularly favourable to adsorption processes, there is a diminution of the reaction velocity even at 17—20°. The adsorption of thrombin by the serum proteins increases with temperature, and is only partly reversible. The conversion of the serum thrombin into its inactive "metathrombin" form is simply due to adsorption; the reactivation by Schmidt's method by means of alkalis being simply the breaking down of the adsorption compound. The general results indicate that there are no facts which are antagonistic to the idea of a fermentative process in clotting.

S. B. S.

Water Drinking. XIV. The Digestive Efficiency of Saliva as Increased by Dilution with Water. OLAF BERGEIM and PHILIP B. HAWK (*J. Amer. Chem. Soc.*, 1913, **35**, 461—476).—Mattill and Hawk (A., 1912, ii, 65) have shown that the drinking of large volumes of water with meals increases the amount of carbohydrate digested. Experiments which have now been made *in vitro* show that the dilution of normal human saliva increases its digestive efficiency. The optimum dilution depends on the nature of the diluent, and is 4 volumes for 0·3% sodium chloride solution and 7 volumes for water. Water, softened by the addition of lime water, exerts an inhibiting effect, due principally to the presence of magnesium hydroxide. E. G.

The Action of Sugar on Digestion. ERWIN THOMSEN (*Zeitsch. physiol. Chem.*, 1913, **84**, 425—436).—Sucrose has no direct action on the stomach, or on the secretion of pancreatic juice and bile. Its action on the small intestine is due to prolongation of gastric digestion without altering the secretions. The lengthening of gastric digestion is due to the occurrence of long pauses in the emptying of the stomach. Sucrose is completely or almost completely absorbed in the small intestine in large quantities, but it delays the absorption of the chyme. W. D. H.

The Pepsin-Chymosin Question. A. RAKOCZY (*Zeitsch. physiol. Chem.*, 1913, **84**, 329—353. Compare A., 1911, i, 827).—The question of the identity of the milk coagulating and protein digesting enzymes is bound up with nature and age of the animal. Hasselt (A., 1911, i, 248), Porter (A., 1911, i, 698), and Burge (A., 1912, i, 148) have all established the presence of a special milk coagulating enzyme in the stomach of the calf. In such infusions where the two enzymes are present they can be separated by Hammarsten's casein method, but with the stomach infusions from other animals which contain no chymosin no such separation could be effected. The power of coagulating milk is inseparably bound up with the peptic enzyme.

In a similar manner elastin may be used to adsorb pepsin, whereas it has no effect on chymosin. This method enables the two enzymes to be separated in the gastric juice of the calf, but not in that of other animals. In slightly acid solution ($N/200$-hydrochloric acid) edestin adsorbs chymosin, but there is no action when the acidity

is increased ($N/80$-acid). On digestion with water, the adsorbed chymosin is recovered from the edestin.

Pepsin in the ox and in the calf appears to have the same properties, and that derived from the two sources is the same.

Milk is coagulated in the stomach in all mammals from the first day of life onwards. The ruminants and such animals as the horse and the pig secrete both pepsin and chymosin. Human beings secrete pepsin only, whilst in dogs and cats neither pepsin nor chymosin is present, and the coagulation is due to other factors which are at present but imperfectly understood. E. F. A.

Formation of Plastein. I. P. GLAGOLEV (*Biochem. Zeitsch.*, 1913, **50**, 162—175).—Formation of plastein has characteristics of a fermentative character, in that it takes place in the presence of minute quantities of the digestive fluid, requires a certain definite reaction of the medium, and does not take place if the digestive fluid is first boiled. It appears to be a generative process, in that when produced by rennin powder (Witte's), natural gastric juice, or papayotin, there is a diminution of the reactive amino-groups, as determined by Sörensen's formaldehyde titration. Plastein formation is a reversible process, and depends on the quantities of ferment, concentration of reacting substances, and reaction of the medium. The reversibility of the reaction can even be detected in very concentrated syrupy solutions. S. B. S.

Synthetic Powers of the Organism of the Dog. WILHELM STEPP (*Zeitsch. physiol. Chem.*, 1913, **84**, 359—360. Compare A., 1911, ii, 1002; this vol., i, 419).—This is a reply to Abderhalden's criticism of the author's work. The death which follows feeding mice on nutriment boiled in alcohol is attributed to destruction of lipoids, and doubt is expressed whether mice possess the synthetic powers to construct these substances from simple cleavage products. W. D. H.

Metabolism Experiments on Parathyroidectomised Dogs. ISIDOR GREENWALD (*J. Biol. Chem.*, 1913, **14**, 363—367).—After removal of the parathyroids, the excretion of phosphorus in the urine is lessened; there is no increase of phosphorus in the fæces; apparently it is retained in the body. This retention appears to be primary, and not secondary to the retention of sodium or potassium, or of both. In no experiments did the retention of the bases precede that of phosphorus. Whether the changes are the cause of tetany is questionable. W. D. H.

The Carbohydrate-sparing Action of Alcohol. O. TÖGEL, E. BREZINA, and ARNOLD DURIG (*Biochem. Zeitsch.*, 1913, **50**, 296—345).—The method of experiment was as follows. A human subject was kept on a carbohydrate-rich diet. A large quantity of dextrose or lævulose was then ingested, and the respiratory quotient was determined at definite intervals afterwards, while the subject was kept in a state of rest. The results thus obtained were com-

pared with those where the experiment was carried out in a similar manner, but where alcohol was ingested in addition to a carbohydrate. After ingestion of 100 grams of dextrose, it was found that the respiratory quotient sank at first, but began to rise after half an hour, until after two hours it gradually rose to 1. After an interval, it gradually sank, until after four hours it reached the original value. Repeated doses of 100 grams of dextrose administered to a subject on carbohydrate-rich diet finally caused only a slight rise in the respiratory quotient. The sugar in this case was neither burnt, excreted as such, nor found in the blood-stream. Lævulose acted in a similar manner, but the action was somewhat more marked than that of dextrose. By repeated doses of 30 grams of lævulose, the respiratory quotient could be maintained for a long time at 1. The general effect of the ingestion of alcohol with the sugar was to depress the respiratory quotient as compared with the control experiments without alcohol. The addition caused no change in the calories used up. In the first period, it was calculated that 70—100 mg. of alcohol were burnt per minute. The depression of the respiratory quotient is not due to the narcotic action of the alcohol, as this is uninfluenced by other narcotics, such as opium. The conclusion is therefore drawn that alcohol exerts a carbohydrate-sparing action in the metabolism.

S. B. S.

Nitrogenous Metabolism. EMIL ABDERHALDEN and ARNO E. LAMPÉ (*Zeitsch. physiol. Chem.*, 1913, **84**, 361—362).—Polemical. A reply to Grafe (this vol., i, 547). W. D. H.

Intermediary Metabolism of Amino-acids. HENRY D. DAKIN (*J. Biol. Chem.*, 1913, **14**, 321—333).—Serine, cysteine, proline, ornithine, and arginine all yield large amounts of sugar in glycosuric dogs. Valine, leucine, *iso*leucine, lysine, histidine, phenylalanine, and tryptophan yield little or no sugar. Arginine is thus the only amino-acid with more than five carbon atoms which yields sugar, and in this case the ornithine moiety is responsible for the action. Amino-acids with branched chains yield little or no sugar. Proline is the only cyclic amino-acid which yields sugar readily; the opening of the ring is the first step in the breakdown. Phenylalanine, tyrosine, and tryptophan all contain an alanine side-chain, but yield no sugar, although alanine itself does; this indicates that the side-chain is broken up.

Ornithine, lysine, arginine, proline, tryptophan, and di-iodotyrosine do not yield acetoacetic acid in marked amounts when added to blood perfusing a dog's liver. W. D. H.

The Behaviour of Some Hydantoin Derivatives in Metabolism. II. 2-Thiohydantoins. HOWARD B. LEWIS (*J. Biol. Chem.*, 1913, **14**, 245—256).—2-Thiohydantoin is toxic for rabbits; the toxicity is increased by the substitution of an alkyl group in the 4-position. 2-Thio-4-methylhydantoin is less toxic, and 2-thiohydantoin-4-acetic acid is not toxic in doses of 2 grams. 2-Thio-

4-methylhydantoin in fatal doses causes albuminuria in rabbits. The sulphur is not oxidised. W. D. H.

Purine Metabolism. I. Uricolysis in the Human Subject. Alonzo E. Taylor and William C. Rose (*J. Biol. Chem.*, 1913, **14**, 419—422).—The nitrogen of milk and eggs was replaced by that in sweetbreads. The purine nitrogen of the urine was increased; this increase is due solely to uric acid. More than half the ingested nitrogen was, however, either destroyed in the alimentary tract before absorption, or was converted in metabolism into non-purine substances, presumably urea. W. D. H.

The Utilisation of Ammonia in Protein Metabolism. Alonzo E. Taylor and A. I. Ringer (*J. Biol. Chem.*, 1913, **14**, 407—418. Compare this vol., i, 548).—In dogs during inanition, and still more in diabetic dogs, ammonium carbonate given by the mouth led to a retention of nitrogen; given under the skin it was promptly eliminated. The administration of urea was followed by complete elimination of all the nitrogen. Ammonia given to man on a protein-free diet was retained to the extent of two-thirds. The presence of carbohydrates in the food is not a necessary factor in the retention of nitrogen from ammonia. It is suggested that the nitrogen is retained because of a reversible reaction that leads to combination with the α-ketonic- or α-hydroxy-acids to form amino-acids, which may be used in the synthesis or sparing of the body proteins. W. D. H.

The Action of Completely Cleaved Nutriment on the Alimentary Canal. Otto Cohnheim (*Zeitsch. physiol. Chem.*, 1913, **84**, 419—424).—Although it has been shown that animals can maintain nitrogenous equilibrium on protein food which is broken down to the simplest constituents, no note has hitherto been made on the effect of such diet on the alimentary canal itself. There are other factors, such as taste, consistence, etc., which influence digestion in addition to chemical composition. In the present research, however, in a dog with a duodenal fistula fed on two commercial specimens of such nutriment (erepton and hapan), no effect on the time of digestion in the stomach or on the amount of digestive juices secreted could be found, when compared with what occurs on a usual diet. These preparations were found to be well absorbed when administered by the rectum. W. D. H.

The Preparation of Dry Animal Organ Material. Albrecht Kossel (*Zeitsch. physiol. Chem.*, 1913, **84**, 354—358).—An elaborate apparatus is described which enables animal organs to be frozen solid by means of carbon dioxide snow, cut into small pieces, and dried below 0°. Colourless or reddish-grey powders are thus obtained from the original organs. E. F. A.

The Relative Influence of Weak and Strong Bases on the Rate of Oxidations in the Unfertilised Egg of the Sea Urchin. Jacques Loeb and Hardolph Wasteneys (*J. Biol. Chem.*, 1913, **14**, 355—362).—Weak bases, which are more efficient in causing

artificial parthenogenesis, are also more efficient in raising the rate of oxidation in the unfertilised egg-cell. This lends support to the view that bases cause parthenogenesis by accelerating oxidation.
W. D. H.

Chemistry of Embryonic Growth. I. Certain Changes in the Nitrogen Ratios of Developing Trout Eggs. Ross A. Gortner (*J. Amer. Chem. Soc.*, 1913, **35**, 632—644).—An account is given of a study of the nitrogenous constituents of trout eggs at various stages of development. It is probable that the egg does not lose any nitrogen before hatching, but afterwards it suffers a rapid loss, until in twenty-one days after hatching, 21·96% of the total nitrogen has disappeared. During its development into the fish, the egg loses 25·35% of its weight, of which 37·26% is due to non-protein matter (fats, etc.) and 62·74% to proteins, and simultaneously basic forms of nitrogen increase at the expense of the monoamino-acids. Urea and uric acid are not produced in any considerable quantity. The composition of the nitrogenous substances which disappear indicates that there is a selective utilisation of the nitrogen compounds by the developing fish. It is probable that some of the energy of development is derived from the shifting of the nitrogen ratios, and it is suggested that as the change from monoamino-acids to basic nitrogen compounds proceeds the energy relations may perhaps be changed and heat liberated.
E. G.

Chemical Differentiation of the Central Nervous System. I. Comparison of the Brain of the Albino Rat at Birth with that of the Fœtal Pig. (Miss) Mathilde L. Koch (*J. Biol. Chem.*, 1913, **14**, 267—279).—Estimation of the constituents of the brain of the rat at birth shows it to be as chemically undifferentiated as the brain of a 50—100 mm. length fœtal pig. The correspondence is further supported histologically. If the nervous systems are assumed to be in corresponding states when motor control is obtained, and Donaldson's law is correct that the nervous system is in the same state at corresponding physiological ages, then the brain of the rat at birth should correspond chemically with the 100 mm. fœtal pig brain. This was found to be the case. W. D. H.

Chemical Differentiation of the Central Nervous System. II. A Comparison of Two Methods of Preserving Nerve-tissue for Chemical Examination. Waldemar Koch and (Miss) Mathilde L. Koch (*J. Biol. Chem.*, 1913, **14**, 281—282).—The material was placed directly in 95% alcohol, and part was dried at 95°. The latter process was found to seriously affect the analyses, the most important change produced being a destruction of phosphatides; this was more marked in brains than in spinal cords.
W. D. H.

Distribution of Nerves in the Heart. (Miss) Winifred C. Cullis and (Mrs.) Enid M. Tribe (*J. Physiol.*, 1913, **46**, 141—150). —After section of the auriculo-ventricular bundle in rabbit and cat,

pilocarpine and muscarine no longer inhibit ventricular activity; they act on the auricles as usual, and are antagonised by atropine; atropine has no effect on the ventricles. Under similar conditions adrenaline produces its normal augmentor effect on the ventricles. From this, it appears that the ventricle does not receive vagus fibres, and that the normal effect of the vagus on the ventricles is therefore indirect through the auricle; further, the ventricle must be supplied with sympathetic fibres, which reach it not only by way of the auriculo-ventricular bundle. W. D. H.

Action of Certain Drugs on Isolated Strips of Ventricle. (Miss) CONSTANCE LEETHAM (*J. Physiol.*, 1913, **46**, 151—158).—Experiments are recorded with isolated strips of ventricle which confirm the findings of Cullis and Tribe (see preceding abstract). W. D. H.

Action of Dyes on the Isolated Frog's Auricle. A. J. CLARK (*Proc. Physiol. Soc.*, 1913, xx; *J. Physiol.*, **46**).—The excised auricle and fibres of the frog's heart beat in Ringer's fluid for some hours. Neutral-red dissolved in the fluid stains the muscular fibres red, but does not injure them. If the alkalinity of the fluid is increased, the fibres remain red as long as they exhibit activity, but when the concentration of alkali is sufficient to arrest activity, they turn yellow. This agrees with Warburg's observations on sea-urchin eggs, and supports the conclusion that normally animal cells are not permeable to hydroxyl ions. W. D. H.

The Presence of Trimyristin and Cephalin in the Liver. ARMANDO FRANK (*Biochem. Zeitsch.*, 1913, **50**, 273—282).—The coagulated and dried ox-liver was extracted by acetone, from which solution, on keeping, a crystalline substance separated, which was identified as trimyristin. The liver powder was then extracted with light petroleum. The extract thus obtained was dissolved in ether and precipitated with acetone. The precipitate was redissolved, filtered, and then reprecipitated with acetone, and this procedure was repeated many times. The substance was, in composition and properties, nearly allied to the cephalin isolated from brain by Thudichum and others. Experiments were carried out which tend to show that the so-called liver jecorin is cephalin contaminated with other substances, such as sugar. S. B. S.

Estimation of Adrenaline. THOMAS R. ELLIOTT (*Proc. Physiol. Soc.*, 1913, xv—xvii; *J. Physiol.*, **46**).—Many workers give adrenaline values which are too low owing to faulty extraction and estimation. At birth nearly all the adrenaline is in the outside paraganglia; in the adult the two suprarenals contain 8—9 mg. In septic conditions it may drop to a quarter of this value. Estimations may be made by the effect on arterial pressure, or by the new colorimetric reaction of Folin and Denis with phosphotungstic acid. The two work out practically the same, but the latter is much the simpler and quicker method. W. D. H.

The Iodine and Phosphorus Contents, Size, and Physiological Activity of the Fœtal Thyroid Gland. FREDERIC FENGER (*J. Biol. Chem.*, 1913, **14**, 397—405).—Functional therapeutic activity and the presence of iodine coincide in the fœtal human thyroid as in extra uterine life. The amount of iodine during the last three months of fœtal life is uniform in the various seasons. The fœtal thyroid is relatively large, and contains more iodine and phosphorus per unit of body weight than those from mature animals. This is especially the case for females. Enlarged thyroid glands were found in small fœtuses. The enlarged glands, as in the adult, contain less iodine and more phosphorus than the normal. Enlargement of the fœtal thyroid is common, and is probably the consequence of insufficient supply or faulty assimilation of iodine on the part of the pregnant animal. W. D. H.

The Changes in Metabolism Produced by the Extirpation of Thyroids and Parathyroids. RAFFAELE PALADINO (*Biochem. Zeitsch.*, 1913, **50**, 497—507).—The experiments were carried out on dogs. The parathyroids and thyroids appear to exert a considerable influence on the phosphorus metabolism, for after extirpation the amount of phosphate excreted (chiefly in the form of phosphates of alkaline earths) increases to three times the normal amount. The amount of calcium excreted diminishes. There is no marked change in the nitrogen excretion. S. B. S.

The Relation of the Corpus Luteum to Lactation. CHARLES H. O'DONOGHUE (*Proc. Physiol. Soc.*, 1913, vi; *J. Physiol.*, **46**).—In rabbits, if the rupture of the Graafian follicles in the ovary is followed by the formation of corpora lutea, there is also growth of the mammary glands, but there is no such growth if corpora lutea do not form. W. D. H.

Biochemistry of the Female Genitalia. III. Enzymes of Ovary, Uterus, and Bladder in Sheep. JACOB ROSENBLOOM and THUISCO A. ERPF-LEFKOVICZ (*Biochem. Bull.*, 1913, **2**, 233—235).—Lipase and amylase are more abundant in the ovary and uterine mucous membrane of pregnant than of non-pregnant sheep. Pregnancy has no effect on the acid-protease of either organ, but increases the alkali-protease. Bladder extracts contained lipase, amylase, and acid-protease, but no alkali-protease. W. D. H.

Biochemistry of the Female Genitalia. IV. Absence of Certain Enzymes from the Human Chorion. JACOB ROSENBLOOM (*Biochem. Bull.*, 1913, **2**, 236—237).—One chorion weighing 10 grams was examined. Extracts made with water and with glycerol were free from amylase, sucrase, maltase, lactase, lipase, peptidase, ereptase, acid-protease, and alkali-protease. The enzymes of the placenta are either developed later, or originate from the maternal moiety (decidua serotina). W. D. H.

The Effect of Small Variations in Concentration of Ringer's Solution on the Response of Isolated Plain Muscle. HENRY H. DALE (*Proc. Physiol. Soc.*, 1913, xix; *J. Physiol.*, **46**).—By adding

salt in small amounts to Ringer's fluid in which plain muscle (uterus) is suspended, the response of the muscle to the anaphylactic reaction and to stimulant drugs is lessened or annulled. If the tonicity of the fluid is lowered by adding water, the responsiveness is increased. The effects are not due to specific ionic action, but are due to alterations in osmotic pressure; solutions of non-electrolytes produce the same effects. W. D. H.

Muscle Chemistry. VI. The Free Amino-acid Nitrogen Titratable by Formaldehyde and the Total Extractive Nitrogen in Muscular Tissue of Animals in a State of Inanition. GIUSEPPE BUGLIA and A. COSTANTINO (*Zeitsch. physiol. Chem.*, 1913, **84**, 243—253).—In dogs to which water only was given for periods varying from twelve to twenty-five days, there was no change in the total nitrogen of the muscles, but there was a small increase in the total extractive nitrogen and in the nitrogen of free amino-acids. This change is not a progressive one, that is, it does not increase as the period of inanition increases. Confirmatory experiments on the octopus are also recorded. W. D. H.

The Lipins (Lipoids) of the Heart Muscle of the Ox. JACOB ROSENBLOOM (*J. Biol. Chem.*, 1913, **14**, 291—294).—Only about 40% of the ether and alcohol extract of heart muscle of the ox is composed of phospholipins (phosphatides), and practically no difference in this percentage was obtained on comparing the extractions carried out in the cold with those carried out at the boiling point of the solvent. W. D. H.

Origin of Fatigue. GAETANO VIALE (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 253—256).—In prolonged muscular work quantities of water are eliminated in the sweat. This water comes from the blood, which in turn withdraws water from the tissues. When a certain point is reached, the necessary water is no longer forthcoming. This is evidenced by decreased secretion of sweat, and by increase in the amount of sodium chloride contained in it. The origin of fatigue is to be found in this removal of water, which causes accumulation of toxins in the blood and disturbs the heat regulation of the organism. In agreement with other workers, the author finds a decrease in red blood corpuscles and in hæmoglobin in fatigue, and this is to be explained as being due to an accumulation of them in the organs. R. V. S.

The Behaviour of the Creatine of Muscle during Fatigue. VITTORIO SCAFFIDI (*Biochem. Zeitsch.*, 1913, **50**, 402—417).—In the muscular tissue of the frog and dog (and probably in all muscular tissue) creatinine does not exist as such in a preformed condition. Care must be taken to exclude high temperatures and acids in the process of its extraction from the tissues. Neither does creatinine appear to be formed in frog's muscle during work; if it is formed, it is either immediately removed or destroyed. Creatine shows certain variations in the quantity found, both in resting and

fatigued conditions, these variations being of about the same order of magnitude in both cases. It was not possible therefore to draw the conclusion that the creatine is formed as a result of work. It is, however, possible that during work creatine is used up, and new supplies are formed from degradation products of the muscle proteins. The condition of the circulation exerted no influence on the creatine metabolism in the frog during muscular work, as similar results were obtained when the circulation was intact, or entirely excluded. S. B. S.

The Effect of Adrenal Secretion on Muscular Fatigue. WALTER B. CANNON and L. B. NICE (*Amer. J. Physiol.*, 1913, **32**, 44—60).—The experiments were performed on cats, rabbits, and dogs; a fatigue curve of a voluntary muscle was obtained by stimulating its nerve. Excitation of the splanchnic nerve increased the height of the muscular contraction. The question was whether this was due to the pouring out of adrenaline into the circulation, and this is answered in the affirmative; the adrenaline appears to act, however, not on the muscle directly, but by improving the circulation of blood through it. Previously reported favouring effects of adrenaline on voluntary muscles (mainly studied in cold-blooded animals) are capable of a similar explanation.
W. D. H.

The Consumption of Fats in the Animal Organism. G. LAFON (*Compt. rend.*, 1913, **156**, 1248—1250).—In order to determine the consumption of fat by the tissues, the author has estimated the amount of fat in the arterial blood and in the venous blood coming from the muscle, first in a state of repose, and then during activity. This has been done in the case of the horse and the ass, working on the muscle of the upper lip, activity being produced by mastication, and in the case of the dog on the muscle of a hind limb, the muscle being electrically excited. The results show that the fat is consumed directly, and to the same extent as dextrose, during the activity of the tissues, and in particular during muscular work. Muscles fatigued by electrical excitation contain less fat than fresh muscle. W. G.

Fluorine in the Animal Organism. I. Skin and its Appendages. ARMAND GAUTIER and PAUL CLAUSMANN (*Compt. rend.*, 1913, **156**, 1347—1353).—Fluorine is to be found everywhere in the organs of plants and animals, but is specially concentrated in a few of them. This paper gives an account of the quantitative examination for fluorine of the skin, and such appendages as the hair, epidermis, nails, tooth enamel, etc., in the case of human beings, animals, birds, and fishes. In their fluorine content, the hair, down, fish-scales, nail, and tortoise-shell resemble the epidermic tissue, whilst the enamel of teeth and the horns differ from it widely, the former parts being rich and the latter poor in fluorine. The fluorine in skin itself appears to accompany the phosphorus and increase with it, for the same organs, without being proportional

to it. It is more abundant at the adult age in human than in animal skin, and diminishes in organs which are in process of decay, such as hair, teeth, etc., of old animals.

The method of estimation consists in incinerating the organ under examination, when dried, with 1 to 1·5% of calcium oxide, and the fluorine is estimated in the alkaline non-fused ash by a method already described (compare A., 1912, ii, 681, 805, 806). W. G.

The Relation of Osmotic Pressure to Absorption Phenomena in the Dog-fish. G. G. SCOTT and WILLEY DENIS (*Amer. J. Physiol.*, 1913, **32**, 1—7).—Dog fishes, of which the spinal cord was largely destroyed, were immersed in various solutions (methylene-blue, boric acid, potassium iodide), and the material being prevented from entering the alimentary canal, the time was noted when they appeared in the blood, urine, etc. The gill membranes appear to be the main channel of absorption, and the physical laws of diffusion suffice to explain the results. W. D. H.

The Action of Ultra-violet Rays on the Ear of the Rabbit Influence of Intensity. Intermittent Radiations. VENCESLAS MOYCHO (*Compt. rend.*, 1913, **156**, 1268—1271. Compare this vol., i, 424).—As the intensity of the radiation increases, the time necessary for the ear to be subjected to it, to produce visible effect, diminishes. The amount of energy necessary to produce minimum visible reaction is practically constant for intensities varying from 4 to 100. If, instead of continuous radiation, the ear is subjected to intermittent treatment, the visible effect is produced when the sum of the short radiations is equal to the continuous radiation, providing that the intervals between the application of the light do not exceed forty-eight hours. W. G.

Chemical Studies on Rhizostoma Cuvieri. RICHARD VON ZEYNEK (*Monatsh.*, 1913, **34**, 581—621).—If a jelly-fish of the above type is removed from water, a mucous substance is exuded which contains innumerable stinging threads; it causes an intense burning when cautiously placed on the tip of the tongue. The mucous substance easily undergoes decomposition; when precipitated by ammonium sulphate and redissolved by a very weak potassium hydroxide solution, acetic acid throws down a flocculent precipitate, which dissolves readily in hydrochloric acid; when heated with this acid, a solution is obtained which reduces Fehling's solution and gives an osazone. The precipitate given by acetic acid contains no phosphorus, whilst the potassium hydroxide solution gives the biuret reaction. The stinging threads are very resistant, and contain very appreciable quantities of silicic acid. When the above mucous substance is allowed to dry on the clothes, the dust causes nasal irritation and acute catarrh, which persists for several hours. The substance to which irritation is due appears to be non-volatile; a careful examination of the mucous substance, however, revealed the presence of an alkaloidal substance.

[With F. AMESEDER.]—Specimens of the Rhizostoma were

analysed, also the water in which one had lived and parts of the organism; the results are to be seen in the original.

The blue colouring matter (zoocyanin) present in *Rhizostoma Cuvieri* varies slightly in tone with the age of the specimen. The fresh aqueous extract is neutral, and the coloured substance is almost entirely precipitated by a 22—27% solution of ammonium sulphate, when it is obtained as a gelatinous mass; it was purified by washing and fractional precipitation with ammonium sulphate solution. The aqueous solution of the substance is turned brown on warming to 55° or on adding alcohol or acetone. Formaldehyde has no effect, but precipitates are obtained with phosphotungstic acid, phosphomolybdic acid, potassium bismuth iodide, potassium mercuri-iodide, and a solution of iodine in potassium iodide. It thus appears that the colouring matter is a protein substance, and the composition is in confirmation of this view. The colour was examined spectroscopically. D. F. T.

Analysis of Human Bile. JACOB ROSENBLOOM (*J. Biol. Chem.*, 1913, **14**, 241—244).—An analysis of a specimen of fistula bile is given, and compared with others previously published. W. D. H.

The Physiology of Secretion in the Kidney. OTTO COHNHEIM (*Zeitsch. physiol. Chem.*, 1913, **84**, 451—467).—Sodium chloride and dextrose are taken up by the surviving kidney at body temperature from solutions, and fixed in loose chemical union, which is dissolved at boiling heat. These combinations, as well as the secretion of these substances by the kidney, have a certain threshold, beneath which the kidney unites with none, and over it with considerable quantities. The chemical combination with the cell-constituents is a preliminary stage in secretion. W. D. H.

The Conditions Affecting the Formation and Excretion of Formic Acid. The Estimation of Formic Acid in Urine. HENRY D. DAKIN, N. W. JANNEY, and ALFRED J. WAKEMAN (*J. Biol. Chem.*, 1913, **14**, 341—354).—The formic acid in urine is partly endogenous. The effect of a number of substances on formic acid excretion was investigated, including amino-, hydroxy-, and saturated fatty acids. Special attention is called to the effect of inanition, which greatly reduces the amount excreted. The acid is largely increased when carbohydrates are given by the mouth or subcutaneously. Protein feeding is followed by a similar but smaller increase. Formic acid is regarded as a product of the intermediary metabolism of carbohydrates and proteins.

Formic acid is estimated in urine by saturating the latter with ammonium sulphate, extracting with ether, removing the formic acid from the ether by sodium carbonate, acidifying with phosphoric acid, distilling in a current of steam, adding mercuric chloride to the distillate, and weighing the calomel formed. W. D. H.

The Excretion of Nitrogen Subsequent to Ligature of Successive Branches of the Renal Arteries. J. D. PILCHER (*J. Biol. Chem.*, 1913, **14**, 389—395).—Ligaturing half the blood

supply of both kidneys causes no noticeable disturbance in renal function. Complete ligature of one artery, and one branch of the other (that is, shutting off three-quarters of the arterial supply), results in prostration, loss of weight, and an increase of excretion of nitrogen; the animals, however, recover gradually. One quarter of the kidney tissue is therefore able to do the work of the whole.

W. D. H.

A Differential Chemical Study of Glucoses from a Case of Pancreatic Diabetes. FREDERIC LANDOLPH (*Biochem. Bull.*, 1913, **2**, 217—222).—The sugar is diabetic urine (one specimen examined) is regarded as a complex of many carbohydrates which can be separated by various treatments. Some of these are dextrin-like, and yield with phenylhydrazine "pseudo-osazones," which are resinous and have low melting points. The work is not yet completed.

W. D. H.

A Modification of Diphtheria Antitoxin. A. T. GLENNY (*J. Hygiene*, 1913, **13**, 63—67).—Evidence is adduced that diphtheria antitoxin is of two kinds, which affect two kinds of the toxin, one of which is lethal, and the other of which produces the local reaction.

W. D. H.

Presence of Propionic Acid in the Secretions of Rheumatic Persons. WILLIAM ŒCHSNER DE CONINCK (*Compt. rend.*, 1913, **156**, 1272).—The urine of rheumatic patients, after a severe attack, has an odour recalling at the same time butyric and acetic acids, and from this urine the author has isolated propionic acid. This acid he has also found in the discharge from eczema sores of such patients.

W. G.

The Action of Nitrites on the Body Temperature of Normal Rabbits, and on those Rendered Hyperthermic by Brain Stimulation. EMANUEL KRAUSS (*Arch. expt. Path. Pharm.*, 1913, **72**, 97—128).—The experiments show that nitrites, as stated by Jacobj, depress the body temperature. Further observations are necessary to explain this, and also why the inhalation of amyl nitrite acts much more markedly on rabbits in a state of hyperthermia.

W. D. H.

Action of Nitrites on the Body Temperature of Rabbits. CARL JACOBJ (*Arch. expt. Path. Pharm.*, 1913, **72**, 129—152).—Nitrites given in various ways (inhalation, subcutaneously, etc.) depress the body temperature of rabbits, especially if they are rendered hyperthermic by stimulation of the brain. These compounds appear to act chiefly on the heat-regulating centres, and secondarily by influencing the calibre of the skin-vessels.

W. D. H.

The Action of Electrolytes on Paramœcium. (Miss) DOROTHY DALE (*J. Physiol.*, 1913, **46**, 130—140).—Experiments were performed to determine the C_H limits fatal to Paramœcium. These for a

given "buffer" are constant for the various cultures used, and are different for different "buffers." The simple tervalent positive ions are more potent than the complex tervalent ions. The action of the former, although similar to that of increased C_H, is not explained by hydrolytic dissociation. The action of various ions on the changes of movement is described. The action of hydrogen and hydroxyl ions and of multivalent cations and anions may possibly be ascribed to the power they possess of conferring electric charges on colloidal materials. W. D. H.

The Mechanism of Histamine Action. C. OEHME (*Arch. expt. Path. Pharm.*, 1913, **72**, 76—96).—Histamine (4-β-iminoethylglyoxaline) is a base which Barger and Dale separated from the intestinal mucous membrane (A., 1911, ii, 217), and is also formed by bacterial action from the intestinal contents (Mellanby and Twort, A., 1912, ii, 853). In minute doses it is fatal to rabbits, producing a great fall of blood pressure, and the other symptoms of anaphylactic shock. The lethal dose is larger if the injection is made into the mesenteric vein instead of into the systemic circulation; it is therefore possible that the liver may have some action in destroying the poison. Slow injection into the jugular vein also lessens its toxicity, and the question is discussed whether this is due to its being destroyed in the blood, or to its removal from the blood. No evidence of actual destruction in the blood itself was discovered, and only traces pass into the urine. When tested on the isolated uterus, the same difference as to whether the injection or addition to Locke's fluid is made rapidly or slowly is noticeable, as in the intact animal. The uterine tissues take up the drug, and this can subsequently be washed out. The question of its activity seems to be related mainly to the concentration. W. D. H.

The Urinary Elimination of Morphine Injected into an Unaccustomed Animal. H. DORLENCOURT (*Compt. rend.*, 1913, **156**, 1338—1340. Compare Totze, A., 1904, ii, 220; Bettink, A., 1905, ii, 546).—In the case of the rabbit the intramuscular injection of morphine hydrochloride to the extent of 0·15 gram per kilo. of body-weight is always followed by urinary elimination of the alkaloid as such. This elimination begins within an hour of injection, is at its maximum from the second to the fourteenth hour, and ends after seventy-two hours. The total elimination amounts to about 4% of the alkaloid injected, and only traces of dioxymorphine could be detected in the urine. The animals employed had never previously had morphine, and received only one injection. W. G.

Influence of Some Derivatives of Quinoline and of Naphthaquinoline on the Elimination of Uric Acid. RICCARDO CIUSA and RICCARDO LUZZATTO (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 305—311).—2-*p*-Methoxyphenylquinoline-4-carboxylic acid, $C_{17}H_{13}O_3N$, forms yellow scales, m. p. 217°. 2-*p*-Dimethylamino-

phenylquinoline-4-carboxylic acid, $C_{18}H_{16}O_2N_2$, forms ruby-red crystals, m. p. 192° (decomp.). 6-Amino-2-phenylquinoline-4-carboxylic acid, $C_{16}H_{12}O_2N_2$, has m. p. 160° (decomp.). 2-Phenyl-β-naphthaquinoline-4-carboxylic acid gives a *methyl* ester, m. p. 124°. In the preparation of the acid, a *dihydro*-derivative, $C_{20}H_{15}O_2N$, is also formed; it has m. p. 226°. A yellow *substance* of acid properties and m. p. 275° also occurs in the preparation of 2-*p*-dimethylaminophenyl-β-naphthaquinoline-4-carboxylic acid.

The authors have investigated the influence of these acids and of a number of others on the excretion of uric acid (compare Nicolaier and Dorn, *Arch. klin. Med.*, 1908, **93**, 331). There is no increase of uric acid after administration of 2-*p*-methoxyphenylquinoline-4-carboxylic acid, 2-*p*-dimethylaminophenylquinoline-4-carboxylic acid or 6-amino-2-phenylquinoline-4-carboxylic acid. A small increase (15—18%) occurs with 2-*o*-hydroxyphenyl-β-naphthaquinoline-4-carboxylic acid. A greater increase (18—27%) is observed with 2-*p*-dimethylaminophenyl-β-naphthaquinoline-4-carboxylic acid, 2-phenyldihydro-β-naphthaquinoline-4-carboxylic acid, and with 2-phenyl-β-naphthaquinoline. Great increases occur after administration of 2-phenylquinoline-4-carboxylic acid ("atophan") and 2-phenyl-β-naphthaquinoline-4-carboxylic acid ("diapurine"). The increase is somewhat less with the latter substance, but it is better tolerated. R. V. S.

Poisoning by Acid. GERTRUDE D. BOSTOCK (*Zeitsch. physiol. Chem.*, 1913, **84**, 468—477).—Subcutaneous injection of glycine in rabbits has no protective action against the fatal effect of acids given by the stomach. The simultaneous administration of ammonium acetate with the acid hastens death. In acid poisoning, the ammonia in the urine increases absolutely and relatively; there is also a rise in total urinary nitrogen. The increase in the ammonia is much greater if glycine or ammonium acetate is given at the same time. W. D. H.

Distribution of Ante-mortem Administered Arsenic in the Human Cadaver. JOHN B. EKELEY (*J. Amer. Chem. Soc.*, 1913, **35**, 483—485).—The analysis of the corpse of a person who had died from arsenical poisoning showed the presence of the following percentages of arsenic (calculated as As_2O_3) in the various parts of the body: Kidneys, 0·02466; stomach walls, 0·02273; liver, 0·00961; intestines, 0·00377; heart, 0·00125; thigh, 0·00039; toes, 0·00031; brain, 0·00012; spinal cord, a trace. E. G.

The Influence of the Intestinal Poisons (*p*-Cresol and Indole) on the Central Nervous System of Animals. S. WLADYCZKO (*Ann. Inst. Pasteur*, 1913, **27**, 336—340).—Continued ingestion of small quantities of *p*-cresol and indole, which are formed by the action of putrefactive bacteria on protein degradation products in the intestine, have no visible action on the general health of the animal, as compared with control animals, as a result of the regressive changes in the blood-vessels of the brain. These

alterations, which are produced by the substances, are less marked in the case of guinea-pigs than of rabbits. They have also been observed in an experiment on *Macacus cynomolgus*. Small doses of *p*-cresol and indole also produce after repeated ingestion a slight destructive change in the cellular elements of the central nervous system.

S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

Tyrosinase from Two Enzymes. MARTINUS W. BEYERINCK (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 932—937).—By the symbiotic action of *Actinomyces* with a common soil bacterium, tyrosine in an agar plate culture is oxidised to melanin, which appears as black spots on the culture plate. Neither organism alone oxidised tyrosine to the same stage. Other species of *Actinomyces* produce blue, red, or yellow pigments, the simultaneous presence of certain varieties of hay bacteria being favourable in the case of blue and red. Dextrose, malates, and nitrates form the chromogeneous food in this case instead of tyrosine. It is considered that the *Actinomyces* produce homogentisic acid from tyrosine, and that the bacterium oxidises this acid to melanin. Plant tyrosinase (from *Euphorbia lathyis*) is a mixture of these two oxidising enzymes. E. F. A.

The Formation of Lactic Acid by Acetic Acid Bacteria. ALFONS OSTERWALDER (*Centr. Bakt. Par.*, 1913, ii, **37**, 353—364).—When inoculated into sterilised red or white wine, two acetic acid bacteria were found to bring about an increase in the amount of lactic acid. This change was observed in both fresh and fermented wines, and was not affected by the addition of sucrose, lævulose, and malic and tartaric acids. The addition of alcohol was followed by an increase in the amount of lactic acid as well as of acetic acid. Malic acid was decomposed by the organisms, while a reduction in the amount of sucrose was accompanied by an increase in total acids, possibly by the formation of gluconic acid. The fermentation is probably without practical significance, since wines possessing a high acetic acid content are regarded as worthless, and those with little acetic acid would only contain traces of lactic acid as a result of fermentation by these organisms. H. B. H.

Natural Variation of B. acidi lactici with Respect to the Production of Gas from Carbohydrates. J. A. ARKWRIGHT (*J. Hygiene*, 1913, **13**, 68—86).—A bacillus of the *B. acidi lactici* group isolated from urine occurred in two varieties, one of which formed gas from sugars and alcohols, and the other of which formed acid, but no gas. Their other characters (serum reactions, etc.) were identical. W. D. H.

Biochemical Activity of Bacillus lactis erythrogenes. MARY LOUISE FOSTER (*J. Amer. Chem. Soc.*, 1913, **35**, 597—600).—An investigation of the action of *Bacillus lactis erythrogenes* on milk has shown that it is progressively catabolic, the proteins being ultimately converted into mono- and di-amino-acids. This proteolytic change is probably due to an enzyme. By precipitation with alcohol, a soluble ferment can be obtained, which decomposes the lactose with formation of formic and acetic acids, and this seems to indicate the presence of an intracellular enzyme, which is set free by the alcohol after it has destroyed the organism. These changes in the milk are accompanied by the production of a pigment, which causes a red to dull brown coloration, and can be extracted with amyl alcohol; it is extracellular, since its formation is dependent on the life of the organism. E. G.

The Inhibitory Selective Action on Bacteria of Substances Related to Monochloroacetic Acid. WILLIAM J. PENFOLD (*J. Hygiene*, 1913, **13**, 35—48).—*B. coli* (Escherlich) when grown on agar to which phenylacetic acid has been added, produces colonies which vary in size, but produce about the same amount of gas from dextrose. When the agar contains monochlorohydrin or sodium monochloroacetate, it throws off variants which ferment alcohol with gas formation, and sugars without gas formation. *B. lactis aërogenes* on monochlorohydrin agar gives rise to variants unable to ferment glycerol. In cases of inhibitory bacterial selection by chemical agents, a comparison of the surviving cells with the original strain indicates what portion or function of the cell is implicated in the cell's intoxication. The cellular enzymes, by virtue of their specific chemical affinities, may play a part in cell intoxication. Phenol, for instance, is rendered more germicidal by the addition of acids; in many media, the cell enzymes produce acids; hence it is probable that phenol selections of bacteria commonly result in the development of new strains with impaired fermenting powers. W. D. H.

Alcoholic Fermentation. ALEXANDER VON LEBEDEV (*Zeitsch. physiol. Chem.*, 1913, **84**, 308).—Polemical (compare Kostytschev, this vol., i, 323). E. F. A.

Influence of Respiratory Chromogens on Alcoholic Fermentation. VLADIMIR I. PALLADIN and S. D. LVOV (*Bull. Acad. Sci. St. Pétersbourg*, 1913, 241—252. Compare this vol., i, 430).—The authors have made experiments to ascertain the cause of the influence exerted on the action of zymase by the oxidising processes due to respiratory chromogens. The yeast employed was treated by von Lebedev's method (A., 1911, i, 248), and the chromogens were obtained from turnips, sugar-beets, or mushrooms.

The fermentation of expressed plant juices by killed yeast in a current of air is accompanied by oxidation of the respiratory chromogen of the juice to a pigment, which greatly retards the action of the zymase; the retardation is especially marked when

the juice is oxidised prior to introduction of the yeast. In the case of boiled juice, which is incapable of converting the prochromogen into chromogen and of oxidising the latter to pigment, alcoholic fermentation proceeds readily. Further, no retardation occurs when the unboiled juice is fermented in a stream of hydrogen, which prevents oxidation of the chromogen to pigment.

In cases where the fermentation is delayed, the proportions of alcohol and of carbon dioxide formed are affected to equal extents.

Consideration of these results and of modern views concerning the mechanism of fermentation renders it probable that, in the above experiments, the pigment withdraws the hydrogen liberated in the formation of the intermediate fermentation products and oxidises it, by means of atmospheric oxygen, to water. The absence of the hydrogen necessary for the subsequent synthesis of the alcohol renders the formation of the latter impossible. T. H. P.

The Use of Ammoniacal Salts in Wine making. René Marcille (*Compt. rend.*, 1913, **156**, 1336—1338).—An examination of some musts, which took several weeks instead of four or five days for complete fermentation, showed them to be deficient in ammoniacal nitrogen. On the addition of ammonium phosphate to the grape-juice, fermentation proceeded at the normal rate. Ammonium sulphate gives slightly better results than the phosphate, but care must be taken with respect to plastering. The wine obtained by the slow fermentation was normal in every respect.

W. G.

The Action of Cyclamine on Alcoholic Fermentation. Johan Lundberg (*Arkiv. Kem. Min. Geol.*, 1913, **4**, No. 32, 1—24).—The rate of fermentation at 30° of a sugar solution by means of yeast in the presence of cyclamine was followed by measuring the volume of carbon dioxide evolved (compare Slator, T., 1906, **89**, 128).

Preliminary treatment of the living yeast with a pure solution of cyclamine has no effect on its power of fermentation; in the presence of sugar, however, the activity of the yeast is greatly diminished by the cyclamine. The action of the poison (cyclamine) thus depends on the physiological condition of the cell.

The amount of cyclamine necessary to poison the yeast is proportional to the quantity of the latter. Above a certain limit of concentration of cyclamine a further increase in quantity does not increase the velocity of poisoning.

It is probable that the poisoning is not a simple chemical reaction, but depends on the individual resistance of the cells.

The action of cyclamine on dry yeast depends only on the active yeast present, and not on the total quantity of dry material.

Even in very small concentrations cyclamine has no stimulating action on the yeast fermentation. T. S. P.

A Ferment of Bitter Wines. E. Voisenet (*Compt. rend.*, 1913, **156**, 1181—1182. Compare A., 1911, ii, 915, 1127).—The ferment from a bitter wine develops in sterile or natural wines, or in wines partly deprived of their alcohol. Thus grown it presents all the

morphological characters of the ferment from the bitter wine. The author names it *Bacillus amaracrylus*. It attacks glycerol, giving acraldehyde, and other products of the fermentation are carbon dioxide, hydrogen, ethyl alcohol, volatile acids, and lactic and succinic acids. It rapidly attacks mannitol and the sugars, acts moderately on dextrin, but does not ferment erythritol, dulcitol, or starch. The fermentation of the sugars, sucrose, lactose, maltose, dextrose, lævulose, and galactose is complete in the presence of calcium carbonate. W. G.

Does the Ferment Causing Bitterness in Wine Consume Cream of Tartar? E. VOISENET (*Compt. rend.*, 1913, **156**, 1410—1412. Compare preceding abstract).—A determination of the tartaric acid in wine before and after it has become bitter shows no difference in the content. Further, if the *B. amaracrylus* is sown on different nutrient solutions containing cream of tartar, no difference can be detected in the tartaric acid content after three months' action. W. G.

Zymase and Reductase in their Mutual Relations. SERGEI LVOV (*Ber. Deut. bot. Ges.*, 1913, **31**, 141—147).—The first or one of the first stages in the alcoholic fermentation of dextrose is the withdrawal of two hydrogen atoms from the dextrose molecule. The hydrogen temporarily attached to the reductase is necessary for the normal course of fermentation.

An exact parallelism exists between the reducing and the fermentative energy of yeast; so that the reducing energy of yeast can be measured by its fermentative energy. The question arises whether reductase exists as a separate, individualised ferment, or whether the reducing properties do not more probably belong to a single, if complicated, fermenting apparatus usually termed zymase? N. H. J. M.

Sugar-free Fermentations of Stereoisomerides. PAUL MAYER (*Biochem. Zeitsch.*, 1913, **50**, 283—287).—Hydroxyfumaric acid, like the corresponding hydroxymaleic acid, undergoes fermentation with yeast, yielding carbon dioxide and acetaldehyde, which was isolated in the form of the *p*-nitrophenylhydrazone. S. B. S.

Replacement of Zinc by Uranium in the Culture of Aspergillus niger. CHARLES LEPIERRE (*Compt. rend.*, 1913, **156**, 1179—1181.* Compare this vol., i, 326, 327).—Uranium, like cadmium and glucinum, can replace zinc in the medium for the culture of *Aspergillus niger*. The weight of crop is normal if the amount of uranium in the form of nitrate is less than 1 in 5000; there is, however, a considerable retardation in attaining the maximum. Sporulation takes place if the amount of uranium is less than 1 in 10,000, but is checked by 1 in 5000. The addition of uranium to media containing zinc produces a marked retardation in growth, but the crop finally attains its normal maximum weight. The uranium is in all cases fixed by the plant. W. G.

* and *Bull. Soc. chim.*, 1913, [iv], **13**, 491—493.

Tannic Acid Fermentation. I. LEWIS KNUDSON (*J. Biol. Chem.*, 1913, **14**, 159—184).—Tannic acid is toxic to many fungi in low concentrations. *Aspergillus niger* is a more vigorous fermentative organism than *Penicillium*. Fermentation is more rapid in the gall-nut infusion than in a synthetic solution, in which tannic acid was the only source of carbon. Certain organic compounds in the infusion protect the gallic acid to some extent. The addition of 5% of sugar did not protect the gallic acid, but simply increased the growth; 10% protected the gallic acid entirely. Fermentation can take place under anaerobic conditions, and 1 mg. of mycelium can effect the transformation of 2·7 grams of tannic acid in ten days. The presence of 10% of sugar does not inhibit the secretion of tannase by *Aspergillus niger*, but it does do so to some extent in *Penicillium*. This enzyme is secreted into the culture solution by submersed mycelium as well as by surface growth. There is no evidence that tannic acid is used directly; it is first transformed into gallic acid. W. D. H.

Tannic Acid Fermentation. II. Effect of Nutrition on the Production of Tannase. LEWIS KNUDSON (*J. Biol. Chem.*, 1913, **14**, 185—202).—There is a progressive increase of tannase in *Aspergillus* and *Penicillium* with increased concentration of tannic acid in Czapek's solution containing 10% sugar. In a full nutrient solution containing 2% tannic acid as a source of carbon, the addition of sucrose decreases the secretion of tannase. *Aspergillus* secretes more tannase (or more active tannase) per unit weight than *Penicillium*. The production of the enzyme is stimulated in both moulds by gallic and especially by tannic acids. W. D. H.

The Catalytic Action of Light on the Germination of Seeds. ERNST LEHMANN (*Biochem. Zeitsch.*, 1913, **50**, 388—392).—Experiments carried out with the seeds of *Epilobium hirsutum* show that in water and in the dark they only germinate very slightly, whereas under otherwise the same conditions 98—100% germinate when exposed to light. The same effect as that produced by light can also be attained by treatment in the dark with solutions of proteoclastic ferments, such as papayotin and trypsin, and by low concentrations of acids (0·05*N*-hydrochloric acid). It appears, therefore, as if light acts catalytically in "mobilising" the proteins of the seeds. S. B. S.

Influence of Cancer Extracts on the Growth of Lupine Seedlings. JACOB ROSENBLOOM (*Biochem. Bull.*, 1913, **2**, 229—232).—The extracts had no deleterious effects; but, on the contrary, growth was accelerated; this may be due to inorganic salts.
W. D. H.

The Action of Poisonous Substances in Different Concentrations on Seeds. The Biochemical Action of Very Concentrated Solutions. V. ARCICHOVSKI (*Biochem. Zeitsch.*, 1913, **50**, 233—244).—The action of the following substances was investi-

gated: formalin, sulphuric acid, and silver nitrate. The seeds were soaked in varying concentrations in water of these substances for varying periods, then washed, and allowed to germinate under sterile conditions. The apparatus for carrying out these various operations is described and figured in the text. The number of seeds (pea-seeds) which germinate, and the percentages which start germinating in given times, were ascertained. The toxicity of these substances increases as the concentration is increased up to a certain optimal point. Further increase in the concentration beyond this point diminishes the toxicity. The causes of this phenomenon are discussed by the author. S. B. S.

Anaerobic Respiration of Various Seed Plants. S. Kostytschev (*Ber. deut. bot. Ges.*, 1913, **31**, 125—129).—Experiments on the amounts of carbon dioxide produced by different plants during anaerobic respiration are described. The ratio CO_2/EtOH varied from 100/100 to 100/0.

It seems to be typical of leaves that about half the carbon dioxide is produced by zymase fermentation. Potato tubers produced only traces of alcohol, if any at all, and thus resemble mushrooms, which, however, contain no carbohydrates.

The results obtained support the view that, in most cases, anærobic respiration is not identical with zymase fermentation. As a rule, zymase fermentation takes place at the same time.

N. H. J. M.

The Evolution of Mineral Substances and Nitrogen in Some Annual Plants. Gustave André (*Compt. rend.*, 1913, **156**, 1164—1167. Compare this vol., i, 233).—An extension of the above study to the case of the common flux, spurrey, and *Camelina sativa* shows that, for these three examples of different families of plants, all the mineral elements, as well as the total nitrogen, steadily increase in weight to the time of complete maturity. W. G.

Experiments with Sterile Cultures of Higher Plants. Ivan Schulov (*Ber. Deut. bot. Ges.*, 1913, **31**, 97—121).—The phosphoric acid of lecithin is not assimilated by maize and peas. Phytin is utilised by peas as source of phosphoric acid.

The roots of maize and peas excrete considerable amounts of reducing sugars; maize also excretes malic acid.

Young plants, supplied with ammonium nitrate, take up more ammonia than nitrate; later on the two forms of nitrogen are utilised in about equal amounts, whilst subsequently chiefly nitric nitrogen is taken up by the plant. The physiologically acid reaction initially produced is undoubtedly of importance in the assimilation of phosphates insoluble in water.

The employment of ammonium nitrate causes an increased secretion of organic acids by the roots, and a greater secretion of sugars. N. H. J. M.

Dry Heating. Carl Thomae (*J. pr. Chem.*, 1913, [ii], **87**, 423—424. Compare A., 1911, ii, 920; this vol., i, 326, 327).—A

further note on the isolation of the fatty and waxy constituents from plant and animal matters by dry distillation, preferably under diminished pressure. Leaves, pine-needles, blossoms, hay, straw, hair, egg-skins, feathers, wood, and articles manufactured from them, such as cloth, paper, linen, leather, cigars, and wadding, all yield a fat or wax on distillation.

Filter paper and linen gave a white, crystalline wax. F. B.

Localisation of Betaine in Plants. VLADIMIR STANĚK (*Zeitsch. Zuckerind. Böhm.*, 1913, **37**, 385—390).—The greatest amount of betaine was found in the leaves, especially in young leaves. Leaves of *Amarantus* contained 2·18, and the roots only 0·48% of betaine. The dry matter of sugar beet-roots contained 0·95 to 1·20%, whilst the leaves contained 2·62%. Beet seeds, without husks, contain only traces of betaine; in seeds of *Chenopodium fœtid.*, no betaine was found. N. H. J. M.

Chemistry of the Floral Pigments. P. Q. KEEGAN (*Chem. News*, 1913, **107**, 181—182).—The colour of blue flowers (gentian, campanula, centaurea, etc.) is attributed to the presence of caffetannin, the only known tannin, except gallotannin, which yields blue oxidation compounds with bases, since it is related to styrene and cinnamic acid. It is doubted whether the presence of an inorganic base is necessary for the production of a blue colour. N. H. J. M.

Chemical Examination of Decoma anomala. FRANK TUTIN and WILLIAM J. S. NAUNTON (*Pharm. J.*, 1913, [iv], **36**, 694—696).—The material employed for this investigation consisted of the entire air-dried plant of *Decoma anomala*, Sond., which had been specially collected in South Africa.

An alcoholic extract of the plant, when distilled in a current of steam, yielded a small amount of an essential oil, b. p. 130—200°/ordinary pressure. The portion of the extract which was soluble in water yielded a small amount of a colourless, crystalline *glucoside*, m. p. 243°, which appeared to possess the formula $C_{39}H_{58}O_{17}$, and a large quantity of a yellow, amorphous, deliquescent product, which, when hydrolysed with alkali, gave 3:4-dihydroxycinnamic acid. The aqueous liquid contained, in addition, a quantity of sugar which yielded *d*-phenylglucosazone, m. p. 218°.

The portion of the extract which was insoluble in water formed a dark-coloured, resinous mass. It consisted largely of amorphous products, some of which gave 3:4-dihydroxycinnamic acid on hydrolysis, and a small amount of an amorphous alkaloid was also present. The following definite substances were, however, obtained from the resin: (1) hentriacontane, $C_{31}H_{64}$, m. p. 68°; (2) a *phytosterol*, $C_{28}H_{46}O$, m. p. 159° (*acetyl* derivative, m. p. 133°), which seems to be a lower homologue of stigmasterol; (3) possibly myricyl alcohol; (4) phytosterolin; (5) palmitic, stearic, arachidic, cerotic, and melissic acids, together with some unsaturated acids, which appeared to consist chiefly of a compound, $C_{16}H_{30}O_2$. H. W.

Occurrence of Gentiopicrin and Gentianose in the Fresh Roots of Gentiana cruciata, L. MARC BRIDEL (*J. Pharm. Chim.*, 1913, [vii], 7, 392—395).—Gentiopicrin and gentianose have been isolated in a crystalline condition from the roots of this species (compare A., 1913, i, 149, 434). T. A. H.

Development of Fat in the Black Walnut (Juglans nigra). II. FRANK M. MCCLENAHAN (*J. Amer. Chem. Soc.*, 1913, **35**, 485—493).—In continuation of the work on this subject (A., 1909, ii, 924), analyses have been made of the ovule of the black walnut at various stages of its development. The fat accumulates rapidly up to a certain point, and afterwards increases but slowly. During the early period of development, the fat is waxy in character, but subsequently becomes liquid. In the very young ovule, phosphatides are greatly in excess of fat, but later their relative importance becomes insignificant. The young ovule contains a large proportion of potassium, but this decreases as the fruit approaches maturity. High percentages of calcium, magnesium, and phosphorus are also present during the early life of the ovule, but are relatively unimportant in the later stages. E. G.

The Anti-toxic Rôle of Calcium with Respect to Some Nutritive Salts in the Culture in Liquid Medium of Peas and Lupins. (Mlle.) C. ROBERT (*Compt. rend.*, 1913, **156**, 915—918). —A comparison of the growth of seedlings of peas and lupins grown on: (*a*) distilled water, (*b*) solutions containing 500 mg. of calcium sulphate per litre, (*c*) solutions containing one of the usual nutrient salts in corresponding strength, (*d*) solutions, being a combination of (*b*) and (*c*). The results show that, with the strength used, calcium is not toxic, but very considerably favours the development of the young plants. The salts of magnesium, potassium, and ammonium are toxic at the concentration used, but the addition of a calcium salt suppresses this toxicity. The development in mixtures of salts of potassium, magnesium, or ammonium with the calcium salt is the same as when the calcium salt alone is used; thus, in the early days of its growth, the salts of those three metals do not seem to act as nutrients to the plant. The white lupin is more sensitive to the toxic action than the pea, very small quantities of potassium salts sufficing to arrest all development. W. G.

Nutritive Value of Maize Proteins. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL (*Proc. Amer. Soc. Biol. Chem.*, 1912–13, xxxi—xxxii; *J. Biol. Chem.*, **14**).—About one-third of the proteins in maize consists of glutelin, which yields all the amino-acids found in most proteins. Zein causes rapid decline in weight, but may be made of greater value by adding tryptophan or other proteins. Gliadin suffices for maintenance, but not for growth. Glutelin is adequate for growth also. W. D. H.

Cotton-seed Meal Intoxication. I. Pyrophosphoric Acid. WILLIAM A. WITHERS and BURTON J. RAY (*J. Biol. Chem.*, 1913, **14**, 53—58).—The results indicate that pyrophosphoric acid is not the cause of the toxicity of cotton-seed meal. W. D. H.

Accumulation of Nitrogen in the Soil by means of Micro-organisms. JOSEF DVOŘÁK (*Zeitsch. landw. Vers. Wesen. Oesterr.* 1912, **15**, 1077—1121).—A detailed account of numerous experiments based on the observations of Stoklasa (A., 1911, ii, 429) and others on the assimilation of nitrogen (atmospheric or otherwise) by plants, and the micro-organisms of the soil.

The influence of various organic substances is studied, and the conclusions arrived at that the ammonium ion is as readily absorbed as the nitrate ion, and that acid soils exhibit the least, and those with a neutral or alkaline reaction the highest, biological absorption. F. M. G. M.

Fixation of Nitrogen by So-called Zeolites. GEORG WIEGNER (*J. Landw.*, 1913, **61**, 11—56).—Experiments were made to ascertain whether the ammonium fixed by zeolites in soils, or any portion of the ammonia, is rendered unavailable to plants. With regard to the amount of ammonia fixed by 100 grams of permutite it is shown that this varies according to the concentration of the ammonia in the solution.

Pot experiments are described in which oats followed by buck-wheat were manured with ammonium sulphate, without and with calcium zeolite in different amounts, and with ammonium zeolite both without and with calcium zeolite.

The results showed that addition of calcium zeolite increased the dry produce, and did not diminish the nitrogen. With large amounts of nitrogen applied as manure, the nitrogen was better utilised in presence of zeolites, possibly owing to losses in the pots without zeolites.

There can be no question of the permanent fixation of a definite and constant amount of ammonia by zeolites, as the amount which is fixed depends on the concentrations, which are variable. The changes are sometimes favourable and sometimes unfavourable to the plants. N. H. J. M.

Action of Histidine and Arginine in Soils. J. J. SKINNER (*Bied. Zentr.*, 1913, **42**, 213—214; from *Proc. 8th Internat. Cong. Appl. Chem.*, 1912).—Histidine and arginine, which are produced in soils as primary cleavage products of proteins, are favourable to the growth of plants except when large amounts of nitrates are present, when they have no appreciable effect. Like creatine and creatinine, both substances can take the place of nitrates. N. H. J. M.

Influence of Sodium Carbonate and the Imperviousness of the Soil on the Growth of Plants. JOHN W. LEATHES (*Bied. Zentr.*, 1913, **42**, 213; from *Proc. 8th Internat. Cong. Appl. Chem.*, 1912).—The result of pot experiments in which alkali soils received

calcium sulphate in amounts sufficient to reduce the sodium carbonate from 0·06 to 0·01% failed to show any appreciable change in the physical properties of the soil. When the sodium carbonate was partly neutralised with calcium sulphate, 33% of the seeds germinated, the best results being obtained with rice and wheat. When the imperviousness of the soil was removed by addition of sodium chloride, 16% of the seeds germinated, but the plants did not ripen.

N. H. J. M.

The Effect of Ignition on the Solubility of Soil Phosphates. CHARLES B. LIPMAN (*J. Ind. Eng. Chem.*, 1912, **4**, 663).—An account of the analysis of five typical soils, as a result of which the author draws the conclusion that the observation of Fraps (A., 1912, ii, 85), that ignition increases the solubility of the phosphates in minerals, does not apply to soils where ignition appears to definitely decrease the solubility of the phosphates; and it is suggested that the increased solubility noted in minerals may be due to mechanical changes induced by heat, which, in disintegrating the particles, increase the amount of surface available for attack by acids.

F. M. G. M.

Zinc as Catalytic Manure. MAURICE JAVILLIER (*Bied. Zentr.*, 1913, **42**, 215; from *Proc. 8th Internat. Congr. Appl. Chem.*, 1912).—Field experiments in which oats, maize, rye, clover, and peas received from 1 to 10 kilos. of crystallised zinc sulphate per hectare. The best results were obtained with maize, which always showed increased production under the influence of zinc sulphate, whilst the other plants gave irregular results.

Laboratory experiments were made with *Aspergillus niger*, showing the effect of zinc on the assimilation of carbohydrates, nitrogen, and minerals, and on the composition of the plant. N. H. J. M.

Aluminium Sulphate as Catalytic Manure. GABRIEL BERTRAND and HENRI AGULHON (*Bied. Zentr.*, 1913, **42**, 215; from *Proc. 8th Internat. Congr. Appl. Chem.*, 1912).—Small amounts of aluminium sulphate (2 mg. per kilo. of soil) increased the yield of barley 18%, or 17% calculated on the dry matter. With 4 mg., the dry produce was not increased, whilst there was a gain in the fresh produce.

N. H. J. M.

Employment of Manganese as Catalytic Manure. GABRIEL BERTRAND (*Bied. Zentr.*, 1913, **42**, 214; from *Proc. 8th Internat. Cong. Appl. Chem.*, 1912).—In pot experiments with peas and barley it was found that addition of manganese sulphate increased the yield by 10—20%. Field experiments gave similar results, oats being increased 9·5% by 60 kilos. of manganese sulphate per acre, peas 20% by 30 kilos., colza 18%, and clover 15% by 40 kilos. of manganese sulphate. The most suitable amounts of manganese sulphate are 30 to 50 kilos. of the anhydrous salt per hectare. N. H. J. M.

Organic Chemistry.

Magnesium in Organic Chemistry. VICTOR GRIGNARD (*Bull. Soc. chim.*, 1913, [iv], **13**, i—xxxvii).—An address delivered to the Chemical Society of France on February 13th, 1913. T. A. H.

Synthesis of Methane by Catalysis. VLADIMIR N. IPATIEV (*J. pr. Chem.*, 1913, [ii], **87**, 479—487; *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 433—442).—According to the author the synthesis of methane from its elements in the presence of metals is not a direct combination of the elements, but consists in a catalytic oxidation of the carbon, by means of the metallic oxide contained in the metal, to carbon dioxide, which then undergoes a catalytic reduction to methane, the water formed in the latter reaction being subsequently decomposed by the metal with the regeneration of the metallic oxide.

In support of this view, the author describes a series of experiments showing (1) that methane is formed by heating carbon at 500—520° in hydrogen under pressure and in the presence of metallic oxides (nickel, copper, tin, iron); (2) that metallic nickel, containing 98·41% of the metal and not further reducible, brings about the catalytic synthesis of methane from carbon and hydrogen under pressure at 500—510°, the amount of methane formed being far greater than that corresponding with the carbon dioxide which could be formed from the oxygen in the apparatus or combined with the metal; (3) that methane in the presence of nickel and water is decomposed under pressure at 485—520° with the formation of hydrogen and carbon dioxide, and (4) that the latter reaction is reversible, a mixture of carbon dioxide and hydrogen, when heated under pressure in the presence of metallic nickel or copper, or the oxides of these metals, yielding water and methane. F. B.

The Relation between the Crystal-Symmetry of the Simpler Organic Compounds and their Molecular Constitution. I. WALTER WAHL (*Proc. Roy. Soc.*, 1913, *A*, **88**, 354—361).—This paper simply contains the experimental data concerning the aliphatic hydrocarbons; general conclusions will be given later. Methane crystallises in the regular system (compare A., 1912, ii, 1044). The crystallographic systems of other hydrocarbons are as follows: ethane, hexagonal; propane is polymorphic, giving rhombic, prismatic needles which, with rise in temperature, give crystals which are either rhombic or monoclinic; β-methylpropane is possibly rhombic, but the matter is uncertain; ββ-dimethylpropane gives cubical crystals, which at low temperature change into crystals which are probably tetragonal; *n*-butane is hexagonal, changing at a temperature close to that of liquid air to rhombic crystals; *n*-pentane is rhombic; *n*-hexane is either monoclinic or triclinic, probably the former; *n*-heptane and *n*-octane are either monoclinic or triclinic, it is uncertain which.

T. S. P.

Polymerisation of Ethylene at High Temperature and Pressure in the Presence of Catalysts. VLADIMIR N. IPATIEV and O. RUTALA (*Ber.*, 1913, **46**, 1748—1755. Compare A., 1911, i, 937).—In a previous paper (*loc. cit.*), it has been shown that the presence of alumina does not affect the nature of the products formed by the polymerisation of ethylene, but has a marked influence on their relative amounts. The present work was undertaken to test the influence of zinc chloride and aluminium chloride.

Ethylene readily undergoes polymerisation when heated under a pressure of about 70 atmospheres at 275° in the presence of zinc chloride. The residual gas has the composition: C_nH_{2n} 36%, H_2 3%, C_nH_{2n+2} 61%. The liquid products were fractionated, and those boiling below 85% found to consist mainly of pentane and hexane, *iso*pentane being isolated from one of them in an approximately pure state. Methyl*cyclo*butane was not detected. In the fractions of b. p. 50—300°, the proportion of ethylenic hydrocarbons increases regularly with increasing temperature, whilst those boiling below 145° contain only ethylene and saturated hydrocarbons.

The individual fractions were treated with fuming sulphuric acid and the residue again fractionated, all the fractions so obtained being unacted on by nitrating mixture or permanganate. Those boiling below 130° consisted almost entirely of paraffin hydrocarbons; in those of higher b. p. an increasing quantity of polymethylene hydrocarbons was found, so that the fraction b. p. 256—265° contained practically only naphthenes.

The portion of the original product of b. p. above 280° was distilled under diminished pressure. The fractions obtained were uniform in ultimate composition and consisted of a mixture of ethylene hydrocarbons and naphthenes.

Ethylene is scarcely affected by commercial aluminium chloride at 240° and about 70 atmospheres pressure. At 280° it gives a charred residue and a gas having the composition C_nH_{2n} 4·0%, H_2 10·0%, C_nH_{2n+2} 86%. With freshly prepared aluminium chloride at 200°, liquid products were not obtained, and only a charred residue remained in the apparatus; liquid products were, however, prepared at the ordinary temperature. These were fractionated as before, and, after removal of unsaturated hydrocarbons by means of fuming sulphuric acid, again distilled, when the fractions, b. p. below 200°, were found to consist mainly of paraffin hydrocarbons, naphthenes being only present in the portion, b. p. above 200°. The polymerisation of ethylene in the presence of aluminium chloride yields, therefore, considerably less naphthenes than with zinc chloride as catalyst. H. W.

$\Delta^{\alpha\gamma\epsilon}$-Hexatriene. PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 1184—1187. Compare van Romburgh and Dorssen, A., 1906, i, 130, 722).—A specimen of $\Delta^{\alpha\gamma\epsilon}$-hexatriene which had been preserved for five years was distilled, when fully 50% passed over below 80° (the hydrocarbon has b. p. 78·5—80°/766 mm.). From the residue a *substance*, b. p. 99·5°/16mm., D^{11} 0·880, n_D^{11} 1·51951, was isolated, which appears to be a dimeride of hexatriene. It readily forms an additive *product* with bromine (1 mol.), whilst, on further

addition of the latter reagent, much hydrogen bromide is evolved. It is rapidly oxidised by potassium permanganate.

[With MULLER.]—$\Delta^{\alpha\gamma\epsilon}$-Hexatriene has been regenerated from its crystalline dibromine additive compound (*loc. cit.*). A solid compound has also been obtained from $\Delta^{\alpha\gamma\epsilon}$-hexatriene and sulphur dioxide, investigation of which is incomplete, but from which the hydrocarbon may also be regenerated. The latter has also been prepared by dehydration of $\Delta^{\alpha\epsilon}$-*hexadiene-δ-ol* by the action of potassium hydrogen sulphate or phthalic anhydride.

[With LE HEUX.]—$\Delta^{\alpha\epsilon}$-Hexadiene-δ-ol has been prepared by the action of allyl bromide, zinc turnings, and absolute ether on acraldehyde. It has b. p. 132·2—132·4°/769 mm., $D_4^{10.5}$ 0·8698, $n_D^{10.5}$ 1·45231. With acetic anhydride and a drop of sulphuric acid, it yields the corresponding *acetate*, b. p. 151·2—152·7°. Phosphorus tribromide converts it into the *bromide*, b. p. 59—63°/35 mm., which very readily absorbs bromine (1 mol.); further quantities of bromine react very slowly without yielding, however, hydrogen bromide.

By reduction of the chloroacetin of *s*-divinyl glycol with a copper-zinc couple in ethereal solution with addition of hydrochloric acid, a liquid, b. p. 77—81°, has been obtained, which, when strongly cooled, becomes crystalline and consists very probably of $\Delta^{\alpha\gamma\epsilon}$-hexatriene. With bromine it gives a dibromide identical with that obtained from the said hydrocarbon. H. W.

Preparation of Chloro-derivatives of the Amyl Series. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 258555).—When the vapour of β-methyl-Δ^{β}-butylene and chlorine are allowed to react at the ordinary temperature and under a pressure of about 50 mm., they give rise to tertiary *iso*amyl chloride and other products which can be employed for the preparation of isoprene. F. M. G. M.

Preparation of Dihalogenated Hydrocarbons. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 259192. Compare this vol., i, 583).—Dichloro*iso*hexane (b. p. 155—160°) is obtained when the vapour of tertiary chloro*iso*hexane is treated with chlorine under reduced pressure; dichloro*iso*butane (b. p. 108—109°) is prepared in a similar manner from chloro*iso*butane, whilst if tertiary bromo*iso*butane (b. p. 72°) is employed it furnishes a satisfactory yield of chlorobromo-*iso*butane. F. M. G. M.

Physical Constants of Certain Chlorinated Hydrocarbons Employed as Solvents. II. WALTER HERZ and W. RATHMAN (*Chem. Zeit.*, 1913, **37**, 621—622).—The following freezing point and specific heat data are recorded: *s*-tetrachloroethane −36°, 0·268; pentachloroethane −22°, 0·266; trichloroethylene −73°, 0·223; tetrachloroethylene −19°, 0·216. The specific heats refer to 20°.

Commercial dichloroethylene consists of a mixture of the *cis*- and *trans*-forms, which can be separated by fractional distillation. The *cis*-form boils at 48·8°/763 mm.; its density is given by the equation: $D = 1{\cdot}2908 - 0{\cdot}00168t$, and its coefficient of expansion is 0·00136. The *trans*-form boils at 59·8°/763 mm.; its density is

given by $D = 1{\cdot}3144 + 0{\cdot}001605t$, and its coefficient of expansion is 0·00127.

The vapour pressures of the two isomerides have also been determined at a series of temperatures. By substitution of the data in Clausius's equation, the latent heat of vaporisation of the *cis*-form is found to be 6930 cal. (43—48·8°), and that of the *trans*-form 7268 cal. (54·8—59·8°). H. M. D.

Some New Properties of Carbon Tetraiodide and its Estimation in Presence of Iodoform. MARCEL LANTENOIS (*Compt. rend.*, 1913, **156**, 1629—1631. Compare this vol., i, 583).—Carbon tetraiodide is attacked by hydrogen at 100°, giving iodoform and hydrogen iodide, and at the same time small amounts of di-iodomethane and methyl iodide are formed. This hydrogenation is readily brought about by alcoholic potassium hydroxide at 30—40°, a small quantity of methane being present in the product. Sodium in liquid ammonia reacts with carbon tetraiodide (3 mols.), giving methane (1 mol.), together with some sodium cyanide, methylamine, and another base, probably guanidine.

Oxygen readily attacks carbon tetraiodide, even in the dark, giving iodine and carbonyl iodide, which is unstable, and yields carbon monoxide with a small proportion of carbon dioxide, the reaction being facilitated by light.

Silver nitrate in aqueous solution (20%) reacts with iodoform, giving carbon monoxide quantitatively. With carbon tetraiodide, it gives both carbon monoxide and carbon dioxide in the proportion of 3 : 1 by volume. One molecule of the tetraiodide gives one molecule of gas, thus giving a means of estimating it alone or in the presence of iodoform. W. G.

Density and Thermal Expansion of Ethyl Alcohol and its Mixtures with Water. N. S. OSBORNE, E. C. MCKELVY, and H. W. BEARCE (*J. Franklin Inst.*, 1913, **175**, 165—167. Compare A., 1912, i, 232).—An abstract of, with a short discussion on, a paper by Pulfrich (*Zeit. für Inst. K.*, **13**, 456), describing different methods of purifying ethyl alcohol, and the varying physical constants exhibited by different specimens thus obtained with an investigation on the thermal expansion of the same when diluted with varying proportions of water. F. M. G. M.

Catalytic Hydrogenation of Acetylenic γ-Glycols in the Presence of Palladium-black. GEORGES DUPONT (*Compt. rend.*, 1913, **156**, 1623—1625).—The reduction of acetylenic γ-glycols in the presence of platinum-black gives the saturated glycol (formula I) together with the alcohol (formula II), but never any of the saturated hydrocarbon (formula III) (compare Lespieau, A., 1910, i, 535):

$$\text{(I.) } OH{\cdot}CRR'{\cdot}[CH_2]_2{\cdot}CRR'{\cdot}OH. \quad \text{(II.) } OH{\cdot}CRR'{\cdot}[CH_2]_2{\cdot}CHRR'.$$
$$\text{(III.) } CHRR'{\cdot}[CH_2]_2{\cdot}CHRR'.$$

If for the platinum-black is substituted palladium-black, in most cases the product of hydrogenation contains only traces of the

glycol with a little of the alcohol, and large quantities of the hydrocarbon.

In the case of the aliphatic glycols of the type dimethylbutinenediol, the hydrogenation is limited and the result is a mixture of the three possible products. With the aromatic glycols, whilst platinum-black gives only the saturated glycol (formula I), palladium-black gives only the saturated hydrocarbon (formula III); thus diphenyldimethylbutinenediol gives quantitatively *βε-diphenylhexane*, a colourless liquid, b. p. 185°/12 mm., D^{15} 0·9634, n_D 1·5440. W. G.

Preparation of Mesityl Oxide from Diacetone Alcohol [*iso*-Hexan-δ-ol-β-one]. MORITZ KOHN (*Monatsh.*, 1913, **34**, 779—780).—The conversion of *iso*hexan-δ-ol-β-one,

$$OH\cdot CMe_2\cdot CH_2\cdot COMe,$$

the primary product in the condensation of acetone to mesityl oxide, into mesityl oxide does not require a large quantity of sulphuric acid as previously supposed. When 290 grams of *iso*hexan-δ-ol-β-one to which sixty drops of sulphuric acid have been added are quickly distilled through a fractionating column, the distillate contains about 190 grams of mesityl oxide. D. F. T.

Action of α-Monochlorohydrin and Epichlorohydrin on Monosodium Glyceroxide. JEAN NIVIÈRE (*Compt. rend.*, 1913, **156**, 1628—1629).—α-Monochlorohydrin is readily prepared by saturating glycerol at 120—130° with hydrogen chloride, a yield of 66% being obtained. The product reacts with monosodium glyceroxide, glycerol being regenerated and at the same time 2—3% of diglyceryl alcohol is produced. Epichlorohydrin, which is readily obtained (95% yield) by the action of strong aqueous potassium hydroxide on αγ-dichlorohydrin under reduced pressure, reacts with monosodium glyceroxide, giving a *polymeride* of the internal anhydride of the diglyceryl alcohol. This is a white, amorphous substance, insoluble in water and the ordinary solvents, and yields a *diacetyl* derivative on boiling with acetic anhydride and anhydrous sodium acetate. Both of these substances decompose without melting.

W. G.

Preparation of Diglyceryl Alcohol. JEAN NIVIÈRE (*Compt. rend.*, 1913, **156**, 1776—1778. Compare preceding abstract).—In an attempt to prepare diglyceryl alcohol the author has prepared the diacetyl derivative of monochlorohydrin and caused it to react with monosodium glyceroxide, the product being a small quantity of the diacetyl derivative of the required alcohol and a considerable residue analogous to the vegetable mucilages.

By warming the internal anhydride of glycerol with anhydrous glycerol in equimolecular proportions on a water-bath for seven hours and acetylating the crude product with acetic anhydride, the *tetracetyl* derivative of the required alcohol is obtained as an oily liquid, b. p. 196—197°/3 mm., D^{17} 1·1835. On saponification with alcoholic sodium hydroxide it yields *diglyceryl alcohol*, $C_6H_{14}O_5$, a pale yellow, very viscous liquid, b. p. 235—240°/6 mm. W. G.

Efficiency of the Preparation of Ethyl Ether from Alcohol and Sulphuric Acid. PERCY N. EVANS and LENA M. SUTTON (*J. Amer. Chem. Soc.*, 1913, **35**, 794—800).—An account is given of experiments made with a view to determine the efficiency of the reaction between ethyl alcohol and sulphuric acid. It has been found that the degree of completeness of the reaction $2Et\cdot OH = Et_2O + H_2O$ amounts to about 40%. This efficiency was maintained in some experiments until the distillate amounted to as much as one hundred and seventy-six times the original volume of the sulphuric acid, or until the ether produced was forty times the volume, or sixteen times the weight, of the acid used. The efficiency decreased abruptly when there remained in the flask a charred, semi-solid residue of about one-twentieth of the weight of the acid originally present. The decrease in efficiency is not due to accumulation of water, as the reaction proceeds normally with dilute sulphuric acid. From 15—20% of the sulphuric acid is lost as sulphur dioxide. E. G.

Crystalline Glycerophosphates. ROGIER and FIORE (*Chem. Zentr.*, 1913, i, 1330—1332; from *Bull. Sci. Pharmacol.*, 1913, **20**, 7—25, 72—86).—Technical sodium glycerophosphate,

$$Na_2PO_3\cdot O\cdot C_3H_7O_2,$$

usually forms small needles with $5H_2O$, but sometimes large tablets with $6H_2O$. The concentrated solution at 18° contains 27·38% anhydrous salt, and may be heated to 120° without decomposition. Cryoscopic methods gave one-third of the calculated molecular weight, so a physiological serum should only contain 35 grams. The following salts have been made by double decomposition. *Calcium* salt, $CaPO_3\cdot O\cdot C_3H_7O_2$, microcrystalline or large crystals by slow evaporation, solubilities, 1% at 0°, 1·68% at 18°, 0·43% at 60°; *barium* salt, with $1H_2O$ which is lost on boiling the solution, solubility 4·50% at 21°; *strontium* salt, leaflets with $2H_2O$, solubility 2·09% at 19°, 0·80% at 60°; *quinine* salt, $B_2PO_3\cdot O\cdot C_3H_7O_2 + 4H_2O$, white needles, m. p. 180—181°, $[\alpha]_D^{21}$ − 133°33′, $[\alpha]_D^{17}$ − 140°24′; *acid strychnine* salt, $BPO_3H\cdot O\cdot C_3H_7O_2,H_2O$, m. p. 260°, $[\alpha]_D^{23}$ − 25°40′; *brucine* salt, $B_2PO_3\cdot O\cdot C_3H_7O_2,11H_2O$, prisms, m. p. 192°, $[\alpha]_D^{22}$ − 29°35′; *basic copper* salt, $Cu[(Cu\cdot OH)PO_3\cdot O\cdot C_3H_7O_2]_2,6H_2O$, dark blue powder; *copper* salt, $CuPO_3\cdot O\cdot C_3H_7O_2,H_2O$, pale blue needles. J. C. W.

Oxidation of Lecithin in Presence of Iron Salts. OTTO WARBURG and OTTO MEYERHOF (*Zeitsch. physiol. Chem.*, 1913, **85**, 412—414).—The mixture of substances known as lecithin is very readily oxidised by atmospheric oxygen in aqueous suspension in presence of iron salts, whereas other important cell constituents are stable under similar conditions. There is a close parallelism between the velocity of lecithin oxidation in vitro and the rate of the oxidation processes in the living cell based on the amount of lecithin present. E. F. A.

The Action of Alkali Arsenite on Ethyl Disulphide. AUGUST GUTMANN (*Ber.*, 1913, **46**, 1474—1475).—Weinland and Rumpf (A., 1897, ii, 257) have shown that sodium disulphide acts on trisodium

arsenite with the formation of trisodium monothioarsenate, Na_3AsO_3S, and sodium sulphide. It was to be expected that ethyl disulphide would act similarly to the sodium disulphide, if it entered into reaction at all, but the author finds that this is not the case, the reaction proceeding readily in the cold with the formation of trisodium arsenate and ethyl mercaptan. This reaction is explained by the author by assigning a peroxide character to the ethyl disulphide, which takes hydrogen from the water, leaving oxygen available for oxidising the arsenite. T. S. P.

Hexadecanesulphonic Acid. ALBERT REYCHLER (*Bull. Soc. chim. Belg.*, 1913, **27**, 110—113. Compare A., 1912, i, 600).—Cetyl iodide reacts with sodium hydrogen sulphide in alcoholic solution to give *cetyl mercaptan*, $C_{16}H_{33}\cdot SH$, which is precipitated as a yellow solid on the addition of water, and on warming this with potassium permanganate solution it is oxidised to the sulphonic acid. The manganese dioxide is filtered off, the solution neutralised with acetic acid, and a slight excess of lead acetate added. The precipitated lead salt is collected, washed, dried, suspended in alcohol, and decomposed by hydrogen sulphide. After filtering and evaporating off the alcohol, *cetylsulphonic* [*hexadecanesulphonic*] *acid*, $C_{16}H_{33}\cdot SO_3H$, is obtained, soluble in alcohol, ether, benzene, and acetic acid, crystallising from the latter in microscopic plates. It behaves like a semi-hard soap, and is a comparatively strong acid, yielding *sodium* and *potassium* salts, which are soluble in water, and closely resemble the alkali palmitates in their behaviour. The *barium* and *lead* salts are insoluble in water. W. G.

The Physico-chemical Properties of Hexadecanesulphonic Acid and Sodium Hexadecanesulphonate. ALBERT REYCHLER (*Bull. Soc. chim. Belg.*, 1913, **27**, 113—128. Compare preceding abstract).—Hexadecanesulphonic acid and its sodium salt in aqueous solution possess the property of emulsifying with toluene, but, unlike the oleates, are only very slightly extracted by that solvent. On the other hand, they possess the property of removing fat from, and cleansing wool in the same manner as, an ordinary soap. The elevation of the boiling point of water on solution either of the acid or its salt does not bear any relation to the concentration of the solutions, and this method gives a wide range of values for the molecular weights. The author has made a complete study of the electrical conductivity of the sodium salt and the free acid at different temperatures and varying concentrations. In the case of the sodium salt, the readings give a sharp indication of the temperature, 38—37°, at which crystallisation takes place. The values obtained for the molecular conductivity in solutions from $0{\cdot}01665N$ to $0{\cdot}0666N$ are practically independent of the concentration. The free acid furnishes an excellent example of a colloidal substance, and permits of the direct examination of the molecular problem and of an intermolecular liquid. The values obtained for the molecular conductivity diminish steadily as the dilution passes from 15 to 30 litres, remains constant from 30 to 60 litres, and finally increases regularly and proportionately as the dilution increases. W. G.

The Use of Calcium Carbonate as Catalyst for Organic Acids and their Anhydrides. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1913, **156**, 1730—1734).—Precipitated calcium carbonate can be employed as a catalyst at 450—500° for the conversion of acids into the ketones, but in the acetic acid series the yield diminishes as the molecular weight increases. Whilst acetic acid gives a theoretical yield of propanone, valeric acid only gives a yield of 32% of dibutyl ketone. Despite blackening due to deposition of carbonaceous products, the calcium carbonate retains its activity and can be employed a great number of times, but its use is not so advantageous as that of thorium oxide (compare Senderens, A., 1912, i, 537) for the higher ketones. Benzoic acid mixed with the aliphatic acids yields mixed ketones under the above conditions. The acids can be replaced by their anhydrides in every case, and whilst benzoic acid alone cannot be converted into benzophenone by this method, a certain amount of this ketone can be obtained by the use of benzoic anhydride.

W. G.

Esters Derived from Octanol by the Author's Method; Observations on the Principle of this Method. JEAN B. SENDERENS and J. ABOULENC (*Compt. rend.*, 1913, **156**, 1620—1623; *Bull. Soc. chim.*, 1913, [iv], **13**, 586—591).—By their method using sulphuric acid (2—3%) as catalyst (compare A., 1911, i, 600, 637; ii, 1080; 1912, i, 694; this vol., i, 42) the authors have prepared the following esters of octanol, of which only the acetate was previously known (compare Bouis, this Journ., 1854, **7**, 280):

Ester.	B. p./74·4 mm.	D_4^{14}.
Formate	184·0°	0·8642
Acetate	194·5	0·8626
Propionate	211·5	0·8611
Butyrate	227·5	0·8592
*iso*Butyrate	220·0	0·8554
*iso*Valerate	236·5	0·8540

The *phenylacetate*, b. p. 195°/35 mm., D_4^{14} 0·9503, is decomposed on distilling at the ordinary pressure.

The authors claim that their method is entirely distinct from that of Fischer and Speier (A., 1896, i, 201), where a large excess of alcohol is used and stronger acid, which merely acts as a dehydrating agent. The organic acids are capable of division into two classes. The first contains the aromatic acids with the carboxyl group attached to the nucleus, in which case their method is useless. The second class contains the fatty acids and aromatic acids with the carboxyl group in a side-chain, and here their dilute acid acts as a true catalyst and an excess of alcohol is unnecessary. A compound of the type $RH \cdot SO_4$ is first formed, and then a cycle of reactions goes on:

$$R \cdot HSO_4 + R \cdot OH = R_2SO_4 + H_2O$$
$$R_2SO_4 + R'CO_2H = R'CO_2R + RHSO_4.$$

W. G.

Graded Degradation of Different Saturated Mono- and Di-basic Acids. PHILIPPE BARBIER and RENÉ LOCQUIN (*Compt. rend.*, 1913, **156**, 1443—1446).—The transformation of a saturated acid of the

type $R·CH_2·CO_2H$ into its next lower homologue can be brought about by first converting the acid into the corresponding tertiary alcohol, $R·CH_2·CMe_2·OH$, by the action of magnesium methyl iodide, and then submitting this to oxidation:

$$R·CH_2·CMe_2·OH + 3O = R·CO_2H + CH_3·CO·CH_3 + H_2O.$$

Thus *iso*valeric acid is first converted into $\beta\delta$-dimethylpentan-δ-ol, which on oxidation with chromic acid yields *iso*butyric acid. Decanoic acid is similarly converted into pelargonic acid.

By the interaction of *iso*amyl bromide and ethyl methylmalonate, *$\alpha\delta$-dimethylhexoic acid*, $CHMe_2·CH_2·CH_2·CHMe·CO_2H$, b. p. 228—230°/760 mm. and 127—130°/18 mm., is obtained, giving a *methyl* ester, b. p. 172—173°, an *acid chloride*, b. p. 69°/16 mm., an *amide*, m. p. 99—100°, and a p-*toluidide*, m. p. 75°. With magnesium methyl iodide it yields *$\beta\gamma\zeta$-trimethylheptan-β-ol*, b. p. 92—95°/18 mm., which on oxidation with dilute nitric acid gives a neutral and an acid product. The acid product is a mixture of acetic, *iso*valeric, and *iso*hexoic acids, whilst the neutral product consists principally of methyl *iso*amyl ketone, together with a small quantity of an unsaturated hydrocarbon, b. p. 160—165°. β-Methyladipic acid on treatment with magnesium methyl iodide and subsequent oxidation yields a certain amount of methylsuccinic acid and some diethylenic hydrocarbon.

With the monobasic acids where the $·CO_2H$ group is attached to a $·CH_2$ group, they are simply converted into their next lower homologue. With an α-substituted acid the principal product is a ketone. The dibasic acids behave in the same way as the monobasic acids, the degradation proceeding simultaneously on the two terminal carboxyl groups. W. G.

Synthesis of the Glycerides of Lauric Acid. B. W. VAN ELDIK THIEME (*Ber.*, 1913, **46**, 1653—1657. Compare A., 1912, i, 333).—A reply to Grün (this vol., i, 157), criticising the latter's experimental results. The author re-affirms that even under the modified conditions stated by Grün (*loc. cit.*) the so-called synthesis of α-dilaurin yields a mixture of trilaurin, crystalline dilaurin, liquid dilaurin, and monolaurin. D. F. T.

Nickel Oxides as Reduction Catalysts in the Addition of Molecular Hydrogen to Unsaturated Fats and Fatty Acids. FRED BEDFORD and ERNST ERDMANN (*J. pr. Chem.*, 1913, [ii], **87**, 425—455; *J. Russ. Phys. Chem. Soc.*, 1913, **45**, 616—643).—Unsaturated fats and fatty acids undergo catalytic reduction at the ordinary pressure in the presence of nickel oxide, the rate of reduction being much greater than when metallic nickel is employed. In addition to its greater activity, the oxide possesses the advantage over the metal in that it is far less sensitive to hydrogen sulphide and other substances which exert a deleterious effect on the activity of the metal. All three oxides of nickel may be used as catalysts, nickelous and nickelic oxides requiring a temperature of 250°, whilst in the presence of the suboxide the reduction proceeds readily at 180—200°.

During the reduction, the higher oxides become converted into the suboxide, which forms a deep black, colloidal solution with the oil or fat.

Nickel suboxide may be distinguished from metallic nickel by its inability to form nickel carbonyl with carbon monoxide, and by its much smaller electric conductivity.

A nickelic oxide, which has already been used in the catalytic reduction, possesses a greater activity than a fresh specimen on account of the presence of suboxide.

The velocity of hydrogenation is increased by employing a voluminous oxide, prepared by gentle ignition of the nitrate, and also by the addition of small quantities of other metallic oxides (Al, Ag, Zr, Ti, Ce, La, Mg).

Nickel salts of organic acids (formic, acetic, oleic, and linolenic) in the presence of unsaturated fats are reduced at 200—250° to the oxide or to metallic nickel, and may therefore be used as catalysts; thus, nickel formate is reduced at 210° to the suboxide and at 250° to metallic nickel. F. B.

Ricinoleic Acid. BERTHOLD RASSOW [with J. RUBINSKY] (*Zeitsch. angew. Chem.*, 1913, **26**, 316—320).—The authors have investigated the action of heat on ricinoleic acid. Since the products formed are amorphous, yield amorphous salts, and have very similar solubilities, their isolation in the pure state has not been accomplished. Their chemical nature is deduced from observations of acid number, saponification number, acetyl number, iodine number, and molecular weight. The following are the main results obtained.

Ricinoleic acid is decomposed at temperatures below 150°, water being the only volatile product formed. At the same time, the acidity sinks to half the original value; in the presence of a trace of sulphuric acid, the acidity can be reduced to one-quarter of the original value, but completely neutral products are never obtained.

Polyricinoleic acids (ester-acids in which the alcoholic hydroxyl group of one molecule is esterified by the carboxyl group of a second molecule) are the sole products of the action of heat on ricinoleic acid. Such products are not uniform, but contain a mixture of difficultly or non-separable polyricinoleic acids with more or less of the original acid. Polyricinoleic acids of high molecular weight are insoluble in alcohol, whilst their barium salts resemble amber and are soluble in ether; those of lower molecular weight are soluble in alcohol, whilst their barium salts dissolve sparingly in ether. A complete separation of the individual polyricinoleic acids was not achieved.

The effect of a variety of substances on the course of the reaction has been investigated. Chlorides of organic acids and neutral salts which do not yield free acid under the conditions of the experiments have but little effect. Traces of strong acids, particularly sulphuric acid, act as positive catalysts, whilst organic bases have the opposite action.

Ricinelaidic acid behaves in the same manner as ricinoleic acid except that it is more readily decomposed by heat. H. W.

Neodymium Oxalate and Some New Compounds of Europium. CHARLES JAMES and J. E. ROBINSON (*J. Amer. Chem. Soc.*, 1913, **35**, 754—759).—A study of the solubility of neodymium

oxalate in solutions of neodymium nitrate of various concentrations at 25° has shown that only one hydrate of neodymium oxalate,

$$Nd_2(C_2O_4)_3,11H_2O,$$

is stable under these conditions. Evidence was obtained of the formation of an oxalonitrate.

Europium *formate*, $Eu_2(CO_2H)_6$, *quinate*,

$$Eu_2[C_6H_7(OH)_4\cdot CO_2]_6,12H_2O,$$

pyromucate, $Eu_2(C_4H_3O\cdot CO_2)_6,2H_2O$, and *m-nitrobenzenesulphonate*,

$$Eu_2(NO_2\cdot C_6H_4\cdot SO_3)_6,6H_2O,$$

are described. E. G.

The Action of Ultraviolet Rays on Aldehydes. ADOLF FRANKE and ERNST POLLITZER (*Monatsh.*, 1913, **34**, 797—809).—When exposed to the radiation from a quartz-mercury lamp, formaldehyde solutions undergo partial decomposition into carbon monoxide, carbon dioxide, hydrogen and methane, and partial polymerisation to glycollaldehyde and higher products (Pribram and Franke, A., 1912, i, 412); the higher aldehydes have been observed to form carbon monoxide, hydrogen, and the hydrocarbon corresponding with the radicle to which the aldehyde group was previously attached (Berthelot and Gaudechon, A., 1910, ii, 814). A re-investigation of the behaviour of the homologues of formaldehyde indicates that they decompose mainly according to the equation $R\cdot CHO = RH + CO$; at the same time condensation takes place to some extent accompanied by polymerisation to resinous substances; no pure condensation product could be isolated. Under the conditions of the experiments, in which moisture and atmospheric oxygen were excluded, no formation of acids or of esters could be dectected, so that the earlier suggestion of Pribram and Franke (*loc. cit.*) that the formic acid obtained in the illumination of formaldehyde solution is produced by the hydrolysis of previously formed methyl formate is hardly probable. From the behaviour of crotonaldehyde, which like benzaldehyde and cinnamaldehyde gives practically no liberation of gas, it appears that the decomposition expressed by the above equation is characteristic of the saturated aliphatic aldehydes.

The aldehyde under examination was contained in a quartz flask of approximately 100 c.c. capacity which was filled to the neck, any evolved gas being collected over water or mercury; the mercury lamp was at a distance of 2 to 3 mm. from the flask, but the temperature of the aldehyde never exceeded 50°.

The substances examined were heptaldehyde, *iso*butaldehyde, propaldehyde, acetaldehyde, crotonaldehyde, benzaldehyde, and cinnamaldehyde. Crotonaldehyde gave only the formation of a resinous substance, whilst the two aromatic aldehydes gave merely red, non-volatile products. The illumination ranged from one to ten days in various cases; only a relatively small proportion of each aldehyde underwent conversion. D. F. T.

Action of Hydrazine and Hydrazine Derivatives on Molten Chloral Hydrate. GUSTAV KNÖPFER (*Monatsh.*, 1913, **34**, 769—777).—Hydrazine reacts with solutions of chloral hydrate, giving an additive product, $CCl_3\cdot CH(OH)\cdot NH\cdot NH_2$, chloralhydrazine (compare A., 1911,

i, 1033); it is now found that if hydrazine sulphate or hydrochloride is dissolved in an excess of molten chloral hydrate, needles of a *substance*, m. p. 187° (decomp.), separate, but the composition is $C_4H_2ON_2Cl_6$, instead of $C_4H_4ON_2Cl_6$, which would be expected from a simple condensation such as that producing anhydrochloralurethane (Feist, A., 1912, i, 566).

The reaction product of benzalazine and chloral hydrate, obtained in a manner similar to the above, has the composition $C_9H_7ON_2Cl_3$, which is again two hydrogen atoms short of the formula for a substance produced by mere condensation; the *substance*, leaflets, m. p. 185°, when heated with potassium hydroxide solution loses a molecule of hydrogen chloride, giving a *substance*, $C_9H_6ON_2Cl_2$, needles, m. p. 86°. The former of these substances is not identical with the isomeric chloralbenzoylhydrazone, $CCl_3\cdot CH{:}N\cdot NHBz$ (Stollé, A., 1905, i, 94), and, as it does not yield chloroform when treated with alkali, it is not likely to be the trichloroacetylhydrazone of benzaldehyde,

$$CCl_3\cdot CO\cdot NH\cdot N{:}CHPh.$$

The loss of the two hydrogen atoms in each case is possibly due to a similar cause to the loss observed by Pinner (A., 1894, i, 385) where the continued action of hydrazine on the imino-ester of benzoic acid gives rise to $NH{:}CPh\cdot NH_2$, $NH{:}CPh\cdot NH\cdot NH\cdot CPh{:}NH$, and

$$CPh{\lessdot}\begin{matrix}N\text{——}N\\NH\cdot NH\end{matrix}{\gtrdot}CPh$$

successively. The structure of the above products, however, remains for the present unsettled. D. F. T.

Keto-enolic Tautomerism. VIII. Formation of Derivatives of Tautomeric Compounds. KURT H. MEYER (*Annalen*, 1913, **398**, 49—65. Compare A., 1912, i, 940, 941).—To the terms "tautomerism," introduced by Laar in connexion with his oscillation theory, and "desmotropy" some confusion has become attached in the course of time and with the increase in the number of examples. The author proposes the following definitions. A substance exhibits tautomerism when it yields two series of derivatives obtained from two isomeric forms differing in the position of a hydrogen atom, and of one or more double linkings. According to the nature of the two isomeric forms, special cases of tautomerism are: (i) desmotropy—the free compounds corresponding with both forms are capable of separate existence or can be separately detected; (ii) pseudomerism—the tautomeric substance is known in only one form, the constitution of which can be determined by methods independent of tautomerism, and which can yield by addition or substitution derivatives of both forms; the other form is unknown and its existence cannot be detected by any method; (iii) cryptomerism—the substance is known in only one form, the constitution of which cannot be definitely determined (by methods independent of tautomerism).

Many reactions of desmotropic substances are explained readily by the desmotropy; each form yields derivatives of its own type by ordinary double decomposition and usually one form reacts, the other being changed to the first by the reagent present. In other reactions the explanation is not so simple; the tautomeric

substance yields a mixture of derivatives of both forms or only one substance, which is generally a derivative of the non-reacting form, for example, the formation of a brominated ketone by the bromination of an enol. Two theories are existent to explain such cases. The substitution theory claims that a substance can only yield derivatives of its own peculiar constitution, and that the production of a derivative of the other form must be due to a transformation of the tautomeride which precedes the substitution. The addition theory of Michael and of Nef assumes that by the direct addition of a reagent and subsequent elimination of a different molecule, a tautomeride of one form can yield derivatives of the other type.

Evidently the test of the two theories lies in the answer to the question, which of the two forms reacts? This answer can only be obtained by an examination of the behaviour of separately stable desmotropic substances. The author quotes numerous examples from his own work, and from that of Dimroth, Hinsberg, Hantzsch, and Herzig and Wenzel to show that the enolic modification is the reactive form, and that, therefore, the additive theory is probably correct.

[With S. LENHARDT.]—Keto-enolic desmotropes and also tautomerides which are known only in the ketonic or the enolic modifications condense with aldehydes (1 or 2 mols.), the resulting compounds losing water in various ways. In order to ascertain whether the ketonic or the enolic modification reacts with the aldehyde, the two desmotropic modifications of methyl mesityl oxide oxalate have been treated with benzaldehyde in the presence of a little piperidine. The ketonic modification, methyl $\alpha\gamma$-diketo-ϵ-methyl-Δ^{δ}-hexene-α-carboxylate, m. p. 67°, is unchanged, but the enolic modification, methyl α-hydroxy-γ-keto-ϵ-methyl-$\Delta^{\alpha\delta}$-hexadiene-α-carboxylate, is converted into the *lactone*, $\begin{matrix}\text{O·CHPh}\\ \text{CO—CO}\end{matrix}\!\!>\!\text{CH·CO·CH:CMe}_2$, m. p. 160°, colourless needles, which does not react with ferric chloride or with alcoholic bromine, and is only slowly attacked by potassium permanganate, and is, therefore, the ketonic modification; the enolic form,

$$\begin{matrix}\text{O·CHPh}\\ \text{CO—CO}\end{matrix}\!\!>\!\text{C:C(OH)·CH:CMe}_2,$$

obtained by dissolving the ketonic modification in cold alcoholic sodium ethoxide, diluting with water, and acidifying, has m. p. 144°, then solidifies and has m. p. 160°, reacts with alcoholic bromine or ferric chloride, and is soluble in alkalis. By prolonged boiling with alcohol and a little piperidine, the enol is converted into the ketonic form; the same change occurs when the fused enol solidifies.

The authors believe that in all desmotropic and tautomeric compounds, condensation occurs by means of the enolic modification.

C. S.

The Characterisation of Chloro-ketones. EDMOND E. BLAISE (*Compt. rend.*, 1913, **156**, 1549—1551).—The most suitable method of characterising the chloro-ketones is to convert them into their semicarbazones under definite conditions, the ordinary methods being unsatisfactory. Semicarbazide hydrochloride (1 to 1·5 mols.) is dis-

solved in water and the chloro-ketone added, when the semicarbazone is rapidly formed, the only exception being methyl trichloromethyl ketone, which requires a cold alcoholic solution of free semicarbazide. Care must be taken in purification. After filtering and washing with water the semicarbazone is heated with an excess of benzene to below 50°, a little anhydrous sodium sulphate is added, the liquid filtered and left for crystallisation. The semicarbazones of the α-chloro-ketones are readily converted into those of the α-hydroxy-ketones by contact with aqueous potassium carbonate for a few hours, and into those of the α-acetoxy-ketones by warming for a few minutes with an alcoholic solution of anhydrous sodium acetate, thus giving three means of identification of the original ketone.

Dichloro-ketones of the type $CHCl_2{\cdot}CO{\cdot}R$ give a normal semicarbazone, but those of the type $CRCl_2{\cdot}CO{\cdot}R'$ give disemicarbazones, $R{\cdot}C(N{\cdot}CH_3ON_2){\cdot}C(N{\cdot}CH_3ON_2)R'$, which are insoluble in organic solvents, except formic and acetic acids.

The following semicarbazones and disemicarbazones have been prepared:

Methyl trichloromethyl ketone semicarbazone, $CCl_3{\cdot}CMe{:}N{\cdot}CH_3ON_2$, fine needles, m. p. 140°.

Dichloromethyl ethyl ketone semicarbazone, m. p. 142°.

Ethylglyoxaldisemicarbazone, $CH{:}(N{\cdot}CH_3ON_2){\cdot}CEt{:}(N{\cdot}CH_3ON_2)$, m. p. above 230°.

Dimethyldiketone disemicarbazone,

$$CMe{:}(N{\cdot}CH_3ON_2){\cdot}CMe{:}(N{\cdot}CH_3ON_2),$$

a white, crystalline powder, m. p. above 230°, soluble only in formic acid.

Chloromethyl chloroethyl ketone semicarbazone,

$$CH_2Cl{\cdot}C{:}(N{\cdot}CH_3ON_2){\cdot}CHClMe,$$

m. p. 140°.

Methyl chloroethyl ketone semicarbazone, micaceous plates, m. p. 148°, which with carbonic acid gives the *semicarbazone*, m. p. 202°, of the corresponding hydroxy-ketone, and with sodium acetate gives *methyl acetoxyethyl ketone semicarbazone*, $CMe{\cdot}C{:}(N{\cdot}CH_3ON_2){\cdot}CHAcMe$, m. p. 161°.

Chloromethyl propyl ketone semicarbazone, m. p. 157°. W. G.

Mannitol Esters of Sulphuric Acid. W. R. Bloor (*J. Amer. Chem. Soc.*, 1913, **35**, 784—794).—In preparing certain mannitol esters of the higher fatty acids by heating the substance with sulphuric acid at 70° (A., 1910, i, 538; 1912, i, 532; ii, 365) unsatisfactory results were obtained, and for this reason a study has been made of the action of concentrated sulphuric acid on mannitol at 39°, 49°, 56°, and 65°.

When mannitol is dissolved in concentrated sulphuric acid, the disulphate is the principal compound produced, but a portion of the mannitol is dehydrated to the form $C_6H_6O(OH)_2$. At low temperatures a lævorotatory ester is produced, but at higher temperatures dextrorotatory compounds are formed together with derivatives which have lost part of their capacity to combine with acid groups. In the presence of the higher fatty acids, esters are produced, presumably

with the mannitol anhydride, but during the processes of separation they are hydrated to mannide and mannitan forms. E. G.

Acetyl-Halogen Sugar Derivatives. W. SLOAN MILLS (*Rep. Brit. Assoc.*, 1912, 444—445).—β-Iodoacetodextrose (E. and H. Fischer, A., 1910, i, 716) may be prepared by the action of dry hydrogen iodide on β-penta-acetyldextrose dissolved in dichloromethane. It is recrystallised rapidly from alcohol. Copper hydride reduces it, yielding a compound $C_{28}H_{44}O_{19}$.

β-*Acetyliodogalactose* is prepared in the same manner from β-penta-acetylgalactose, and has m. p. 93—94°. Octoacetylmaltose yields an iodo-derivative, m. p. 62—66°. Acetyliodolactose, from acetyl-lactose, has m. p. 142°. C. H. D.

Gentiobiose. GÉZA ZEMPLÉN (*Zeitsch. physiol. Chem.*, 1913, **85**, 399—407).—Octa-acetylgentiobiose crystallises well and is relatively easily isolated from highly impure crude products. Acetylation may thus be used to obtain gentiobiose from plant products, and its preparation from gentian roots is described. *Octa-acetylgentiobiose* sinters at 192°, m. p. 195°, $[\alpha]_D^{20}$ $-5\cdot6°$. Gentiobiose is equivalent to 130 c.c. of Fehling's solution, maltose reducing 128·5 c.c. The phenylosazone crystallises in citron-yellow, stellate needles, or from hot water in short, pointed prisms, m. p. 160—170° (decomp.), $[\alpha]_D^{20}$ $-76\cdot1°$ in pyridine and alcohol. E. F. A.

Deflocculation of Starch and Solution of Dextrose. GIOVANNI MALFITANO and (Mlle.) A. MOSCHKOV (*Compt. rend.*, 1913, **156**, 1681—1684. Compare this vol., i, 593).—A further discussion of the difference between the phenomenon of deflocculation of starch and that of the solution of dextrose and a description of the difference in behaviour of solutions of these pseudo-crystals of starch and crystals of dextrose under different conditions. W. G.

Diastatic Degradation of Starch. WILHELM BILTZ (*Ber.*, 1913, **46**, 1532—1536).—The degradation of potato starch under the influence of enzymes has been studied, the course of the reaction being followed qualitatively by the iodine reaction and quantitatively by the withdrawal of portions of the solution at definite intervals, addition of boiling water, and precipitation of the dextrins by the addition of so much alcohol that the mixture contained 80—90% of the latter, the treatment being repeated until the product was free from sugar. The approximate mean molecular weight of the dextrins was then determined by measurement of the viscosity of their aqueous solution (compare this vol., i, 593).

The following are the main results obtained:

The diastatic degradation of starch to sugar takes place with intermediate formation of erythrodextrins and achroodextrins which are themselves ultimately transformed into sugar. The velocity of saccharification of the achroodextrins is smaller than that of the erythrodextrins, and this is again smaller than that of the amylodextrins.

The existence of erythrodextrins is established.

The mean molecular weights for the achroodextrins is about 3700; for the erythrodextrins, 6200—7000; for the amylodextrins, above 10,000. Since purified specimens of achroodextrin I, achroodextrin II, and erythrodextrin II*a* have molecular weights 1800, 1200 and 3000 respectively, it would appear that, besides these and the amylodextrins, other dextrins of high molecular weight must exist which are indifferent towards iodine and belong to the class of achroodextrins.

Philoche's determinations of the velocity of the conversion of starch into sugar (A., 1908, i, 712; ii, 470) show that this rapidly diminishes at first, but then becomes constant when the reaction appears to be unimolecular. The author's experiments show that the first phase of the reaction is complicated by the presence of amylo- and erythrodextrins in the mixture, and that reaction only follows a simple law when only one type of substances, namely, the achroodextrins, are undergoing saccharification. H. W.

Partial Hydrolysis of Cellulose. GÉZA ZEMPLÉN (*Zeitsch. physiol. Chem.*, 1913, **85**, 180—191).—On treatment of cellulose with strong sulphuric acid a mixture of various depolymerised products is obtained. Even after prolonged treatment, cellobiose acetate is obtained on acetolysis and not dextrose pentacetate. Crystalline products were not obtained on acetolysis of xylan and mannan preparations or of chitin.

E. F. A.

Chemical Composition of Cork Substance. GÉZA ZEMPLÉN (*Zeitsch. physiol. Chem.*, 1913, **85**, 173—179).—Cork when treated by Cross and Bevan's method with chlorine yields a product, which in its external properties and solubility resembles cellulose, but on treatment with acetic anhydride and sulphuric acid by Skraup's method gave no cellobioseocta-acetate. One hundred grams of cork meal contained about 4 grams of this cellulose-like product. E. F. A.

Betonicine and Turicine. ALBERT KÜNG and GEORG TRIER (*Zeitsch. physiol. Chem.*, 1913, **85**, 209—216).—The mixture of betaines in *Betonica officinalis* has been resolved into two isomerides, a lævorotatory base betonicine, and a dextrorotatory base turicine. Both are betaines of the natural hydroxyproline, and on exhaustive methylation of this compound the same mixture of the two betaines is obtained as exists in *Betonica officinalis*, *Stachys silvatica*, etc. According to the method of isolation sometimes one and sometimes the other isomeride has been isolated, in reality both are present.

Betonicine crystallises in four-sided, stunted pyramids, m. p. 243—244° (decomp.). It reacts neutral, tastes sweet, and has $[\alpha]_D^{15} -36{\cdot}6°$. The *hydrochloride* crystallises in lustrous prisms, m. p. 222—223° (decomp.), $[\alpha]_D^{15} -24{\cdot}79°$. The *aurichloride* separates in dull yellow-coloured plates aggregated in fan-shaped clusters, m. p. 242°. The *platinichloride* forms short prisms, m. p. 226°.

Turicine crystallises in long, transparent, lustrous, flat prisms, or in slender, glistening needles, m. p. 249° (decomp.), $[\alpha]_D +36{\cdot}26°$. It tastes sweet and is not hydroscopic. The *hydrochloride* crystallises in slender, lustrous needles, m. p. 223°, and reacts acid, $[\alpha]_D +24{\cdot}65°$.

The *aurichloride* is a yellow powder crystallising in obliquely-cut, lustrous prisms, m. p. 232°. The crystalline *platinichloride* has m. p. 223°. E. F. A.

Synthesis of Betonicine and Turicine. ALBERT KÜNG (*Zeitsch. physiol. Chem.*, 1913, **85**, 217—224. Compare preceding abstract).—γ-Hydroxyproline prepared by E. Fischer's method from gelatin can be methylated by means of potassium hydroxide in methyl alcohol and methyl iodide. The product, hydroxyprolinebetaine,

$$\mathrm{HO{\cdot}CH}<\begin{array}{l}\mathrm{CH_2{\cdot}CH{-}CO}\\ \qquad\;\,|\qquad\;\;|\\ \mathrm{CH_2{\cdot}NMe_2{\cdot}O}\end{array},$$

is a mixture of betonicine and turicine in equal quantities. The nature of the isomerism between these two betaines has not been established. E. F. A.

Compounds of Hexamethylenetetramine with Various Silver Salts. LUDWIG VANINO and PAULA SACHS (*Arch. Pharm.*, 1913, **251**, 290—293. Compare Grützner, A., 1899, i, 6).—The authors have prepared the compound of hexamethylenetetramine with silver nitrate, obtained by Grützner (*loc. cit.*), and also *compounds* with the following silver salts: silver fluoride, $C_6H_{12}N_4,AgF,3H_2O$, slender needles; silver chloride, B,4AgCl, prismatic crystals (compare Délepine, A., 1895, i, 261); silver bromide, B,3AgBr, microscopic crystals; silver iodide, B,3AgI, amorphous; silver chlorate, $B,AgClO_3,H_2O$, amorphous, explodes on warming; silver oxalate, $B,Ag_2C_2O_4$; globular masses of slender needles. T. A. H.

The Methylation of Glycine by means of Formaldehyde. WALTHER LÖB (*Biochem. Zeitsch.*, 1913, **51**, 116—127).—If formaldehyde is allowed to act on glycine in neutral solution in the cold, a compound, $CH_2{:}N{\cdot}CH_2{\cdot}CO_2H$, is formed, with separation of the elements of water, which under the influence of acids or alkalis readily undergoes scission again into formaldehyde and glycine. If, however, the substances are allowed to act on one another in hot acid solution, a stable *methylenediglycine*, $CH_2(NH{\cdot}CH_2{\cdot}CO_2H)_2$, is formed, which can be readily isolated in the form of a dihydrochloride, from which, by means of silver oxide, the free base can be obtained in platelets, melting about 199°. In alkaline solution, formaldehyde does not act on glycine. If formaldehyde in the presence of acid and zinc is allowed to act on glycine (at 100°), a mixture of sarcosine and dimethylaminoacetic acid is produced. The mechanism of this reaction is explained by assuming that methylenediglycine is reduced to a mixture of an equal number of molecules of methylglycine and glycine. By the action of formaldehyde on the former, methylenedi(methylglycine) can be produced, which, on reduction, yields an equal number of molecules of dimethyl- and monomethyl-glycines. S. B. S.

Behaviour of α-Amino-acids and Polypeptides to Neutral Salts. PAUL PFEIFFER and J. VON MODELSKI (*Zeitsch. physiol. Chem.*, 1913, **85**, 1—34. Compare A., 1912, i, 949).—The compounds of lithium chloride or bromide with glycine of the composition

$$LiX,NH_2{\cdot}CH_2{\cdot}CO_2H,H_2O$$

are readily prepared by evaporating an aqueous solution of the components until crystallisation begins. They form colourless needles, m. p. 136° (the chloride) and 175—176° (the bromide) respectively.

The compounds of the type $LiX,2NH_2\cdot CH_2\cdot CO_2H,H_2O$ are obtained by crystallising rapidly at room temperature from strong solutions after inoculation. They crystallise in colourless, transparent plates, m. p. 186—190° (the chloride) and 223° (the bromide).

The compound of lithium chloride and alanine,

$$LiCl,NH_2\cdot CHMe\cdot CO_2H,H_2O,$$

has m. p. 128—129°.

Monoglycine calcium chloride, $CaCl_2,NH_2\cdot CH_2\cdot CO_2H,3H_2O$, forms tiny, lustrous plates, which do not melt. *Diglycine calcium chloride*, $4H_2O$, crystallises in long, colourless needles. *Triglycine calcium chloride* separates in lustrous, transparent platelets which do not melt at 250°. *Triglycine lanthanum chloride*,

$$LaCl_3,3NH_2\cdot CH_2\cdot CO_2H,3H_2O,$$

forms colourless, transparent, prismatic needles.

Monoalanine lithium chloride, $LiCl,NH_2\cdot CHMe\cdot CO_2H,H_2O$, crystallises in colourless, lustrous platelets, m. p. 127—128°. *Dialanine calcium chloride*, $3H_2O$, yields colourless, transparent needles, m. p. 77° to a viscid, clear liquid.

Monodiglycylglycine calcium chloride,

$$CaCl_2,NH_2\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2H,3H_2O,$$

separates in well-formed, colourless, transparent platelets.

Monobetaine potassium bromide, $KBr,C_5H_{11}O_2N,2H_2O$, crystallises in transparent, tabular plates, which soften completely at 90—93°, m. p. about 110°. *Monobetaine potassium iodide* forms long, thin, colourless plates consisting in part of parallel, intergrown, flat needles, which sinter at 100°, begin to melt at 115°, and form a clear liquid at 140°. *Dibetaine potassium iodide* $KI,2C_5H_{11}O_2N,2H_2O$, forms colourless, tabular crystals with oblique faces, m. p. 148°. *Monobetaine barium chloride*, $4H_2O$, crystallises in long, thin, colourless, prismatic needles. *Monobetaine barium bromide*, $4H_2O$, also separates in similar needles.

The constitution of the salts described is discussed; they are regarded as amphi-salts in which both the basic and acid groups of the amino-acid are neutralised. E. F. A.

Methyl Derivatives of δ-Aminovaleric Acid and *dl*-Ornithine. EMIL FISCHER and MAX BERGMANN (*Annalen*, 1913, **398**, 96—124).—By hydrolysis with hydrochloric acid, D 1·19, in a sealed tube in the water-bath, δ-*m*-nitrobenzoylamino-α-methylaminovaleric acid (A., 1909, i, 793) readily yields *δ-amino-α-methylaminovaleric acid dihydrochloride*, $NH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH(NHMe)\cdot CO_2H,2HCl$, m. p. 207—210° (decomp., corr.), colourless plates or prisms, which forms a precipitate with phosphotungstic acid, but not with potassium bismuth iodide even in considerably concentrated solutions. From the dihydrochloride, the *picrate*, $C_6H_{14}O_2N_2,2C_6H_3O_7N_3$, m. p. 205—206° (decomp., corr.), and the *platinichloride*, $C_6H_{14}O_2N_2,H_2PtCl_6,H_2O$ (or $4H_2O$), decomp. 218° (corr.), when anhydrous, have been prepared.

By treating an aqueous solution of the dihydrochloride with silver

sulphate, removing the excess of silver by hydrochloric acid and the sulphuric acid by barium hydroxide, and evaporating the filtrate at 10—20 mm., all the operations being performed in an atmosphere of carbon dioxide, *δ-amino-α-methylaminovaleric acid*, m. p. 82—100°, is obtained as a crystalline mass. Its aqueous solution reacts strongly alkaline, precipitates ferric hydroxide, and dissolves precipitated copper hydroxide.

By hydrolysing *dl*-benzoylornithine with boiling hydrochloric acid (D 1·19) and treating the resulting *dl*-ornithine with 2*N*-sodium hydroxide and benzenesulphonyl chloride (3 mols.) at 46—48°, and acidifying, *αδ-dibenzenesulphonyldiaminovaleric acid* (dl-*dibenzenesulphonylornithine*), $C_{17}H_{20}O_6N_2S_2,H_2O$, m. p. 155—157° (corr., anhydrous), microscopic needles, is obtained. By treatment with 2*N*-sodium hydroxide and methyl iodide at 65°, it yields, after acidification, *αδ-dibenzenesulphonyldimethyldiaminovaleric acid*,

$$SO_2Ph{\cdot}NMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(NMe{\cdot}SO_2Ph){\cdot}CO_2H,$$

m. p. 141—142° (corr.), microscopic plates, by the hydrolysis of which by hydrochloric acid (D 1·19) at 100° is obtained N-*dimethylornithine-αδ-dimethyldiaminovaleric acid*), $NHMe{\cdot}[CH_2]_3{\cdot}CH(NHMe){\cdot}CO_2H$, which is isolated by precipitation with phosphotungstic acid; the *hydrochloride*, $C_7H_{16}O_2N_2,2HCl$, and *platinichloride*, $C_7H_{16}O_2N_2,H_2PtCl_6$, m. p. 220° (decomp., corr.), are described, and the *aurichloride* and *picrate* are mentioned. A 0·5% aqueous solution of dimethylornithine dihydrochloride and aqueous potassium bismuth iodide yield a brick-red precipitate after a few hours.

dl-Ornithine, obtained by the hydrolysis of δ-benzoylornithine, has been isolated in a crystalline state.

δ-Benzenesulphonylaminovaleric acid, 2*N*-sodium hydroxide, and methyl iodide at 63—65° yield, after acidification, *δ-benzenesulphonylmethylaminovaleric acid*, $SO_2Ph{\cdot}NMe{\cdot}[CH_2]_4{\cdot}CO_2H$, m. p. 70—71° (corr.), colourless needles or prisms, by the hydrolysis of which by hydrochloric acid (D 1·19) is obtained *δ-methylaminovaleric acid*, m. p. 121—122° (corr.), needles or prisms, which is isolated by means of phosphotungstic acid. The acid is very hygroscopic, and its aqueous solution gives immediately a brick-red precipitate with potassium bismuth iodide; the *picrate*, $C_6H_{13}O_2N,C_6H_3O_7N_3,H_2O$, has m. p. 70—71° (corr.). At 130—160°, δ-methylaminovaleric acid loses water and is converted into 1-*methyl*-2-*piperidone*, $NMe{<}{\begin{matrix}CO{-}CH_2\\CH_2{\cdot}CH_2\end{matrix}}{>}CH_2$, b. p. 94—95° (corr.)/9 mm.

3-Amino-2-piperidone, prepared from ornithine, reacts readily with benzaldehyde to form the *benzylidene* compound,

$$CHPh{:}N{\cdot}CH{<}{\begin{matrix}CO{-}NH\\CH_3{\cdot}CH_2\end{matrix}}{>}CH_2,$$

m. p. 140—142° (corr.), almost colourless crystals.

Glycine, *p*-toluenesulphonyl chloride, and 2*N*-sodium hydroxide at 67—70° yield, after acidification, p-*toluenesulphonylglycine*, $C_9H_{11}O_4NS$, m. p. 149—150° (corr.), slender needles, which is converted by 3*N*-sodium hydroxide and methyl iodide at 67° and subsequent

acidification into p-*toluenesulphonylsarcosine*, $C_{10}H_{13}O_4NS$, m. p. 150—152° (corr.), by the hydrolysis of which sarcosine is obtained.

The reaction of alcoholic sodium ethoxide, α-chloro-γ-bromopropane, and ethyl malonate in the presence of ether leads to the production of *ethyl γ-chloropropylmalonate*, $CH_2Cl\cdot CH_2\cdot CH_2\cdot CH(CO_2Et)_2$, b. p. 154—155° (corr.)/17 mm., which reacts with bromine in chloroform to form *ethyl bromo-γ-chloropropylmalonate*

$$CH_2Cl\cdot CH_2\cdot CH_2\cdot CBr(CO_2Et)_2,$$

b. p. 175—176° (corr.)/17 mm. Ethyl γ-chloropropylmalonate and 33% aqueous methylamine react at the ordinary temperature to form *γ-chloropropylmalonmethylamide*, $CH_2Cl\cdot CH_2\cdot CH_2\cdot CH(CO\cdot NHMe)_2$, m. p. 158—162° (corr.), leaflets or needles.

A by-product in the preparation of ethyl γ-chloropropylmalonate under certain conditiods is *ethyl di-γ-chloropropylmalonate*,

$$C(CH_2\cdot CH_2\cdot CH_2Cl)_2(CO_2Et)_2,$$

m. p. 51—52°, b. p. 195—197° (corr.)/14 mm., flattened crystals, which is converted by methyl alcoholic ammonia at 100° into a *substance*, $C_9H_{14}O_2N_2$, m. p. 330° (decomp., corr.), colourless, microscopic prisms, which is probably *bis-2-piperidone-3 : 3'-spiran*,

$$CH_2{<}{\substack{CH_2\cdot CH_2\\ NH-CO}}{>}C{<}{\substack{CH_2\cdot CH_2\\ CO-NH}}{>}CH_2.$$

C. S.

The Oxidative Degradation of a Synthetic Tripeptide. OTTO EISLER (*Biochem. Zeitsch.*, 1913, **51**, 45—52).—By the oxidation of alanylglycylglycine with calcium permanganate, using as much of the latter as is equivalent to 8—10 atoms of oxygen to one molecule of the peptide, an acid in the form of a crystalline calcium salt was isolated, the formula of which corresponded approximately with

$$C_6H_5O_7N_3Ca,6H_2O.$$

On hydrolysis by acids, one molecule gives rise to two molecules of oxalic acid. Two alternative formulæ are suggested by the author.

S. B. S.

Anhydride Formation with a Diaminohydroxy-acid. MORITZ KOHN and ALFONS OSTERSETZER (*Monatsh.*, 1913, **34**, 781—786). —It has been shown (Kohn, A., 1908, i, 819; Kohn and Bum, A., 1910, i, 136) that *iso*hexan-δ-ol-β-one on treatment with potassium cyanide and ammonium chloride, or the hydrochloride of an amine, gives rise to an aminolactone. When equimolecular quantities of *iso*hexan-δ-ol-β-one, ethylenediamine dihydrochloride, potassium cyanide, and potassium hydroxide are heated together with a little water at 60° for five to six hours, and the resulting nitrile hydrolysed by treatment with concentrated hydrochloric acid, a *substance*, $C_9H_{18}O_2N_2$, prismatic crystals, m. p. 174°, is obtained, which gives a crystalline *picrate*,

$$C_9H_{18}O_2N_2,C_6H_3O_7N_3,$$

m. p. 154°, and an *oxalate*, $C_9H_{18}O_2N_2,2C_2H_2O_4,\frac{1}{2}H_2O$, tablets, m. p. 160° (decomp.).

The structure of the substance is probably that of a diaminolactone or of a hydroxylactam, but the point is at present undecided.

D. F. T.

The Electrolytic Formation of Carbamide and Acetamidine Nitrate. FRITZ FICHTER, KARL STUTZ, and FRITZ GRIESHABER (*Verhand. Naturfors. Ges. Basel*, 1912, **23**, 222—263).—It is shown that small quantities of carbamide are produced by the electrolysis of solutions of ammonium carbamate. The best yields, which are nevertheless very small, are obtained when the anode current density (C_a) lies between 0·130 and 0·555 ampere per sq. cm. Between these values the yield is practically constant and amounts to about 0·60 gram per 100 ampere-hours. It is shown that the yield is increased if the concentration of the carbamate is increased, and also increase of free ammonia increases the yield, the latter factor being of much more importance than the former. The best yield is obtained with a solution containing 12 gram-equivalents of ammonia and 8 gram-equivalents of ammonium carbamate. It is also shown that carbamide is decomposed by the oxidising action of the current and converted into ammonium nitrate, and that the amount of decomposition is greatest when there is no free ammonia present and that it decreases, rapidly as the concentration of ammonia is increased. The gases evolved at the anode were collected and analysed, and the relationship between their composition and the temperature and excess ammonia concentration determined. It is shown that at 18° with $C_a = 0·044$ ampere per sq. cm., the percentage of oxygen slowly decreases, whilst the nitrogen increases with the concentration of free ammonia up to 7 gram-equivalents per litre, and that on further increasing the free ammonia concentration the nitrogen increases rapidly until at 12 gram-equivalents per litre it has reached 100%. From a solution containing 9 gram-equivalents of ammonia the percentage of nitrogen in the gas was 24·8% at 6°, whilst at 18° it had increased to 99·1%. A theory is put forward to represent the electrolytic oxidation of ammonia which can be shortly represented by the scheme:

$$\begin{array}{ccccc} NH_3 & \longrightarrow & NH_2{\cdot}OH & \longrightarrow & H_2N_2O_2 \\ & & & & \downarrow \\ & & & & N_2O + H_2O \end{array}$$

and

$$\begin{array}{ccccc} NH_4{\cdot}ON{:}N{\cdot}OH & \longrightarrow & NH_4NO_2 & \longrightarrow & NH_4NO_3 \\ & & \downarrow & & \\ & & N_2 + H_2O & & \end{array}$$

Nitrous oxide is found in the gases collected at the anode, and the other steps in the process are generally confirmed by the observations. The formation of carbamide by the electrolysis of ammonium carbamate is explained by the following scheme:

$$O{:}C(NH_2){\cdot}ONH_4 + 2NH_2{\cdot}OH = 2{\cdot}O{:}CH{\cdot}NH_2 + H_2N_2O_2 + 2NH_3 + 2H_2O$$
$$O + NH_3 + O{:}CH{\cdot}NH_2 = NH_2{\cdot}CO(NH_2) + H_2O$$

According to this, formamide is produced by the interaction of hydroxylamine, produced as above, and ammonium carbamate, and this is then electrolytically oxidised in the presence of ammonia to carbamide. In proof of this theory the authors quote the work of Jouve (A., 1899, i, 420), who showed that when carbon monoxide is heated with ammoniacal cuprous chloride, carbamide is produced. Further, Hofmeister and Halsey (A., 1898, ii, 529) have shown that a large number

of organic substances when treated with potassium permanganate in ammoniacal solution yield carbamide. These substances are all oxy-acids, ketones, and ketonic acids, that is, substances which give carbon monoxide on oxidation. Carbamide was next obtained by electrolysing a solution of ammonium acetate containing methyl alcohol; this is represented by

$$CH_3{\cdot}OH \longrightarrow CO \longrightarrow H{\cdot}CO{\cdot}NH_2 \longrightarrow NH_2{\cdot}CO{\cdot}NH_2.$$

When ethyl alcohol was electrolysed in ammoniacal solution a small quantity of acetamidine nitrate was obtained. It was found that the addition of ammonium nitrate increased the yield of the amidine nitrate, and that if no ammonium nitrate had been added, often there was no yield at all. The formation is represented by the scheme:

$$CH_3{\cdot}CH_2{\cdot}OH \longrightarrow CH_3{\cdot}CHO + NH_3 \longrightarrow$$
$$CH_3{\cdot}CH(OH){\cdot}NH_2 + O + NH_3 \longrightarrow CH_3{\cdot}C(NH)NH_2$$

The authors show in confirmation of the above that aldehyde ammonia can be oxidised to the amidine by calcium permanganate, ammonium persulphate and hydrogen peroxide, and isolated provided that excess of ammonia and some ammonium nitrate are present. The corresponding propionamidine nitrate and butyramidine nitrate were obtained by the electrolysis of ammoniacal solutions of propyl and butyl alcohols respectively. In the case of butyl alcohol only the smallest yield was obtained, and with higher alcohols amidine nitrates could not be obtained in any case. J. F. S.

The Fixation of Nitrogen by Mixtures of Barium Oxide and Charcoal. THOMAS EWAN and THOMAS NAPIER (*J. Soc. Chem. Ind.*, 1913, **32**, 467—474).—The first set of experiments were carried out by heating a mixture of two parts of barium carbonate and one part of well-burned wood charcoal, contained in an iron boat, in a porcelain tube is a current of nitrogen. The results obtained were as follows (compare Kühling and Berkhold, A., 1908, i, 143): the absorption of nitrogen begins between 900° and 930°. The amount absorbed under the same conditions increases very rapidly with the temperature, for example, if 4 mols. of nitrogen are passed over 1 mol. of $BaCO_3$ in two hours, about 1% of the barium will combine with it at 930°, about 14% at 960°, and about 40% at 1000°. The greater part of the nitrogen fixed is in the form of cyanide. Under the conditions used by the authors, about 2·5% of the nitrogen used is fixed at 960° and about 10% at 1000°. The addition of quantities of potassium carbonate up to 11% seems to improve the results, but the improvement is no more than would be produced by a difference of 10—20° in temperature.

No cyanide is formed until some 30% of the barium carbonate has been converted into oxide, and the quantity of carbon monoxide in the gas has fallen to about 30%; the percentage of carbon monoxide falls steadily as the formation of cyanide progresses.

The authors draw the conclusion that the fixation of nitrogen is due to one or both of the reversible reactions: $BaO + 2C + N_2 \rightleftarrows BaCN_2 + CO$, $BaO + 3C + N_2 \rightleftarrows Ba(CN)_2 + CO$; and further experiments indicate that the barium compounds mix in the solid (or fused) mixture, so that the ratio of the partial pressures of carbon monoxide and nitrogen in

the gas when equilibrium is attained at any given temperature depends on the relative quantities of cyanide, cyanamide, and oxide in the mixture. The reaction appears to be arrested at half-conversion of the barium oxide, which may be explained by assuming the formation of a compound $BaO,Ba(CN)_2$, in which the barium oxide is much less active than in the free state.

Pure barium cyanide is readily obtained by suspending anhydrous barium hydroxide, in the form of a fine powder, in light petroleum, and adding an emulsion of the theoretical quantity of anhydrous hydrocyanic acid in light petroleum. It fuses at 600° and is distinctly volatile even at its melting point. The fused product contains barium cyanamide, the amount of which depends, among other things, on the temperature and the length of time the fusion is heated; the presence of finely divided iron in the cyanide increases the amount of cyanamide formed.

When barium ferrocyanide is heated in a vacuum or in an atmosphere of nitrogen, decomposition begins at about 500°, nitrogen is evolved, and a mixture of carbon, iron, and barium cyanide and cyanamide remains behind.

When mixtures of barium oxide, cyanide, and cyanamide are heated in nitrogen, the combined nitrogen passes more and more into the form of cyanide as the mixture is more and more diluted with barium oxide.

T. S. P.

Some Aliphatic Cyanoacetylamines. MARIA CLOTILDE BIANCHI (*Atti R. Accad. Sci. Torino*, 1912–1913, **48**, 654—659).—*Cyanoacetomethylamide*, $CN\cdot CH_2\cdot CO\cdot NHMe$, is prepared with almost the theoretical yield by passing gaseous methylamine into an alcoholic solution of ethyl cyanoacetate; it crystallises in prisms, m. p. about 104—105°. *Cyanoacetoethylamide*, $CN\cdot CH_2\cdot CO\cdot NHEt$, is similarly prepared and forms prismatic laminæ, m. p. 74—75°; it is oxidised by potassium permanganate at the ordinary temperature.

Dicyanoacetopropylenediamide, $(CN\cdot CH_2\cdot CO\cdot NH)_2C_3H_6$, obtained by keeping a mixture of ethyl cyanoacetate and propylenediamine for twenty-four hours, crystallises in colourless needles, m. p. 161—162°.

Dicyanoacetotrimethylenediamide, $CH_2(CH_2\cdot NH\cdot CO\cdot CH_2\cdot CN)_2$, prepared by mixing ethyl cyanoacetate and trimethylenediamine, crystallises in slightly yellow needles, m. p. 163—165°.

Cyanoacetamide, after recrystallisation from ether, has m. p. 124—125°, which is higher than the m. p. given in the literature.

R. V. S.

Photochemical Synthesis of a New Compound, Carbonyl Cyanide, by means of Ultra-violet Rays. DANIEL BERTHELOT and HENRY GAUDECHON (*Compt. rend.*, 1913, **156**, 1766—1768).—Carbon monoxide and cyanogen when mixed and subjected to the ultra-violet rays ($\lambda < 0{\cdot}25\ \mu$) from a mercury-quartz lamp combine to form *carbonyl cyanide*, $CO(CN)_2$, a yellow, amorphous compound, which does not volatilise at 200°, but gives off small quantities of nitrogen. It is soluble in alkalis, giving a yellow solution, and slowly

undergoes hydrolysis on the addition of acid, giving carbon dioxide and hydrogen cyanide. It burns only very slowly in oxygen at a red heat.

W. G.

[Potassium Manganicyanide.] JULIUS MEYER (*Zeitsch. anorg. Chem.*, 1913, **81**, 385—405).—See this vol., ii, 599.

Some Azides of Carbamic Acid. VI. E. OLIVERI-MANDALÀ and F. NOTO (*Gazzetta*, 1913, **43**, i, 514—520).—The azides described in this paper were prepared by the action of azoimide on carbimides. Methylcarbamazide can be obtained in this way. *Chloromethylcarbamazide* (from chloromethylcarbimide in benzene solution) decomposes rapidly on exposure to the air. Alcoholic ammonia converts it into a substance, $(C_2H_5ON_2Cl)_3$, having the composition of a *trimeride* of the *chloromethylcarbamide* to be expected; it decomposes above 300°, evolving hydrogen chloride.

Bromomethylcarbamazide is similarly obtained from *bromomethylcarbimide*, which can be prepared by Schroeter's method (A., 1909, i, 773); this azide is also very unstable. When it is treated with alcoholic ammonia, a *trimeric bromomethylcarbamide*, $(C_2H_5ON_2Br)_3$, is produced; it decomposes above 300°.

Propylcarbimide, prepared from silver cyanate and propyl iodide, has b. p. 82—85°. The *azide*, $C_4H_8ON_4$, has b. p. 85—86°/28 mm. When heated for two hours with aniline in alcoholic solution, it yields s-*phenylpropylcarbamide*, $C_{10}H_{14}ON_2$, m. p. 114—116°.

iso*Propylcarbamazide*, $C_4H_8ON_4$, crystallises in long needles, m. p. 44°. s-*Phenyl*iso*propylcarbamide*, $C_{10}H_{14}ON_2$, obtained from this azide, forms needles, m. p. 142—143°.

iso*Butylcarbamazide*, $C_5H_{10}ON_4$, has b. p. 94°/22 mm. s-*Phenyl*iso*butylcarbamide*, $C_{11}H_{16}ON_2$, crystallises in small needles, m. p. 158°.

R. V. S.

A New Class of Lipoid Arsenic Compounds. EMIL FISCHER and GEORG KLEMPERER (*Therapie der Gegenwart*, Jan., 1913; Reprint 8 pp.).—When behenolic acid is heated with arsenic trichloride and the product of action is afterwards treated with bases, an acid containing arsenic and chlorine in approximately equivalent quantities is formed. It has been obtained so far as a coloured oil, which is not sufficiently pure for analysis. The strontium salt, containing about 13% arsenic and 6% chlorine, has been employed under the name of elarson as a medicament containing arsenic in a relatively non-toxic form, and satisfactory therapeutic results are claimed for it in cases requiring treatment by arsenic.

S. B. S.

Hydro-aromatic Substances. ARTHUR W. CROSSLEY, WILLIAM H. PERKIN, MARTIN O. FORSTER, and HENRY R. LE SUEUR (*Rep. Brit. Assoc.*, 1912, 124—125).—See Crossley and Renouf, T., 1912, **101**, 1524; Crossley and Smith, P., 1912, 332.

C. H. D.

Preparation of Several Dicyclohexylbutanes. PAUL SABATIER and MARCEL MURAT (*Compt. rend.*, 1913, **156**, 1430—1434. Compare A., 1912, i, 547, 617, 757).—By direct hydrogenation with reduced

nickel the authors have prepared five of the nine possible *dicyclo*hexylbutanes, three being derivatives of *n*-butane and two of *iso*butane; *aδ-dicyclohexylbutane*, $C_6H_{11}\cdot[CH_2]_4\cdot C_6H_{11}$, colourless crystals, m. p. 9°, b. p. 304—306° (corr.), D_0^{21} 0·8772, n_D^{21} 1·475, is obtained by the reduction of aδ-diphenylbutane.

Phenyl ethyl ketone reacts with magnesium benzyl chloride at 450° in the presence of thorium oxide to give phenylbenzylethylcarbinol, which by distillation under reduced pressure yields diphenyl-Δ^a-butylene, b. p. 296° (corr.), D_0^{18} 1·0124, n_D^{18} 1·593 (compare Klages and Heilmann, A., 1904, i, 487). This hydrocarbon on hydrogenation in the presence of slightly active nickel gives *aβ-diphenylbutane*, a colourless liquid, b. p. 285—287° (corr.), D_0^{18} 1·0092, n_D^{18} 1·587, which on further hydrogenation over very active nickel at 170° yields *aβ-dicyclohexylbutane*, a colourless liquid, b. p. 276—278° (corr.), D_0^0 0·9104, D_0^{18} 0·9084, n_D^{18} 1·500.

aa-Diphenyl-Δ^a-butylene, b. p. 295—297° (corr.), D_0^{16} 1·0039, n_D^{16} 1·595, obtained by the interaction of magnesium phenyl bromide and ethyl butyrate and subsequent dehydration, on hydrogenation at 150° with slightly active nickel yields *aa-diphenylbutane*, b. p. 286—288° (corr.), D_0^{16} 0·9748, n_D^{16} 1·554. If this hydrogenation is carried out at 250° the product is diphenylmethane, m. p. 27°, b. p. 262°, described by Klages and Heilmann (*loc. cit.*) as *aa*-diphenylbutane. The *aa*-diphenylbutane, now described, on hydrogenation at 170° with very active nickel yields *aa-dicyclohexylbutane*, b. p. 280—282° (corr.), D_0^0 0·8922, D_0^{16} 0·8842, n_D^{16} 1·485.

By the interaction of benzophenone and magnesium *iso*propyl iodide or by the action of magnesium phenyl bromide on ethyl *iso*butyrate, and subsequent dehydration of the carbinol formed, *aa-diphenyl-β-methylpropylene*, b. p. 293°, D_0^{16} 1·0240, n_D^{16} 1·596, is obtained, and this on gentle hydrogenation at 180° yields *aa-diphenyl-β-methylpropane*, b. p. 285—286° (corr.), D_0^{16} 0·978, n_D^{16} 1·560. This hydrocarbon by more active hydrogenation at 170° gives *aa-dicyclohexyl-β-methylpropane*, b. p. 278—279° (corr.), D_0^0 0·9017, D_0^{16} 0·8906, n_D^{15} 1·492.

aγ-Diphenyl-β-methylpropylene, b. p. 304° (corr.), D_0^{16} 1·0181, n_D^{16} 1·593, obtained in the usual way from magnesium methyl iodide and dibenzyl ketone, on hydrogenation at 170° with very active nickel yields *aγ-dicyclohexyl-β-methylpropane*, b. p. 290—292° (corr.), D_0^0 0·8916, D_0^{19} 0·8840, n_D^{19} 1·484. W. G.

Partial Reduction of Aromatic Polynitro-compounds by Electrochemical Methods. III. KURT BRAND and TH. EISENMENGER (*J. pr. Chem.*, 1913, [ii], **87**, 487—507. Compare A., 1906, i, 80; 1907, i, 755).—The present paper deals with the electrolytic reduction of 2:4:6-trinitrotoluene, 2:4-dinitroanisole, and 4-chloro-*m*-dinitrobenzene in alkaline, acid and almost neutral solution.

On reduction in alkaline solution at a mercury cathode, 4-chloro-*m*-dinitrobenzene yields 4-chloro-*m*-nitroaniline and 6-chloro-*m*-nitroaniline, together with 2:4-dinitrophenol; under the same conditions, 2:4-dinitroanisole is reduced to *5:5′-dinitro-o-azoxyanisole*, which separates from benzene in slender, almost colourless leaflets, m. p. 209°. The constitution of the azoxy-compound has been established by its

preparation from 5-nitro-2-methoxyphenylhydroxylamine by the action of sodium hydroxide in alcoholic solution. The reduction of 2 : 4 : 6-trinitrotoluene in alkaline solution yielded no definite product. In hydrochloric acid solution and in the presence of cupric chloride, 2 : 4 : 6-trinitrotoluene is reduced at a copper cathode to 2 : 6-dinitro-*p*-toluidine and 4 : 6-dinitro-*o*-toluidine.

The last-named compound forms orange-yellow crystals, which have m. p. 135° and not 155° as given by Holleman and Böeseken (A., 1898, i, 303). It yields an *acetyl* derivative, crystallises in white needles, m. p. 224°, and when diazotised and boiled with alcohol is converted into 2 : 4-dinitrotoluene and 2 : 4-*dinitroindazole*,

$$C_6H_2(NO_2)_2<\begin{matrix}CH \\ | \\ N\end{matrix}>NH,$$

which crystallises in almost white needles, m. p. 203°, and dissolves in aqueous alkalis, yielding yellow solutions.

On reduction in acid solution under the same conditions as given above for 2 : 4 : 6-trinitrotoluene, 2 : 4-dinitroanisole yields 4-nitro-*o*-anisidine (Meldola, Woolcott, and Wray, T., 1896, **69**, 1321), whilst 4-chloro-*m*-dinitrobenzene gives rise to 4-chloro-*m*-nitroaniline and 6-chloro-*m*-nitroaniline, which are separated by crystallisation of their acetyl derivatives from alcohol.

In almost neutral solution, 2 : 4 : 6-trinitrotoluene is reduced at a silver cathode to 2 : 6-dinitro-*p*-tolylhydroxylamine (Cohen and Dakin, T., 1902, **81**, 27) and 4 : 6-*dinitro*-o-*tolylhydroxylamine*, which forms light yellow crystals, m. p. 109°.

The constitution of 2 : 6-dinitro-*p*-tolylhydroxylamine has been confirmed by its reduction with copper powder and hydrochloric acid to 2 : 6-dinitro-*p*-toluidine, and conversion of the latter compound by diazotisation and boiling with alcohol into 2 : 6-dinitrotoluene. When boiled with strong hydrochloric acid, 2 : 6-dinitro-*p*-tolylhydroxylamine yields 3 : 5 : 3′ : 5′-*tetranitro*-p-*azoxytoluene*, colourless needles, m. p. 216°; on treatment with phosphorus pentachloride in ethereal solution it gives rise to 3 : 5 : 3′ : 5′-*tetranitro*-p-*azotoluene*, which crystallises in orange needles, m. p. 248—250°.

Reduction of 4-chloro-*m*-dinitrobenzene in almost neutral solution yields a small amount of 2 : 2′(or 4 : 4′)-*dichloro*-5 : 5′-*dinitroazobenzene*, m. p. 164°, together with a brown oil, containing 4- and 6-chloro-*m*-nitrophenylhydroxylamines, which, however, could not be isolated from the product, and were therefore identified by oxidation of the cathode liquid with ferric chloride to the corresponding nitroso-compounds.

1-*Chloro*-4-*nitro*-2-*nitrosobenzene* forms white needles, m. p. 95°, and has also been prepared by the oxidation of 6-chloro-*m*-nitroaniline with Caro's acid.

1-*Chloro*-2-*nitro*-4-*nitrosobenzene*, prepared from 4-chloro-*m*-nitroaniline in a similar manner, forms white needles, m. p. 120°.

In neutral solution, 2 : 4-dinitroanisole is reduced at a silver cathode to the above-mentioned 5 : 5′-dinitro-*o*-azoxyanisole and 5-*nitro*-2-*methoxyphenylhydroxylamine*, which forms a brownish-red, sandy, crystalline powder, m. p. 129°, is reduced by copper powder and hydrochloric acid to 4-nitro-*o*-anisidine, and on oxidation with ferric chloride yields a

compound, $C_{16}H_{16}O_8N_4$, m. p. 121°, the constitution of which has not yet been determined. F. B.

The Transformation of Aromatic Nitroamines and Allied Substances, and its Relation to Substitution in Benzene Derivatives. FREDERICK S. KIPPING, KENNEDY J. P. ORTON, SIEGFRIED RUHEMANN, and JOHN T. HEWITT (*Rep. Brit. Assoc.*, 1912, 116—123).—See Orton and Jones, T., 1912, **101**, 1708, 1720.

C. H. D.

A Photochemical Reaction. FRÉDÉRIC REVERDIN (*Bull. Soc. chim.*, 1913, [iv], **13**, 485—486 *).—A solution of 3 : 5-dinitro-4-nitromethylaminotoluene in alcohol on exposure to sunlight slowly undergoes partial transformation into 3 : 5-dinitro-4-methylaminotoluene.

T. A. H.

Hexylenic Ethers. R. DIONNEAU (*Bull. Soc. chim.*, 1913, [iv], **13**, 519—525).—A more detailed account, with some new data, of work already recorded (A., 1910, i, 353). Phenoxyhexylene, D_4^0 0·9553, reacts with bromine in chloroform to give a *dibromide*, D_4^0 1·5415, b. p. 208°/35 mm. (decomp.), and with excess of hydriodic acid to form di-iodohexane, D_4^0 2·047, whilst with 1 mol. of the acid it gives iodophenoxyhexane, D_4^0 1·4385, b. p. 205°/33 mm., and a *substance*, D_4^0 1·516, b. p. 84°/33 mm. or 183°/760 mm., which may be iodohexylene. Iodophenoxyhexane through its magnesium derivative yields phenoxyhexane, from which Franchimont and Zincke's hexyl iodide is obtainable by heating with hydriodic acid; thus showing that in phenoxyhexylene the radicle C_6H_{11} is linear and carries the phenoxy-group on the first carbon atom. On oxidation with permanganate or ozone, phenoxyhexylene yields phenoxyvaleric and formic acids. These observations indicate that it has the formula $OPh\cdot[CH_2]_4\cdot CH{:}CH_2$.

Ethoxyhexylene (*loc. cit.*) has been prepared by the action of allyl iodide on the magnesium derivative of iodoethoxypropane.

T. A. H.

Aliphatic Dihalogen Compounds. JULIUS VON BRAUN (*Ber.*, 1913, **46**, 1782—1792).—A series of experiments is described on (1) the synthesis of brominated esters, (2) the preparation of polymethylene dibromides in which one $-CH_2-$ group is replaced by $-N(CN)-$, (3) ring-formations with sodium cyanamide, and (4) certain other ring-formations.

(1) Diprimary chloro-, bromo-, and iodo-compounds react readily with alkali phenoxides and alkoxides with the formation of halogenated ethers (for example, $Br[CH_2]_x\cdot OPh$), the use of which in synthetic operations is greatly limited by the difficulty of removing the phenoxy-radicle without completely decomposing the molecule. The author has, therefore, examined the halogen derivatives of alkyl carboxylates (compare A., 1909, i, 419) in this respect. When dry sodium benzoate (1 mol.) is heated with 1·5 mols. of various dibromides, the nature of the product formed depends greatly on the distance of the bromine atoms

* and *J. pr. Chem.*, 1913, [ii], **88**, 90—91.

from one another. Ethylene dibromide yields almost exclusively ethylene dibenzoate, bromoethyl benzoate, $CH_2Br\cdot CH_2\cdot O\cdot COPh$, not being detectable; in the trimethylene series, the yield of brominated ester is 30%, in the tetramethylene series 45%, in the pentamethylene series above 60%, and in the heptamethylene series nearly 75%. These esters are readily saponifiable by acid or alkali, or even by protracted action of water and alcohol.

Trimethylene bromide and sodium benzoate yield trimethylene dibenzoate, m. p. 57°, and γ-bromopropyl benzoate, b. p. 162—164°/14 mm. When warmed with sodium iodide in alcoholic solution, the latter yields *γ-iodopropyl benzoate*, pale yellow oil, b. p. 175—178°/12 mm. *δ-Bromobutyl benzoate*, b. p. 176—178°/14 mm., together with tetramethylene dibenzoate, is similarly obtained from tetramethylene bromide. ε-Bromoamyl benzoate, b. p. 188—190°/12 mm., is most readily obtained from α:ε-dibromopentane and sodium benzoate at 200—210°. The corresponding pentamethylene dibenzoate is a liquid. ε-Bromoamyl benzoate is readily saponified by aqueous alcoholic potassium hydroxide with formation of pentamethylene oxide (compare Clarke, T., 1912, **101**, 1802). *η-Bromoheptyl benzoate* is an oil, b. p. 205—210°/11 mm., which does not solidify. With sodium iodide it yields *η-iodoheptyl benzoate*, pale yellow oil, b. p. 220—224°/11 mm.

(2) The observation that in phenoxypropylbromoamylcyanamide (A., 1909, i, 507) the phenoxy-group is replaced by bromine more readily than the nitrile group is saponified under the action of hydrobromic acid has led the author to examine the possibility of introducing two phenoxy-alkyl residues into sodium cyanamide (compare Traube and Engelhardt, A., 1911, i, 955) with the ultimate object of replacing the phenoxy-groups by bromine,

$$N(CN)[(CH_2)_xOPh]_2 \longrightarrow N(CN)[(CH_2)_xBr]_2,$$

and thus obtaining polymethylene dibromides in which one $-CH_2-$ group is replaced by $CN\cdot N<$.

γ-Phenoxypropyl iodide in alcoholic solution reacts readily with commercial sodium cyanide, yielding allyl phenyl ether and *diphenoxypropylcyanamide*, b. p. 295—300°/13 mm. The yield of the latter is nearly 60% of that theoretically possible. Fuming hydrobromic acid converts it into *dibromopropylcyanamide*, $CN\cdot N([CH_2]_3\cdot Br)_2$, a pale brown, heavy oil which is not volatile with steam, and cannot be distilled without decomposition. When dissolved in dry ether, it reacts readily with metallic sodium, yielding a product which is only partly volatile in a vacuum. The volatile portion, b. p. 110—120°/11 mm., was hydrolysed with hydrochloric acid, and identified as hexamethyleneimine; the non-volatile portion was not identified. Phenoxyethyl bromide scarcely reacts with sodium cyanamide, but the corresponding *iodide*, m. p. 31—32°, yields phenylvinyl ether and *diphenoxyethylcyanamide*, white leaflets, m. p. 96°. In this compound the cyano- and phenoxy-groups are more simultaneously affected by hydrobromic acid than is the case with diphenoxypropylcyanamide, so that an approximately pure *dibromide* could only be obtained in small quantity. From β-iodoethyl ethyl ether, $I\cdot[CH_2]_2\cdot O\cdot C_2H_5$, and sodium cyanamide, the corresponding unsaturated ether is produced, whilst

ϵ-iodoamyl phenyl ether gives a product which is decomposed during distillation into amylene phenyl ether, $CH_2:CH\cdot[CH_2]_3\cdot OPh$.

(3) When sodium cyanamide is boiled with an alcoholic solution of $\alpha:\epsilon$-pentamethylene dibromide, and the product treated with water, an oil is obtained which below 100°/12 mm. yields a small unsaturated fraction, at 110°/12 mm. gives a trace of 1-cyanopiperidine, and leaves a viscous, non-volatile oil. Similar results are obtained with $\alpha:\epsilon$-di-iodopentane and $\alpha:\delta$-di-iodobutane. From *o*-xylylene bromide and sodium cyanamide, a viscous product is obtained from which a small amount of a crystalline *product*, m. p. 235—236°, can be separated by methyl alcohol; the substance appears to be a polymeride of cyanodihydro*iso*indole.

(4) $\alpha:\eta$-Dibromoheptane forms with ethyl sodioacetoacetate an *oil*, which is decomposed on distillation, and on saponification yields *β:μ-diketotridecane*, $COMe\cdot[CH_2]_9\cdot COMe$, m. p. 72° (*semicarbazone*, m. p. 184°), together with nonanedicarboxylic acid and small quantities of the *keto-acid*, $COMe\cdot[CH_2]_9\cdot CO_2H$, m. p. 59—62°. The latter was not obtained in the pure state.

An attempt was made to synthesise suberone from $\alpha:\delta$-dibromobutane and ethyl acetonedicarboxylate. The desired substance was only obtained in very small quantity.

Attempts were further made to form cyclic compounds containing mercury, by the action of sodium amalgam on $\alpha:\delta$-di-iodobutane and $\alpha:\epsilon$-di-iodopentane respectively. The substances obtained were only partly volatile in a vacuum, and probably consisted of polymerides of the substances required. H. W.

Amino-alcohols. Derivatives of Phenyl Glyceryl Ethers. P. BRENANS (*Bull. Soc. chim.*, 1913, [iv], **13**, 525—535).—In continuation of the work of Fourneau (A., 1910, i, 246, 822), a number of new amino-alcohols of these types have been prepared with a view to the investigation of their therapeutic properties.

o-*Nitrophenoxypropanediol*, $NO_2\cdot C_6H_4\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$, m. p. 45°, results from the action of monochlorohydrin on *o*-nitrophenol in presence of potassium hydroxide; it crystallises in yellow spangles, and on reduction with tin and hydrochloric acid yields o-*aminophenoxypropanediol hydrochloride*, m. p. 170°, crystallising in silky needles; the free *base* is very soluble in water. o-*Nitrophenyl glycide ether*, $NO_2\cdot C_6H_4\cdot O\cdot CH_2\cdot CH{<}\overset{CH_2}{\underset{O}{|}}$, m. p. 51—52°, formed by the action of dichlorohydrin on *o*-nitrophenol in presence of alkali, crystallises in pale yellow needles. In this reaction some dinitrodiphenoxypropanol, m. p. 122° (compare Fourneau, *loc. cit.*), is formed.

p-*Nitrophenoxypropanediol*, m. p. 58°, prepared by the general method (above and *loc. cit.*), crystallises in slender, colourless needles, and on reduction furnishes the corresponding *amino*-compound, m. p. 133°, crystallising in ragged tablets and becoming brown in the light; the *hydrochloride*, m. p. 166°, forms colourless scales.

Tetranitrodiphenoxypropanol, $OH\cdot CH[\cdot CH_2\cdot O\cdot C_6H_3(NO_2)_2]_2$, m. p.

79°, obtained by the action of epichlorohydrin on the potassium derivative of 2 : 4-dinitrophenol, in presence of excess of alkali, or, better, on the silver derivative of the phenol, forms large, yellow-tinted crystals. On reduction with tin and hydrochloric acid, it yields the corresponding *tetra-amino*-compound *hydrochloride*, crystallising from methyl alcohol in small, yellow prisms and decomposing below 200° when heated.

o-*Nitro*-p-*tolyl glycide ether*, $NO_2\cdot C_7H_6O\cdot CH_2\cdot CH<\begin{matrix}CH_2\\ | \\ O\end{matrix}$, m. p. 66—67°, prepared by the action of dichlorohydrin on 2-nitro-*p*-cresol in presence of alkali, crystallises in bright yellow prisms. When heated with dimethylamine at 100° during ten hours, it yields γ-*dimethylamino*-α-2-*nitro*-p-*tolyloxypropanol*,

$$NO_2\cdot C_7H_6O\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot NMe_2,$$

as a thick, yellow oil, giving a crystalline *benzoyl* derivative, m. p. 179°.

o-*Iodophenoxypropanediol*, m. p. 95°, prepared from *o*-iodophenol by the general method, crystallises in silky, colourless needles. o-*Iodophenyl glycide ether*, b. p. 200—202°/20 mm., is a colourless liquid, which, with dimethylamine, yields γ-*dimethylamino*-α-o-*iodophenoxypropanol*, b. p. 210°/20 mm. (decomp.), as a colourless syrup from which the *benzoylated hydrochloride*, m. p. 169—170°, may be obtained as slender, prismatic needles.

5-*Iodoguaiacyloxypropanediol*, $OMe\cdot C_6H_3I\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$, m. p. 109°, crystallises in slender, colourless, odourless needles.

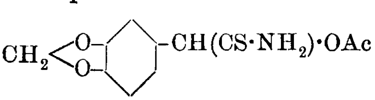
γ-*Dimethylamino*-α-o-*tolyloxypropanol*, b. p. 175—178°/28 mm., gives a benzoyl derivative, the *hydrochloride* of which has m. p. 138° and crystallises in colourless, silky needles.

p-*Nitrobenzoyl*-γ-*dimethylamino*-α-*thymoxypropanol hydrochloride*, m. p. 161°, crystallises in large, yellow, octahedra from a mixture of alcohol and ether; the meta-*isomeride*, m. p. 187°, forms small, hard prisms from alcohol.

m-*Tolyl glycide ether*, b. p. 136·5°/14 mm., on treatment with dimethylamine gives γ-*dimethylamino*-α-m-*tolyloxypropanol*, b. p. 178—180°/14 mm., as a colourless syrup; the *benzoylated hydrochloride*, m. p. 138—139°, crystallises in rectangular tablets from acetone.

T. A. H.

Preparation of Derivatives of Aldehydo- and Keto-cyanohydrins containing Sulphur. AUGUST ALBERT (D.R.-P. 259502).



—The crystalline *compound* (annexed formula), decomp. 145°, is obtained when a benzene solution of methylenedioxyacetylmandelonitrile, $CH_2<\begin{matrix}O\\O\end{matrix}>C_6H_3\cdot CH(CN)\cdot OAc$, is treated with alcoholic ammonia and the solution saturated at 0° with hydrogen sulphide; after some time the product separates in crystalline form.

The *compound* from benzoyl-*o*-nitromandelonitrile crystallises with 1 mol. of ethyl alcohol and decomposes at 160°. F. M. G. M.

Chloroquinolsulphonic Acids and Their Conversion into Chloro-*p*-benzoquinonesulphonic Acids. ALPHONSE SEYEWETZ and J. PARIS (*Bull. Soc. chim.*, 1913, [iv], **13**, 486—491. Compare A., 1911, i, 360; this vol., i, 492).—Part of this work has been described already (*loc. cit.*). Chloroquinol on sulphonation by the method already described (*loc. cit.*) yields *sodium chloroquinolsulphonate*,

$$C_6H_2Cl(OH)_2\cdot SO_3Na,$$

colourless leaflets, soluble in water, but not in alcohol, which acts as a photographic developer in presence of alkalis, and on oxidation by sodium dichromate and sulphuric acid yields *sodium chloro*-p-*benzoquinonesulphonate,* bright yellow needles, soluble in water but not in alcohol, which has oxidising properties, and in aqueous solution liberates iodine from iodides in presence of acids. T. A. H.

Unsaturated Compounds. Method of Reaction of Enols and Phenols. KURT H. MEYER and S. LENHARDT (*Annalen*, 1913, **398**, 66—82).—It has been shown (this vol., i, 704) that the enolic grouping represents one of the most reactive states in organic chemistry. The additive capacity of the double linking is enormously increased by the presence of the hydroxyl group, as is proved by comparative experiments on the rate of addition, of alcoholic bromine and of *p*-nitrobenzenediazonium hydroxide, to pairs of substances differing only by the one containing a hydroxyl group where the other contains a hydrogen atom, as, for example, styryl methyl ketone and benzoylacetone. The reactivity of the enolic grouping is not connected, as Hinsberg supposes, with the dissociability of the hydrogen atom, because alkyl ethers of enols, which do not contain the mobile hydrogen atom, are also extremely reactive.

Recent researches on the action of ozone, potassium permanganate, and hydrogen on benzene have shown that the latter behaves like a substance containing very slowly reacting ethylenic linkings. The comparatively great reactivity of phenol, therefore, is explicable as being due to the activating influence of the hydroxyl group on the double linking. This view is supported by the fact that phenolic ethers are almost as reactive as phenol itself. Phenol, anisole, resorcinol, resorcinol dimethyl ether, α-naphthol, α-naphthyl methyl ether, β-naphthol, β-naphthyl methyl ether, and anthranol each reacts instantly with alcoholic bromine at 0°. The preceding ethers with the exception of anisole react as readily as phenol with diazo-hydroxides; *benzeneazophloroglucinol trimethyl ether*, m. p. 82·5°, garnet-red crystals, easily soluble in dilute mineral acids, p-*nitrobenzeneazophloroglucinol trimethyl ether*, m. p. 150·5°, brown needles with violet lustre, p-*nitrobenzeneazoresorcinyl dimethyl ether*, m. p. 152°, red needles, and p-*nitrobenzeneazo-α-naphthyl methyl ether*, m. p. 169°, red needles, are described. α-Naphthyl methyl ether in glacial acetic acid reacts readily with nitrous acid, yielding nitroso-α-naphthol, methyl alcohol being eliminated.

It is probable that all substances containing the groups $\cdot CH\!:\!C\cdot OR$ or $\cdot CH\!:\!C\cdot NR$ contain an activated ethylenic linking. Examples of the latter kind are found in the reactivity of pyrroles with aldehydes, halogens, and diazo-compounds; 1 : 2-dimethylindole condenses with

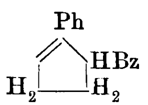
p-nitrobenzenediazonium hydroxide in glacial acetic acid to form a *substance*, $C_{16}H_{14}O_2N_4$, m. p. 204—205°, dark red crystals. C. S.

Aromatic Telluretine Compounds. II. KARL LEDERER (*Ber.*, 1913, **46**, 1810—1812. Compare this vol., i, 615).—The methyl, ethyl, and propyl esters of α-bromopropionic acid have been heated to 50° with diphenyl telluride and the telluretine compounds isolated with difficulty and in poor yields. *Methyl diphenyl-α-propionyltelluretine bromide* [*α-bromodiphenyltelluripropionate*], $TePh_2Br{\cdot}CHMe{\cdot}CO_2Me$, and the *ethyl* and *propyl* esters, and also *methyl diphenyl-α-*iso*butyryltelluretine bromide* [*α-bromodiphenyltelluri*iso*butyrate*],

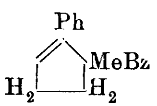
$$TePh_2Br{\cdot}CMe_2{\cdot}CO_2Me,$$

are white, amorphous substances with indefinite melting points.
J. C. W.

1-Benzoyl-2-phenyl-Δ²-*cyclo*pentene. ÉDOUARD BAUER (*Compt. rend.*, 1913, **156**, 1470—1472).—The conversion of αδ-dibenzoylbutane into the two cyclic compounds 1-benzoyl-2-phenyl-Δ^1-and-Δ^2-*cyclo*pentenes by the action of sodium ethoxide (compare A., 1912, i, 777) is equally well brought about by sodamide. 1-Benzoyl-2-phenyl-Δ^2-*cyclo*pentene, thus constituted, should behave as a dialkylacetophenone (compare Haller and Bauer, A., 1909, i, 108), and the author has now proved this to be the case. It reacts with sodamide in anhydrous benzene, giving a sodium derivative which, on the addition of methyl iodide, is converted into the the corresponding *1-benzoyl-2-phenyl-1-methyl-*Δ^2-cyclo*pentene* (formula II), b. p. 223—224°/23 mm., a viscid oil instantly decolorising potassium permanganate solution in the cold. This



(I.)



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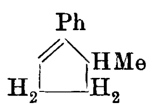

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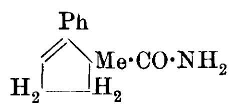


(IV.)

methyl derivative reacts further with sodamide (compare Haller and Bauer, *loc. cit.*) and is decomposed, giving a mixture of *2-phenyl-1-methyl-*Δ^2-cyclo*pentene* (formula III), b. p. 116—117°/20 mm., and benzamide on the one hand, and benzene and *2-phenyl-1-methyl-*Δ^2-cyclo*pentene-1-carboxylamide* (formula IV), m. p. 165°, on the other.
W. G.

1-Benzoyl-2-phenyl-Δ¹-*cyclo*pentene. ÉDOUARD BAUER (*Compt. rend.*, 1913, **156**, 1684—1686. Compare A., 1912, i, 777; preceding abstract).—Sodamide acts on 1-benzoyl-2-phenyl-Δ^1-*cyclo*pentene in the same manner as on benzophenone (compare A., 1908, i, 987), giving 2-phenyl-Δ^1-*cyclo*pentene-1-carboxylamide and benzene and 1-phenyl-Δ^1-*cyclo*pentene and benzamide.

On boiling 1-benzoyl-2-phenyl-Δ^1-*cyclo*pentene with sodamide in benzene a brick-red precipitate is obtained, which is decolorised on treatment with water. This product is separable by crystallisation from ether into benzamide and *2-phenyl-*Δ^1-cyclo*pentene-1-carboxylamide*, needles, m. p. 135—136°, which rapidly reduces alkaline permanganate

and decolorises bromine in chloroform. On hydrolysis with alcoholic potassium hydroxide it yields a mixture of two isomeric acids,

$C_{12}H_{12}O_2$,

separable by crystallisation from ether into 2-*phenyl*-Δ^1-cyclo*pentene-carboxylic acid*, m. p. 157°, and an *acid*, m. p. 124—125°, differing from the other only in the position of the ethenoid linking in the nucleus, and which gives the corresponding *amide*, m. p. 178—179°.

From the original benzene solution, after distilling off the solvent, there is obtained 1-*phenyl*-Δ^1-cyclo*pentene*, m. p. 23°, b. p. 120—121°/20 mm., D_4^{25} 0·98617, n_α^{25} 1·56723, n_D^{25} 1·5734, n_β^{25} 1·59017, which yields a *picrate*, m. p. 64·5°. On reduction by sodium in absolute alcohol it gives phenyl*cyclo*pentane. W. G.

Preparation of Nitriles from Thiocarbamides [and from Thiocarbimides]. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 259363, 259364).—It has been shown by Weith (A., 1875, 901, 908, 1241) that nitriles (in very small yield) can be obtained by the action of copper powder on thiocarbamides, and this reaction has now been carried out with cheaper material, such as iron, in the presence of machine or paraffin oils or anthracene.

o-Toluonitrile is obtained in 64% yield when a mixture of iron (20 parts) and paraffin (100 parts) is slowly treated at 280° with 10 parts of *o*-ditolylthiocarbamide. The preparation of the following compounds is also described: *m*-toluonitrile in 62% yield, *p*-toluonitrile in 75% yield, *β*-naphthonitrile in 75% yield, *m*-xylonitrile in 65% yield, *p*-methoxybenzonitrile in 67% yield, *p*-chlorobenzonitrile in 51% yield from *p*-dichlorophenylthiocarbamide, *p*-cyanoquinoline in 21% yield from *p*-diquinolylthiocarbamide, octonitrile in 61% yield from diheptylthiocarbamide, and phenylacetonitrile in 20% yield from dibenzylthiocarbamide.

The second patent describes the preparation of many of the preceding compounds by substituting the corresponding thiocarbimides for the thiocarbamides, the average yield of product being about the same.

F. M. G. M.

Polymerisation. ABRAHAM KRONSTEIN (*Ber.*, 1913, **46**, 1812—1814).—A claim for priority in the study of polymerisation from the chemical, physical, technical, and also physiological points of view (compare Liebermann and Kardos, this vol., i, 476). J. C. W.

Preparation of Diphenyleneacetic Acid (9-Fluorenecarboxylic Acid) from Benzilic Acid and Aluminium Chloride. DANIEL VORLÄNDER and ALFRED PRITZSCHE (*Ber.*, 1913, **46**, 1793—1796).—The fact that Vorländer and Huth assumed the formation of the unknown nitrile of benzilic acid as an intermediate stage in the condensation of benzoyl cyanide to 9-cyanofluorene (A., 1911, i, 867) has led to the study of benzilic acid itself, with the result that a good method for the preparation of 9-fluorenecarboxylic acid has been discovered. Triphenylacetic acid could not be detected in the product, and therefore diphenylchloroacetic acid cannot represent an intermediate stage. Carbon disulphide, or preferably benzene, may be used as a solvent, but they do not enter into the reaction. The fluorene-

carboxylic acid was characterised by conversion into the unstable chloride with thionyl chloride, then into the *amide*,

$$\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>CH \cdot CO \cdot NH_2,$$

microscopic needles, m. p. 250°, and finally into the nitrile (Wislicenus and Russ, A., 1910, i, 840).

Phenylglyoxylic acid also condenses with benzene in presence of aluminium chloride, forming benzilic acid, and subsequently the above 9-fluorenecarboxylic acid. Ethyl phenylglyoxylate gives the same result, whereas the action of magnesium phenyl bromide leads to the formation of ethyl benzilate and, with an excess, benzopinacone. In toluene solution, phenylglyoxylic acid condenses to p-*methylfluorenecarboxylic acid*, $C_{15}H_{12}O_2$, which has m. p. 210°, and yields p-*methylfluorene* in leaflets, m. p. 88°, on distillation with soda-lime.

The alkaline solution of the condensation product of diphenyleneglycollic acid and benzene has a violet fluorescence and contains a little 9-*phenylfluorenecarboxylic acid*, $C_{20}H_{14}O_2$, which crystallises in white needles, m. p. 183°, and is easily transformed into 9-phenylfluorene (Kliegl, A., 1905, i, 187). J. C. W.

Pimaric Acid. LEO A. TSCHUGAEV and P. TEEARU (*Ber.*, 1913, **46**, 1769—1774. Compare Vesterberg, A., 1886, 365, 1038; 1888, 249; 1906, i, 92; 1907, i, 213).—The authors confirm Vesterberg's conclusion that galipot must contain at least three acids. *d*-Pimaric acid has m. p. 211—212°, $[\alpha]_C$ +55·40°, $[\alpha]_D$ +72·52°, $[\alpha]_E$ +97·20°, $[\alpha]_F$ +123·0°, $[\alpha]_F/[\alpha]_C$ 2·20°. 2·129 Grams of acid are soluble in 100 grams of absolute methyl alcohol at 25°. The acid is monobasic. The sodium salt has $[\alpha]_C$ +30·12°, $[\alpha]_D$ +38·86°, $[\alpha]_E$ +52·42°, $[\alpha]_F$ +67·37°, $[\alpha]_F/[\alpha]_C$ 2·23° in methyl-alcoholic solution (c = 2·174). Methyl pimarate, m. p. 69°, obtained by the action of methyl sulphate on an aqueous alcoholic solution of sodium pimarate in the presence of an excess of sodium hydroxide or carbonate, has $[\alpha]_C$ +46·30°, $[\alpha]_D$ +60·45°, $[\alpha]_E$ +81·36°, $[\alpha]_F$ +102·7°, $[\alpha]_F/[\alpha]_C$ 2·22.

In the presence of spongy platinum, hydrogen converts *d*-pimaric acid into *dihydropimaric acid*, m. p. 240—241°; 100 grams of absolute methyl alcohol dissolve 0·478 gram acid. In ethyl alcoholic solution (c = 0·566) at 20° the latter has $[\alpha]_C$ +14·57°, $[\alpha]_D$ +19·43°, $[\alpha]_E$ +26·05°, $[\alpha]_F$ +37·53°, $[\alpha]_F/[\alpha]_C$ 2·57. It is monobasic, and forms salts closely resembling those of pimaric acid. The *sodium* salt has in methyl alcoholic solution (c = 3·568) at 20°, $[\alpha]_C$ +4·41°, $[\alpha]_D$ +5·46°, $[\alpha]_E$ +7·84°, $[\alpha]_F$ +11·14°, $[\alpha]_F/[\alpha]_C$ 2·56. The *ammonium* salt crystallises in long, thin needles.

The authors consider that pimaric acid is probably a tetracyclic compound with one double bond. H. W.

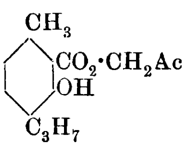
Preparation of Phenolcarboxylic Acids. JOSEPH ZELTNER and MAX LANDAU (D.R.-P. 258887. Compare A., 1876, ii, 632; 1877, i, 77; ii, 415).—The action of chloroform or carbon tetrachloride on phenols has been studied (*loc. cit.*), and the reaction is now found to proceed smoothly under atmospheric pressure in the presence of copper powder, or a salt of copper.

When phenol (9·4 parts), a 40% solution containing potassium hydroxide (39·2 parts), carbon tetrachloride (16 parts), and 0·3 part of copper, are boiled together during eight hours under reflux, it gives rise to a mixture of salicylic acid (25%) and *p*-hydroxybenzoic acid (30%).

The preparation of the following compounds is also described: 4-hydroxy-*m*-toluic acid, m. p. 146—147°, in 60% yield from *p*-cresol; an 80—85% yield of a mixture of 6- and 4-hydroxy-*m*-toluic acids from *o*-cresol. A 45% yield of 3-nitrosalicylic acid (compare Hasse, *loc. cit.*) from *o*-nitrophenol; and of 5-chlorosalicylic acid (in 75% yield) from *p*-chlorophenol. Guaiacol furnished vanillic acid, m. p. 207°, and quinol gave rise to gentisic acid. Salicylic acid gave a 70—75° yield of a mixture of phenol-2 : 4- and 2 : 6-dicarboxylic acids separable by means of their barium salts, whilst *m*-cresotic acid furnished α-coccinic acid (A., 1897, i, 539), and *o*-cresotic acid yielded 1-hydroxy-2-methylbenzene-4 : 6-dicarboxylic acid (α-hydroxyuvitic acid), m. p. 294—295°.

F. M. G. M.

Preparation of Acetylcarbinyl *o*-Thymotate. ADOLF DIEFENBACH and RICHARD ZAHN (D.R.-P. 258936).—The methyl and ethyl esters of *o*-thymotic acid are known (A., 1910, i, 38), and *acetylcarbinyl o-thymotate*, m. p. 75° (annexed formula), has now been prepared by the action of monochloroacetone on sodium *o*-thymotate.



F. M. G. M.

α-Hydroxy-γ-phenylcrotonic Acid; its Preparation; New Isomerisation. J. BOUGAULT (*Compt. rend.*, 1913, **156**, 1468—1470. Compare A., 1912, i, 770; this vol., i, 269).—α-Hydroxy-γ-phenylcrotonic acid is most readily prepared from its amide by choice of suitable hydrolysing agents, which will not bring about its isomerisation into benzylpyruvic or benzoylpropionic acids. Aqueous solutions of alkali carbonates or hydrogen carbonates boiled for thirty to forty minutes with the amide convert 30—40% into the acid required, with only a small admixture of its isomerides. As acid hydrolysing agents, the best are aqueous solutions of oxalic or phosphoric acids, oxalic acid (7½%) giving a yield of 80% of the acid required.

The author has isolated a new isomeride, m. p. 91°, which appears to be the *enolic* form of benzoylpropionic acid, and to have the constitution $C_6H_5·C(OH)⁚CH·CH_2·CO_2H$. It is readily converted by alkalis and strong acids into the ketonic form.

W. G.

Preparation of Halogen Alkyl Esters of *o*-Acetoxybenzoic Acid. RICHARD WOLFFENSTEIN (D.R.-P. 258888. Compare A., 1912, i, 556, 768).—The crystalline *ester*, $OAc·C_6H_4·CO·O·CHMe·CCl_3$, m. p. 52°, is obtained when *o*-acetoxybenzoyl chloride is heated with trichloro*iso*propyl alcohol in the presence of dimethylaniline, whilst the tribromo-*tert.*-butyl *o*-acetoxybenzoate, m. p. 90°, is prepared by the action of *o*-acetoxybenzoyl chloride on acetonebromoform [tribromo-*tert.*-butyl alcohol], $OH·CMe_2·CBr_3$, and the *compound* formed when the latter constituent is replaced by dichloro*iso*butyl alcohol is also mentioned.

F. M. G. M.

Benzoylcyanohydrins of Ketones, and Amides, and Hydroxy-acids Derived from Them. JULES ALOY and CHARLES RABAUT (*Compt. rend.*, 1913, **156**, 1547—1549. Compare A., 1912, i, 462).—Benzoylcyanohydrins can be readily obtained from ketones by the gradual addition of benzoyl chloride (1/10th mol.) to a solution of potassium cyanide (1/10th mol.) in 100 c.c. of water containing the ketone (1/10th mol.). The mixture is shaken for three hours and then extracted with ether, from which the cyanohydrin crystallises. They are, in general, quite crystalline and stable, and are hydrolysed by sulphuric acid, giving the corresponding benzoylamide, which is further hydrolysed by sodium hydroxide to benzoic acid and the hydroxy-acid.

Thus acetone gives *propylidenebenzoylcyanohydrin*, $OBz\cdot CMe_2\cdot CN$, m. p. 36—37°, yielding the *amide*, $OBz\cdot CMe_2\cdot CO\cdot NH_2$, m. p. 142—143°, which is hydrolysed to *α-hydroxy-α-methylpropionic acid*, m. p. 79°.

Methyl propyl ketone yields *β-amylidenebenzoylcyanohydrin*, a syrupy liquid, hydrolysing to the *benzoylamide*, m. p. 126°, which on further hydrolysis yields *α-hydroxy-α-methylvaleric acid*, $OH\cdot CPrMe\cdot CO_2H$, m. p. 46—47°.

Diethyl ketone gives a small yield of *γ-amylidenebenzoylcyanohydrin*, a liquid, which furnishes an *amide*, $OBz\cdot CEt_2\cdot CO\cdot NH_2$, m. p. 149—150°.

*cyclo*Hexanone gives cyclo*hexylidenebenzoylcyanohydrin*,

$$OBz\cdot C_6H_{10}\cdot CN,$$

m. p. 71°, yielding an *amide*, m. p. 118°, which is hydrolysed to *cyclo*hexanol-1-carboxylic acid.

3-Methyl*cyclo*hexanone gives a *benzoylcyanohydrin*, m. p. 125—126°, yielding the *amide*, m. p. 135—136°, which on hydrolysis gives 3-methyl*cyclo*hexanol-1-carboxylic acid.

4-Methyl*cyclo*hexanone is converted into the *benzoylcyanohydrin*, m. p. 86°, this giving an *amide*, m. p. 122°, which finally yields *4-methyl*cyclo*hexanol-1-carboxylic acid*, m. p. 80—81°. W. G.

The Action of Nitric Acid on the Dihydroxybenzoic Acids. FRANZ VON HEMMELMAYR (*Monatsh.*, 1913, **34**, 811—820).—Of the dihydroxybenzoic acids it is not the compound in which the carboxyl group is most firmly attached which can be nitrated most satisfactorily, but the important condition apparently is resistance to oxidation by the nitric acid; for example, β-resorcylic acid can be nitrated successfully, whilst gentisic acid, the nitro-derivative of which is much more stable, is for the greater part oxidised to oxalic acid. The author has therefore compared the behaviour of these acids towards nitric acid (D 1·4), and finds that the acids derived from catechol and quinol are oxidised almost entirely to oxalic acid. It is an interesting fact that those acids in which the meta-positions are unoccupied and in which at least one of these vacant positions is in a para-position to a hydroxy-group, more readily undergo nitration (compare von Hemmelmayr, this vol., i, 468).

3:4-Dihydroxybenzoic (protocatechuic) acid with the nitric acid alone or in acetic acid solution gave much oxalic acid, together with orange-red needles of a *substance*, $C_6O_{10}N_4$, possibly tetranitro-*o*-benzoquinone.

2 : 3-Dihydroxybenzoic acid gave a vigorous reaction with production of oxalic acid.

3 : 5-Dihydroxybenzoic (α-resorcylic) acid reacted vigorously, giving mainly oxalic acid together with a small quantity of an impure yellow, crystalline *substance*. By allowing the nitration to proceed in ethereal solution, the oxidising effect of nitric acid is diminished, and a *nitro-3 : 5-dihydroxybenzoic* acid, deep red needles, m. p. 210° (decomp.), could be isolated in small quantity.

2 : 6-Dihydroxybenzoic (γ-resorcylic) acid gave a vigorous reaction from the product of which a *trinitrohydroxybenzoic acid*, brownish-red, microscopic needles, decomp. at 240°, could be isolated.

2 : 5-Dihydroxybenzoic (gentisic) acid, when nitrated in cold ethereal solution, gave an approximately 30% yield of nitrogentisic acid (compare Klemenc, this vol., i, 49), which crystallises with $2H_2O$.

D. F. T.

Preparation of Anthraquinone-α-carboxylic Acids. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 259365. Compare A., 1911, i, 279; 1912, i, 979; this vol., i, 49).—1-*Chloroanthraquinone*-4-*carboxylic acid*, m. p. 229—230°, is prepared by heating together phthalic anhydride and *p*-chlorotoluene in nitrobenzene solution, and introducing chlorine at a temperature of 160—170°.

When phthalic anhydride and *m*-xylene are condensed in the presence of chlorine, they furnish 3-methylanthraquinone-1-carboxylic acid, m. p. 246—247°, and apparently identical with that previously prepared by Wachendorff and Zincke (A., 1878, 232), whilst oxidation of the sodium salt with potassium permanganate furnishes *anthraquinone*-1 : 3-*dicarboxylic acid*, m. p. above 300°. F. M. G. M.

Preparation of Phenylmethylphthalide. ALFONS OSTERSETZER (*Monatsh.*, 1913, **34**, 795—796).—From analogy to the behaviour of the *o*-aldehydic acids which yield alkyl substituted phthalides (Mermod and Simonis, 1908, i, 342; Simonis, Marben and Mermod, 1906, i, 32), it might be expected that *o*-ketonic acids when treated with a Grignard reagent should yield dialkyl substituted phthalides.

The reaction product of *o*-benzoylbenzoic acid and magnesium phenyl bromide is an oil, but magnesium methyl iodide gave phenylmethylphthalide, $C_6H_4<\begin{matrix}CMePh\\CO\end{matrix}>O$, leaflets, m. p. 76°; the intermediate hydroxy-acid could not be isolated. D. F. T.

The Action of Phthalylacyl Chlorides on Benzene and Aluminium Chloride. ERNST PFAEHLER (*Ber.*, 1913, **46**, 1700—1702).—Although phthalylphenylglycyl chloride (Pfaehler, this vol., i, 751) behaves similarly to phthalylglycyl chloride and the aliphatic homologues of this substance towards benzene and aluminium chloride, some of its higher homologues, such as phthaliminophenylpropionyl chloride, act in a different manner.

Phthaliminophenylpropionyl chloride,

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N\cdot CH(CH_2Ph)\cdot COCl,$$

m. p. 131—132°, was obtained from the corresponding *acid*, m. p. 176—177°, which is produced when phthalaminobenzylmalonic acid, m.p. 160—170° (compare Sörensen, A., 1903, i, 834), is heated. When warmed with an equimolecular quantity of aluminium chloride in benzene solution, 2-phthalimino-1-hydrindone,

$$C_6H_4{<}{\genfrac{}{}{0pt}{}{CO}{CO}}{>}N\cdot CH{<}{\genfrac{}{}{0pt}{}{CH_2}{CO}}{>}C_6H_4,$$

m. p. 191°, is obtained by intramolecular elimination of hydrogen chloride; it was not found possible to produce this substance by direct dehydration of the free acid. By heating the phthaliminohydrindone in acetic acid solution with fuming nitric acid at first in the open and afterwards in a sealed tube at 135°, the phthalyl nucleus is oxidised with the production of 2-amino-1-hydrindone hydrochloride,

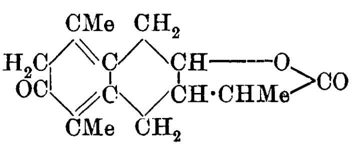
$$C_6H_4{<}{\genfrac{}{}{0pt}{}{CH_2}{CO}}{>}CH\cdot NH_2,HCl$$

(compare Gabriel and Stelzner, A., 1897, i, 61). D. F. T.

Hydrogenation of Santonic Acid. GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 507—510).—When sodium santonate is treated with hydrogen in presence of platinum-black until no more gas is absorbed, a *tetrahydrosantonic acid*, $C_{15}H_{24}O_4$, is formed; it crystallises in prisms or in leaflets, m. p. 190° (decomp.). The same tetrahydro-derivative was obtained in an experiment in which only one-fourth of the requisite amount of hydrogen was employed, and a corresponding quantity of santonate remained unaltered. In this experiment was also isolated a small quantity of a *substance*, which formed acicular prisms, m. p. about 99°, and gave a green fluorescence with alcoholic potassium hydroxide. This compound of m. p. 99° gives an *oxime*, which crystallises in lustrous needles, m. p. about 235°. Tetrahydrosantonic acid dissolves in carbonates in the cold, gives no coloration with alcoholic potassium hydroxide, and has no bitter taste. When treated with acids it loses water. It dissolves readily in concentrated hydrochloric acid; the solution becomes greenish-brown, and if left exposed to the air deposits a *substance*, which after recrystallisation forms large, colourless, prismatic crystals, m. p. 88°. This compound does not dissolve in carbonates in the cold, but when its alkaline solution (obtained in the warm) is acidified, an *acid* separates in laminar crystals, which at first have m. p. about 130°, but after exposure to the air acquire the m. p. of tetrahydrosantonic acid. The substance of m. p. 88° crystallises from light petroleum in laminæ or in prisms of m. p. 102°, and these are converted into tetrahydrosantonic acid by boiling with potassium hydroxide. Conversely, if tetrahydrosantonic acid is boiled with *N*-sulphuric acid the substance of m. p. 102° is obtained. Tetrahydrosantonic acid yields an *oxime*, which crystallises in colourless prisms, m. p. 222° (decomp.), and on boiling with dilute sulphuric acid yields the above-mentioned compound of m. p. 102°. When an acetic acid solution of the oxime is treated with nitrous acid, a crystalline *compound* of m. p. 130° is formed; it yields a blue coloration with a sulphuric acid solution of diphenylamine. On treatment with concentrated sulphuric acid the oxime is converted into a *substance* which crystallises in rectangular tablets,

m. p. 235° (not sharply); this compound does not dissolve in carbonates in the cold, and it reduces Fehling solution after hydrolysis with acid. The two oximes which have been mentioned can be obtained directly from the raw product of the hydrogenation, but together with them there is then observed a third *oxime*, which forms small, colourless needles, m. p. 240° (decomp.). From alkali solutions of this substance sulphuric acid precipitates a *compound*, crystallising in regular, hexagonal laminæ, m. p. 160—162°. R. V. S.

Hydrogenation of Santonin. YASUHIKO ASAHINA (*Ber.*, 1913, **46**, 1775—1777).—*Tetrahydrosantonin*, $C_{15}H_{22}O_3$, is formed by the action of hydrogen on a solution of santonin in glacial acetic acid in the presence of platinum-black. It consists of thin, white leaflets, m. p. 155—156°, $[\alpha]_D^{25}$ +60·56°, in chloroform solution. It yields a clear solution after protracted boiling with saturated aqueous barium hydroxide, from which the original substance is reprecipitated on acidification, and thus contains the lactonic group intact. In glacial acetic acid solution, it is stable towards permanganate. It yields an *oxime*, $C_{15}H_{23}NO_3$, m. p. 225°, $[\alpha]_D^{20}$ −17·78°, in chloroform solution.



The author is led to the conclusion that the annexed formula for santonin most readily harmonises with the above data. H. W.

Methylcarbonato-derivatives of Phenolcarboxylic Acids and their Use for Synthetic Operations. IX. Derivatives of Pyrogallolcarboxylic Acid. EMIL FISCHER and MAX RAPAPORT (*Sitzungsber. K. Akad. Wiss. Berlin*, 1913, 493—506).—When an excess of methyl chloro-formate is allowed to act on pyrogallolcarboxylic acid the trimethylcarbonato-compound is obtained. Phosphorus pentachloride converts it into the corresponding chloride, which crystallises from ether and has been used for the following synthetic operations.

Benzene and aluminium chloride convert it into a product yielding 2 : 3 : 4-trihydroxybenzophenone on hydrolysis, which is identical with the dye alizarin-yellow-A; the structure of this is thus established.

By interaction of the chloride in alkaline solution with *p*-hydroxybenzoic acid and subsequent elimination of the methylcarbonato-groups the didepside, *pyrogallolcarboyl*-p-*hydroxybenzoic acid*,

$$C_6H_2(OH)_3 \cdot CO \cdot O \cdot C_6H_4 \cdot CO_2H,$$

isomeric with galloyl-*p*-hydroxybenzoic acid is obtained.

The new term, carboyl, denoting the carboxylic acid radicle is derived in a similar way to benzoyl from benzoic acid—the radicle of pyrogallolcarboxylic acid is thus pyrogallolcarboyl.

When dextrose is shaken with the chloride and quinoline in chloroform solution, five trimethylcarbonatopyrogallolcarboyl residues are introduced into the sugar. On cautious hydrolysis a tannin is obtained isomeric with pentagalloyldextrose.

Trimethylcarbonatopyrogallolcarboxylic acid, $C_6H_2(O \cdot CO_2Me)_3 \cdot CO_2H$,

crystallises in tiny, colourless platelets, m. p. 122—124° (corr.). The pure acid gives hardly any coloration with ferric chloride.

The corresponding *chloride* crystallises in colourless, lancet-shaped needles, m. p. 67—68° (corr.).

The *methyl* ester, $C_6H_4(O{\cdot}CO_2Me)_3{\cdot}CO_2Me$, crystallises in microscopic, stout double pyramids, m. p. 82—84°, the homologous *ethyl* ester crystallises in tiny, oblique plates, m. p. 91—94° (corr.).

Trimethylcarbonatopyrogallolcarboyloxybenzoic acid,

$$C_6H_2(O{\cdot}CO_2Me)_3{\cdot}CO{\cdot}O{\cdot}C_6H_4{\cdot}CO_2H,$$

crystallises in slender, microscopic platelets, m. p. 198—199° (corr.). Ammonia converts it into *pyrogallolcarboyl*-p-*hydroxybenzoic acid*, $C_6H_2(OH)_3{\cdot}CO{\cdot}O{\cdot}C_6H_4{\cdot}CO_2H$. The didepside crystallises in very small, lustrous crystals aggregated in bunches, m. p. 235—238° (corr., decomp.). With ferric chloride a blue or bluish-violet coloration is produced.

Penta-[trimethylcarbonatopyrogallolcarboyl]-dextrose,

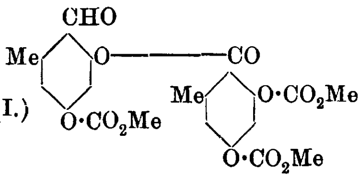
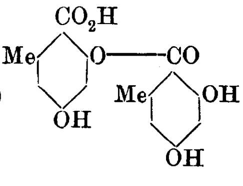
$$C_6H_7O_6[CO{\cdot}C_6H_2(O{\cdot}CO_2Me)_3]_5,$$

forms a colourless, amorphous powder which sinters at 100°, m. p. about 130°, $[\alpha]_D^{18}$ +27°.

Pentapyrogallolcarboylglucose forms also a colourless, amorphous powder, which sinters about 160°, m. p. 200° (decomp.), $[\alpha]_D^{18}$ +69·1°. It differs from tannic acid and pentagalloylglucose in being sparingly soluble in water. E. F. A.

Synthesis of *o*-Diorsellinic Acid. EMIL FISCHER and HERMANN O. L. FISCHER (*Sitzungsber. K. Akad. Wiss. Berlin*, 1913, 507—512).—Two didepsides are derived from orsellinic acid according as coupling takes place in the ortho- or para-positions. The product previously obtained (this vol., i, 477), identical with the natural lecanorcic acid, was considered to be the *p*-diorsellinic acid, and this is now confirmed by the synthesis of the ortho-isomeride.

Methylcarbonato-orcylaldehyde (Hoesch, this vol., i, 474) is readily coupled with dimethylcarbonato-orsellinyl chloride in alkaline solution, yielding the following compound (I). The corresponding acid is

(I.)  (II.) 

obtained on oxidation with permanganate, and it is converted into the *o*-diorsellinic acid on elimination of the methyl carbonato-groups by means of dilute ammonia. The *o*-diorsellinic acid (II) differs from lecanoric acid in solubility, melting point, and in its behaviour towards ferric chloride. It differs also from the gyrophoric acid described by Hesse (A., 1901, i, 151).

Trimethylcarbonato-orsellinoylorcylaldehyde crystallises in slender, pliable needles, m. p. 112—113° (corr.).

Trimethylcarbonato-o-*diorsellinic acid* separates in tiny, six-sided

platelets which sinter at 150°, m. p. 158° (corr., decomp.). With ferric chloride only a yellow coloration is obtained.

o-Diorsellinic acid (formula II) forms colourless, tiny needles much intergrown, but appears somewhat yellow in bulk. It has m. p. 120—125°, becomes solid, and melts again at 180—185°. E. F. A.

Angeli-Rimini Reaction of the Aldehydes. LUIGI BALBIANO (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 575—579).—Polemical. A reply to Angeli (A., 1912, i, 626). R. V. S.

Quantitative Investigation of the Photochemical Transformation of *o*-Nitrobenzaldehyde into *o*-Nitrosobenzoic Acid. ANTON KAILAN (*Ber.*, 1913, **46**, 1628—1634).—Polemical. The author maintains the sufficiency of his methods and the accuracy of the results obtained by him (this vol., i, 51) against the criticism of Weigert and Kummerer (this vol., ii, 370). R. V. S.

Some Derivatives of Methyl*cyclo*pentan-3-one. MARCEL GODCHOT and FÉLIX TABOURY (*Compt. rend.*, 1913, **156**, 1779—1781. Compare this vol., i, 278).—By the action of dry chlorine on methyl*cyclo*pentan-3-one in diffused light at a temperature below 25°, *2-chloromethyl*cyclo*pentan-3-one*, C_6H_9OCl, is obtained as a colourless oil, b. p. 80—82°/8 mm., D^{22} 1·128, n_D^{22} 1·465. On boiling this chloro-derivative with water it yields a mixture of *methyl*cyclo*pentan-2-ol-3-one*, b. p. 83—85°/12 mm., and *2-methyl-Δ^1-*cyclo*penten-5-one*, b. p. 50°/12 mm. The former of these compounds is a pale yellow, syrupy liquid, giving a violet coloration with ferric chloride, and yielding an unstable *phenylhydrazone*. On oxidation the ketone-alcohol is converted into α-methylglutaric acid. 2-Methyl-Δ^1-*cyclo*penten-5-one is a colourless liquid, having b. p. 157—158°, D^{26} 0·9712, n_D^{26} 1·4714. It is very soluble in water, and gives a *semicarbazone*, m. p. 230°, and an *oxime*, m. p. 127°. W. G.

Reduction of Ketones and Aldehydes to the Corresponding Hydrocarbons by means of Amalgamated Zinc and Hydrochloric Acid. ERIK CLEMMENSEN (*Ber.*, 1913, **46**, 1837—1843).—The application of amalgamated zinc has led to very good results in the reduction of fatty-aromatic ketones, and of aliphatic ketones and aldehydes to the corresponding hydrocarbons. In practice, an excess of granulated zinc is left for an hour with 5% mercuric chloride, drained, and then heated with the substance and concentrated hydrochloric acid under reflux, care being taken that the evolution of hydrogen is brisk enough to keep the two liquids well mixed.

By this means acetophenone gives ethylbenzene, or by using only the theoretical amount of acid, styrene. Propiophenone or phenylacetone give 90% yields of *n*-propylbenzene; butyrophenone or benzylacetone give 88—100% yields of *n*-butylbenzene, and methyl α-naphthyl ketone is reduced to α-ethylnaphthalene. Aromatic aldehydes are too susceptible to the action of mineral acids, but, notwithstanding, a 46%

yield of toluene was obtained from benzaldehyde. Heptaldehyde, however, gives a good yield of *n*-heptane. The following reductions of aliphatic ketones give almost theoretical yields; methyl *n*-nonyl ketone to *n*-undecane, methyl *n*-heptadecyl ketone to *n*-nonadecane, di-*n*-heptadecyl ketone (stearone) to *n*-pentatriacontane. The method is being extended to other classes of compounds. J. C. W.

Dynamic Isomerism. HENRY E. ARMSTRONG, THOMAS M. LOWRY, SIDNEY YOUNG, CECIL H. DESCH, JAMES J. DOBBIE, MARTIN O. FORSTER, and ARTHUR LAPWORTH (*Rep. Brit. Assoc.*, 1912, 115—116).—See Lowry and Glover, T., 1913, **103**, 913. C. H. D.

Synthesis of Violanthrone. CHRISTIAN SEER and ROLAND SCHOLL (*Annalen*, 1913, **398**, 82—96).—The constitution of violanthrone has been now proved, since the orientation of the benzoyl groups in the dibenzoyl-αα-dinaphthyl used in its synthesis (this vol., i, 59) has now been definitely settled.

αα-Naphthidine in 3% hydrochloric acid at 0° is treated with sodium nitrite, and the tetrazotised solution is filtered into aqueous potassium cyanide and copper sulphate at 60°, whereby 4 : 4′-*dicyano-α : α′-dinaphthyl*, m. p. 280—281°, pale yellow needles, is obtained. The latter is hydrolysed by alcoholic sodium hydroxide at 160—190°, and the resulting *αα-dinaphthyl-4 : 4′-dicarboxylic acid*, m. p. 349—350°, colourless crystals, is converted by phosphoric and phosphoryl chlorides into the acid *dichloride*, pale brown crystals, from which 4 : 4′-dibenzoyl-αα-dinaphthyl is obtained by means of aluminium chloride and benzene in nitrobenzene at 70—75°. 4 : 4′-Dibenzoyl-αα-dinaphthyl has now been prepared in orange-yellow needles, m. p. 146—147°; it is converted into violanthrone by aluminium chloride at 95—100° (*loc. cit.*).

By treatment with hydriodic acid, b. p. 127°, and red phosphorus at 190° for ten hours, violanthrone is converted into a substance which is apparently its parent hydrocarbon, *violanthrene*, $C_{34}H_{20}$; it is a dark powder which is not attacked by alkaline sodium hyposulphite, and forms in concentrated sulphuric acid a blue solution with a brown fluorescence.

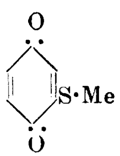
5-*Iodo*-1-*naphthoic acid*, m. p. 253—254°, colourless needles, prepared in the usual manner from 5-amino-1-naphthoic acid, forms a *methyl* ester, $C_{12}H_9O_2I$, m. p. 81—82°. By heating the latter with copper powder at 220—240° in a current of carbon dioxide, *methyl αα-dinaphthyl-5 : 5′-dicarboxylate*, $C_{24}H_{18}O_4$, m. p. 173—174°, faintly yellow needles, is obtained. The *acid*, $C_{22}H_{14}O_4$, m. p. 359—360°, microscopic needles, is converted into the crude *chloride*, m. p. about 150°, by phosphorus pentachloride, and the chloride is heated with aluminium chloride, benzene, and nitrobenzene at 70—80°, whereby 5 : 5′-*dibenzoyl-αα-dinaphthyl*, $C_{34}H_{22}O_2$, m. p. 248—250°, glistening leaflets, is obtained. By heating the latter with aluminium chloride at 145°, neither *Bz*-1 : 1′-dibenzanthronyl nor violanthrone is produced, but benzanthrone; whether this is present as such in the crude 5 : 5′-dibenzoyl-αα′-dinaphthyl or is produced during the reaction was not determined.

C. S

Conversion of 3-Dimethylaminophenyl Methyl Sulphide into 3-Methylthiol-*p*-benzoquinone. THEODOR ZINCKE and JOHANNES MÜLLER (*Ber.*, 1913, **46**, 1777—1781. Compare this vol., i, 355).—*3-Methylthiol-4-nitrosodimethylaniline hydrochloride* separates in red needles when a solution of sodium nitrite is added to a well-cooled solution of 3-dimethylaminophenyl methyl sulphide in hydrochloric acid. The free *base* is best obtained by addition of sodium acetate, and forms green needles melting at 143° to a deep blue liquid. When boiled with *N*-sodium hydroxide, it yields dimethylamine and *4-nitroso-3-methylthiolphenol*, yellow needles, m. p. 186°, which is converted by acetic anhydride and sodium acetate into the corresponding *acetyl* derivatives, yellow needles, m. p. 165°. *4-Amino-3-methylthiolphenol* is obtained by reduction of a boiling ammoniacal solution of 4-nitroso-3-methylthiolphenol by hydrogen sulphide, and, after purification by sublimation in a vacuum, forms nearly colourless needles, m. p. 154°, which readily oxidise on exposure to air. The *alkali* salts and the *hydrochloride* are readily soluble; the *sulphate* is more sparingly soluble. The *diacetyl* derivative forms small, white crystals, m. p. 100°, which contain ½ mol. acetic acid. When warmed with salicylaldehyde in alcoholic solution, the free base yields a *substance*,

$$C_{14}H_{13}O_2NS,$$

yellowish-brown needles, m. p. 134°.



3-Methylthiol-p-benzoquinone (annexed formula) is obtained by addition of dichromate solution to a solution of 4-amino-3-methylthiolphenol in dilute sulphuric acid and subsequent oxidation of the bluish-black *product* so obtained with nitric acid in acetic acid solution. An excess of nitric acid causes the elimination of the methylthiol group. It is therefore preferable to reduce the above quinhydrone to the quinol and oxidise the latter with dilute sulphuric acid and dichromate solution. 3-Methylthiol-*p*-benzoquinone forms red needles, m. p. 148°. Concentrated nitric acid (D 1·4) dissolves it without change; sulphurous acid reduces it to the corresponding quinol. When dissolved in chloroform and treated with chlorine, it gives tetrachloro-*p*-benzoquinone, whilst with aniline in hot glacial acetic acid solution it yields 2 : 5-dianilino-*p*-benzoquinone and methyl mercaptan.

3-Methylthiolquinol forms white needles, m. p. 83°, which are readily oxidised on exposure to air. With acetic anhydride and sodium acetate it yields a *diacetyl* compound, m. p. 101°. H. W.

2-Aminoanthraquinone. FRITZ ULLMANN and ROBERT MEDENWALD (*Ber.*, 1913, **46**, 1798—1809).—Two iminoanthraquinone nuclei have been linked together by an ethylene group, the sulphonic acid derived from aminoanthraquinone has been shown to be the 3-sulphonic acid, the preparation of the 1-nitro- and 3-nitro-2-aminoanthraquinones is described, and the condensation of 1 : 3-dibromo-2-aminoanthraquinone with bases has been studied.

Toluene-p-sulpho-2-anthraquinonylamide, $C_{14}H_7O_2 \cdot NH \cdot SO_2 \cdot C_7H_7$, from 2-aminoanthraquinone and *p*-toluenesulphonyl chloride in pyridine,

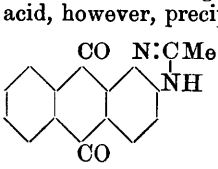
forms yellow needles, m. p. 304° (corr.), which give a red solution in hot alkalis or cold concentrated sulphuric acid. Excess of the sulphonyl chloride gives rise to the *disulphonamide*, $C_{28}H_{21}O_6NS_2$, in yellowish-brown crystals, m. p. 256° (corr.), whereas methyl sulphate yields *toluene*-p-*sulpho-2-anthraquinonylmethylamide* in yellow crystals, m. p. 195° (corr.), from which *2-methylaminoanthraquinone*, $C_{14}H_7O_2{\cdot}NHMe$, may be obtained in long, ruby-red needles, m. p. 226—227° (corr.), by warming with concentrated sulphuric acid. When condensed with ethylene dibromide in a sealed tube, the original sulphonamide yields *ethylenebistoluene*-p-*sulpho-2-anthraquinonylamide*, $C_{44}H_{32}O_8N_2S_2$, in yellow crystals, m. p. 301° (corr.), which on hydrolysis with concentrated sulphuric acid give *ethylenebis-2-aminoanthraquinone*,

$$C_6H_4{<}{}^{CO}_{CO}{>}C_6H_3{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}C_6H_3{<}{}^{CO}_{CO}{>}C_6H_4.$$

This forms small, orange-yellow crystals, m. p. 400°, and gives a red vat with sodium hyposulphite, cotton being dyed orange.

Fuming sulphuric acid (18—20% SO_3) converts 2-aminoanthraquinone into *2-aminoanthraquinone-3-sulphonic acid*, $C_{14}H_9O_5NS$, a faintly yellow powder, which forms a white sulphate by the addition of water to the red solution in concentrated sulphuric acid, and also a golden-yellow *sodium* salt. Its constitution is determined by the formation of Scholl's 1 : 3-dibromo-2-aminoanthraquinone [A., 1907, i, 541, m. p. 249·5° (corr.), and not 239°] under the influence of bromine water, and the transformation into 2-chloroanthraquinone by eliminating the amino-group and then replacing the sulphonic group through the medium of sodium chlorate and hydrochloric acid.

The chief product of the nitration of 2-acetylaminoanthraquinone is *1-nitro-2-acetylaminoanthraquinone*, $C_{16}H_{10}O_5N_2$, which forms long, silvery needles, m. p. 277—278° (corr.), and is hydrolysed by warm concentrated sulphuric acid to 1-nitro-2-aminoanthraquinone, m. p. 310° (corr.) (Terres, this vol., i, 738, gives m p. 267°). Bayer & Co. (A., 1906, i, 677) also obtained the latter compound by nitrating the carbamate of 2-aminoanthraquinone, m. p. 279—280°, and hydrolysing the carbamate of 1-nitro-2-aminoanthraquinone, m. p. 205°. The addition of glacial acetic acid to the solution in fuming nitric acid, however, precipitates the isomeric *carbamate* of *3-nitro-2-amino-anthraquinone*, $C_{17}H_{12}O_6N_2$, in faintly yellow needles, m. p. 225° (corr.), thus affording a means of obtaining 3-nitro-2-aminoanthraquinone (Scholl, A., 1905, i, 70). When the 1-nitroamine or the urethane is reduced with sodium sulphide, 1 : 2-diaminoanthraquinone is obtained, m. p. 303—304° (compare Terres, *loc. cit.*). Reduction of the acetylated base, however, gives rise to *2-methyl-a-anthraquinoneiminazole* (annexed formula). This crystallises in yellow leaflets, m. p. 326° (corr.), which form a colourless hydrochloride and an orange-red sodium salt.



1 : 3-Dibromo-2-aminoanthraquinone condenses with *p*-toluidine in presence of anhydrous potassium acetate to form *3-bromo-2-amino-1-toluidinoanthraquinone*, $C_{21}H_{15}O_2N_2Br$, in long, dark red, sparkling needles, m. p. 181° (corr.), which on oxidation with lead peroxide yields

3-*bromoanthraquinone*-1 : 2 : 1′ : 2′ : 4′-*methylphenazine*,

$$C_6H_4<{CO \atop CO}>C_6HBr<{N \atop N}>C_6H_3Me,$$

in pale brown needles, m. p. 247° (corr.). The dye gives a blue hyposulphite vat which colours cotton light blue, but the shade changes to pale yellow in the air. J. C. W.

Preparation of Nitroaminoanthraquinones. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 259432).—When the anthraquinonenitroamines (A., 1905, i, 447) are treated with mineral acids (such as hydrochloric or phosphoric) they are converted into nitroaminoanthraquinones; thus anthraquinone-1-nitroamine (*loc. cit.*) when left in contact with concentrated sulphuric acid for one hour furnishes a mixture of 1 : 2- and 1 : 4-nitroaminoanthraquinones.

Anthraquinone-2-nitroamine prepared by the action of sodium hypochlorite on anthraquinone-2-*iso*diazoxide yields 1-nitro-2-aminoanthraquinone (A., 1906, i, 677), and this on reduction (by ordinary methods) gives rise to 1 : 2-*diaminoanthraquinone*, m. p. 242—244°.

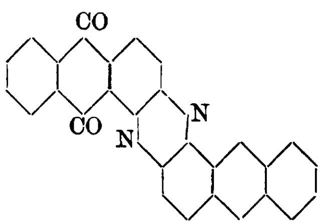
Anthraquinone-1 : 5-dinitroamine furnishes a mixture of 2 : 6-dinitro- and 4 : 8-dinitro-1 : 5-diaminoanthraquinones, whilst anthraquinone-2 : 6-dinitroamine gives rise to 1 : 5-*dinitro*-2 : 6-*diaminoanthraquinone*, brown crystals, m. p. over 300°, which on reduction yields 1 : 2 : 5 : 6-*tetra-aminoanthraquinone*. F. M. G. M.

1 : 2-Diaminoanthraquinone and a Synthesis from it of Indanthrene. ERNST TERRES (*Ber.*, 1913, **46**, 1634—1647).—Indanthrene can be obtained from 1 : 2-diaminoanthraquinone and 1 : 2-anthraquinone, and the author also describes other angular azines obtained by the interaction of 1 : 2-diaminoanthraquinone with diethyl oxalate, benzil, 1 : 2-naphthaquinone, and phenanthraquinone. The two last-named have already been obtained (Farbenfabriken vorm. Friedr. Bayer & Co., A., 1906, i, 905). The nomenclature employed is that proposed in a former paper (Bally and Scholl, *Ber.*, 1911, **44**, 1662). The paper also records a reducing action of potassium copper cyanide, which reacts with 2-methylanthraquinonyl-1-diazonium sulphate, yielding 2-methylanthraquinone. The nitrile simultaneously formed is removed by saponifying it to the corresponding acid, which is soluble in water.

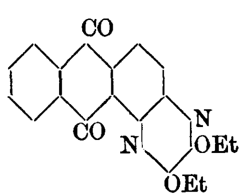
In order to exclude the formation of isomeric products, 1 : 2-diaminoanthraquinone was made (but with poor yield) by a new method, starting from 1-nitro-2-methylanthraquinone. Oxidation of this substance (best effected by concentrated nitric acid and chromic anhydride. Badische Anilin- & Soda-Fabrik, D.R.-P. 228394) yields 1-nitroanthraquinone-2-carboxylic acid, m. p. 283°. On treatment of this acid with sodium sulphide solution on the water-bath, 1-*amino-anthraquinone*-2-*carboxylic acid*, $C_{15}H_9O_4N$, is obtained; it forms brownish-red, shimmering needles, m. p. 286°. When 1-nitroanthraquinone-2-carboxylic acid is boiled for several hours with phosphorus pentachloride in benzene solution, the acid *chloride* (which crystallises in yellow needles) is produced, and if the reaction mixture is poured into cold alcoholic ammonia solution, the *amide*, $C_{15}H_8O_5N_2$, is

obtained; it forms yellow leaflets or large, almost colourless prisms, m. p. 299—301°. On reduction with ammonium sulphide, the amide yields 1-*aminoanthraquinone*-2-*carboxylamide*, $C_{15}H_{10}O_3N_2$, which crystallises in red needles, m. p. 279—281°. 2-Amino-1-nitroanthraquinone, m. p. 266—267° (Farbenfabriken vorm. Friedr. Bayer & Co., A., 1906, i, 677) can be obtained from 1-nitroanthraquinone-2-carboxylic acid by warming it with bromine, potassium hydroxide, and water, but it is necessary that the acid should be freshly precipitated (by pouring an acetic acid solution of it into water). 1 : 2-Diaminoanthraquinone is obtained by heating 2-amino-1-nitroanthraquinone with ammonium sulphide solution for five hours on the water-bath.

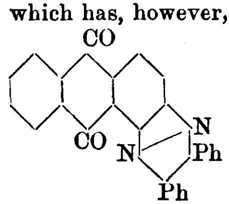
When a mixture of 1 : 2-diaminoanthraquinone and 1 : 2-anthraquinone in acetic acid is boiled, transbisangular *anthroanthraquinoneazine* (annexed formula) is rapidly deposited as a brownish-red, crystalline paste. It gives a dark green solution in cold, concentrated sulphuric acid, and from this solution water precipitates at first the dark blue sulphate. In concentrated nitric acid the substance dissolves, giving a bluish-green solution, which becomes blue and finally wine-red on warming. Alkali hyposulphite solution yields an insoluble, bluish-green vat salt. It is possible that the above product contains also the *cis*-isomeride. That the *trans*-form is present is shown by the fact that, by oxidation with chromic acid to anthraquinoneazine and reduction of the latter by means of boiling quinoline, indanthrene is obtainable, although only in very minute quantities and by working in very definite conditions.



Condensation of ethyl oxalate with 1 : 2-diaminoanthraquinone (by boiling in acetic acid solution) yields 2 : 3-*diethoxypyrazinoanthraquinone* (annexed formula), which crystallises in red needles, m. p. 276—277°. This azine gives a bright yellow solution in sulphuric acid. With hyposulphite solution it yields a red vat, which has, however, little affinity for unmordanted vegetable fibres.



Benzil yields by a similar condensation 2 : 3-*diphenylpyrazinoanthraquinone* (annexed formula), which forms yellow needles, m. p. 282—283°. Concentrated sulphuric acid dissolves the substance with production of a dark reddish-brown coloration. Alkali hyposulphite yields a bluish-black, insoluble vat salt.

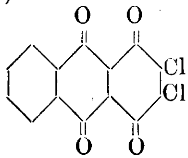
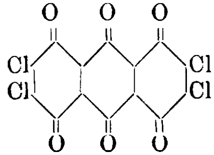


R. V. S.

Preparation of Anthraquinone Derivatives Containing Halogens. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 258556).—When 1 : 4-diamino- or 1-amino-4-hydroxy-anthraquinone is treated with chloric acid it furnishes a chlorinated quinone.

1 : 4-Diaminoanthraquinone (50 parts) dissolved in concentrated sulphuric acid (1000 parts) at 5° is slowly treated during about four hours with finely powdered potassium chlorate (250 parts); the *product*, a grey powder, crystallises from xylene, contains 23·1% of chlorine, and no nitrogen.

By modifying the reaction, a *compound* (I) having a higher chlorine content is obtained, and when diaminoanthrarufin (46 parts) with potassium chlorate (450 parts) is employed it gives rise to *tetrachlorotriquinone* (II):

(I.)  (II.) 

These compounds condense with aromatic amines (eliminating one atom of chlorine), furnishing dyes. F. M. G. M.

[Derivatives of] Some Aromatic Diketones. LUIGI ALESSANDRI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 517—519).—When phenanthraquinone is boiled with an ethereal solution of diazomethane until no more diazomethane remains, nitrogen is evolved, and a *substance*, $C_{15}H_{10}O_2$, is formed; it crystallises in thin, orange-yellow needles, m. p. 167°. The compound is stable towards permanganate. R. V. S.

The Aliphatic Sequiterpene-Alcohol, Farnesol. MAX KERSCHBAUM (*Ber.*, 1913, **46**, 1732—1737).—The author has investigated a number of derivatives of farnesol, an alcohol which is widely distributed in flower-blossom oils (compare A., 1904, i, 513; Soden and Treff, A., 1904, i, 439).

Farnesol, obtained from *Hibiscus Abelmoschus*, L., and purified by the phthalic ester method, has b. p. 160°/10 mm., D^{18} 0·885, n_D 1·48809, α_D ±0°. It may be preserved in closed vessels for years without alteration. Solid derivatives have not been obtained. The *acetate* has b. p. 169—170°/10 mm., and is practically odourless. When heated with potassium hydrogen sulphate at 160—170°, farnesol loses water, forming *farnesene*, a colourless, mobile oil, b. p. 129—132°/12 mm., D^{18} 0·877, n_D 1·49951, α_D ±0°. Oxidation of farnesol by means of chromic acid and dilute sulphuric acid leads to the formation of farnesaldehyde, which, after purification by means of the solid bisulphite *compound*, has b. p. 172—174°/14 mm., D^{18} 0·893, n_D 1·49951, α_D ±0°. The corresponding *semicarbazone*, leaflets, m. p. 133—135° after slight previous softening, is well adapted for the identification of farnesol.

Attempts to determine the constitution of farnesol by a study of the products of the action of potassium permanganate on it were not completely successful. Acetone was, however, isolated. When, however, *farnesaldoxime* was converted into the corresponding *nitrile* and the latter saponified by alcoholic sodium hydroxide, *farnesenic acid*, b. p. 202—206°/16 mm., acetic acid, and a ketone were obtained. The latter substance was identified as dihydro-ψ-ionone by

means of its semicarbazone. Since the constitution of the latter follows from its synthesis from geranyl chloride and ethyl sodioacetoacetate followed by saponification of the ethyl geranylacetoacetate by sodium hydroxide, the following formula is ascribed to farnesol: $CMe_2:CH\cdot[CH_2]_2\cdot CMe:CH\cdot[CH_2]_2\cdot CMe:CH\cdot CH_2\cdot OH$ (compare following abstract).

Dihydro-ψ-ionone is converted by methyl magnesium bromoacetate into a *methyl hydroxydihydrofarnesenate*, which, on prolonged heating with acetic anhydride and sodium acetate at 160—165°, loses water, and yields *methyl farnesenate*, b. p. 177—185°/10 mm. The corresponding free acid has a b. p. identical with that of the acid obtained from farnesol. Solid derivatives could not, however, be prepared.

Reduction of methyl farnesenate by sodium and absolute alcohol gives rise to a mixture of dihydro-ψ-ionol. dihydrofarnesol, and, probably, farnesol. The presence of the latter could not, however, be definitely established. H. W.

Farnesol. CARL HARRIES and REINHOLD HAARMANN (*Ber.*, 1913, **46**, 1737—1741).—A study of the action of ozone on farnesol has confirmed the formula ascribed to the latter by Kerschbaum (preceding abstract).

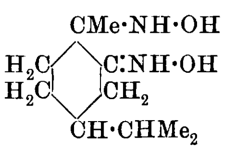
When farnesol is ozonised in hexane solution, a gelatinous *diozonide* is obtained, which, on further treatment with azone in chloroform solution, is transformed into the *triozonide*. The latter, when boiled with water, gave the tests for hydrogen peroxide, for the group $C\cdot CO\cdot C\cdot C\cdot CHO$ and for aldehydes, whilst acetone, formic and acetic acids, lævulinaldehyde, and lævulic acid were identified among the products formed.

The action of ozone on farnesene was also investigated, the latter substance having been obtained by the fractionation of a specimen of crude farnesol which had been preserved during several years and which had undergone decomposition to a considerable extent with elimination of water. In carbon tetrachloride solution, the hydrocarbon yields a stable, glassy *tetra-ozonide*, which is decomposed by boiling water with formation of lævulinaldehyde. The latter was identified by conversion into phenylmethyldihydropyridazine, m. p. 197° (Harries, A., 1898, i, 233). H. W.

Methylcamphoroxime, Methylcampholenonitrile, and Methylcampholenic Acid. ALBIN HALLER and ÉDOUARD BAUER (*Compt. rend.*, 1913, **156**, 1503—1506).—The mixture of methyl- and dimethyl-camphor obtained by the action of methyl iodide on sodium camphor (compare A., 1909, i, 594) can be separated by the action of hydroxylamine zinc chloride, the methylcamphor being converted into its oxime, m. p. 60°, b. p. 134—135°/11 mm., $[\alpha]_D^{22}$ +25·15° (compare Glover, T., 1908, **93**, 1285). It gives a *phenylurethane*, prismatic crystals, m. p. 112—113°, $[\alpha]_D^{22}$ +24·8°, and at the same time a small quantity of slender needles, m. p. 110—111°, which are inactive. The oxime is hydrolysed by hydrochloric acid into the nitrile, b. p. 105—106°/15 mm., $[\alpha]_D^{23}$ +45° (compare Glover, *loc. cit.*). In solution in alcohol it has $[\alpha]_D^{23}$ +53·9°. The nitrile is hydrolysed by

alcoholic potassium hydroxide to *methylcampholenamide*, m. p. 91—92°, which is completely inactive, and this in its turn is hydrolysed by more concentrated alkali to *methylcampholenic acid*, m. p. 30°, b. p. 153°/20 mm., which is also inactive. It is probable that the methylcampholenonitrile by reason of its optical activity is analogous to α-campholenonitrile, but in the course of hydrolysis undergoes transformation, its derivatives being of the β-type. W. G.

*iso*Nitroamines of the Terpenes. GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1913, [v], 22, i, 616—622. Compare Cusmano and Linari, A., 1912, i, 272).—*Carvomenthone-αβ-hydroxylamineoxime* (annexed formula) is obtained by the action of hydroxylamine on carvomenthone bisnitroso-chloride; it forms tufts of long, colourless needles, m. p. 118°. From the mother liquor the following substances can be isolated in small quantity: active carvotanacetoneoxime, oxytetrahydrocarvoneoxime, and two other *oximes* of m. p. 120° and 160° respectively. The hydroxylamineoxime reduces ammoniacal silver nitrate and Fehling solution. When treated with ferric salts, it yields an amorphous, yellow powder, which is soluble in ether and contains iron. This *substance* gives Liebermann's reaction, and when shaken in ethereal solution with concentrated hydrochloric acid, it loses its iron, and is converted into a blue *compound*. The hydroxylamineoxime yields a *benzylidene* derivative, $C_{17}H_{23}O_2N_2$, which crystallises in hard, colourless prisms, m. p. 141°. The p-*nitrobenzylidene* derivative is a yellow powder.



*Carvomenthone-αβ-*iso*nitroamineoxime*, $C_{10}H_{19}O_3N_3,H_2O$, obtained by the action of sodium nitrite on the hydrochloride of the hydroxylamineoxime above described, forms rectangular tablets, m. p. 64°. It gives blue colorations with sulphuric acid solutions of phenol and diphenylamine. The *ammonium* and *silver* salts were prepared. When the aqueous solution of the *potassium* salt is boiled, the active oxime of carvotanacetone is produced. The *iso*nitroamineoxime is fairly stable towards acids; after prolonged boiling with acetic acid or hydrochloric acid only small quantities of tanacetone are formed. When the *iso*nitroamineoxime is dissolved in the equimolecular quantity of potassium carbonate and the solution is placed over sulphuric acid, nitrous oxide is evolved, and the *salt* of oxycarvomenthoneoxime is produced. If this is decomposed with carbonic acid, the *oxime*, $C_{10}H_{18}O(NOH)$, is obtained in rhomboidal leaflets, m. p. 102°. On evaporating a solution of the oxime in ethyl nitrite the *pernitrosyl* compound is deposited as an oil, and this reacts with semicarbazide to form *oxycarvomenthonesemicarbazone*, m. p. 172°.

If concentrated methyl-alcoholic solutions of hydroxylamine and 8-*iso*nitroaminomenthone are mixed (being cooled meanwhile with ice and salt) the *hydroxylammonium* salt, $C_{10}H_{18}O_3N_2\cdot NH_2\cdot OH$, is precipitated in long, colourless needles, m. p. 68°. Acids decompose the salt in the cold, yielding the original *iso*nitroamine, whilst cold alkalis convert it into pulegone. The salt remains unaltered for a long time in the solid state, but in alcoholic or ethereal solution it is rapidly

transformed into *menthoneisonitroamineoxime*, $C_{10}H_{19}O_3N_3$, which forms large, prismatic crystals, m. p. 77°. This substance gives blue colorations with sulphuric acid solutions of diphenylamine and phenol. It is very stable towards heat, remaining unaltered for a long period at 150°. The *potassium* salt, $C_{10}H_{18}O_3N_3K,2H_2O$, explodes above 350°. The *sodium* salt, $C_{10}H_{18}O_3N_3Na,4H_2O$, has m. p. 66°, or when anhydrous, 220° (decomp.). The *ammonium* salt dissociates at about 100° into its components. R. V. S.

The Constituents of Ethereal Oils. Synthesis of the Diterpene, α-Camphorene, $C_{20}H_{32}$, and of the Sesquiterpene *cyclo*Isoprenemyrcene, $C_{15}H_{24}$. FRIEDRICH W. SEMMLER and K. G. JONAS (*Ber.*, 1913, **46**, 1566—1571. Compare Semmler and Rosenberg, this vol., i, 377).—Unsuccessful attempts have been made to synthesise α-camphorene from isoprene, and also by the addition of two isoprene radicles to limonene.

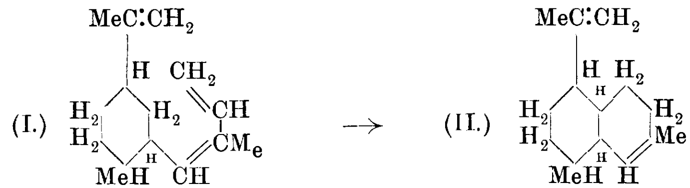
Myrcene was heated in a sealed tube at 250—260° for four hours, and the product subjected to fractional distillation, whereby a portion, b. p. 175—195°/8 mm., was obtained, analyses of which gave results agreeing with the formula $C_{20}H_{32}$. When a cooled, absolute ethereal solution of the product was saturated with dry hydrogen chloride, a crystalline product was obtained identical in all respects with α-camphorene tetrahydrochloride. Successive treatment with glacial acetic acid and sodium acetate, and with alcoholic potassium hydroxide, converted it into α-camphorene identical with the substance obtained from camphor oil of high boiling point, from which the tetrahydrochloride could be regenerated. The mother liquor obtained from the α-camphorene tetrahydrochloride, on treatment with glacial acetic acid and sodium acetate and, subsequently, with alcoholic potassium hydroxide, yielded other diterpenes which appeared to be bicyclic.

Since myrcene is a butadiene and undergoes condensation when heated, attempts were made to obtain a condensation product from myrcene and isoprene. When these substances were heated in a sealed tube for three and a-half hours at 225° and the product fractionated, the following fractions were obtained: (i) unchanged isoprene; (ii) b. p. 52—65°/8 mm., consisting of dipentene obtained partly from the condensation of two isoprene molecules, and partly by the isomerisation of myrcene; (iii) b. p. 120—150°/8 mm., which, on subsequent distillation, yielded cyclo*isoprenemyrcene*, b. p. 125—135°/8 mm., n_D 1·49166, $\alpha_D \pm 0°$, D^{18} 0·8685. The latter yielded a *trihydrochloride*, m. p. 83°, from which the hydrocarbon could be regenerated in the usual manner, and again converted into the hydrochloride; (iv) b. p. 175—195°/8 mm., n_D 1·5034, $\alpha_D \pm 0°$, D^{20} 0·8890, and (v) a considerable residue. H. W.

The Constituents of Essential Oils. The Constitution of Zingiberene. Transformation of the Monocyclic Zingiberene into the Bicyclic *iso*Zingiberene. FRIEDRICH W. SEMMLER and A. BECKER (*Ber.*, 1913, **46**, 1814—1822).—Of the naturally-occurring monocyclic sesquiterpenes, only limene and zingiberene have been studied. The former can be regenerated from its trihydrochloride, but

the latter gives a dihydrochloride which no longer yields the original oil with alkalis. The conclusion is therefore drawn that the hydrochloride contains a different ring system. In addition, the abnormal molecular refraction, 68·37 instead of 67·86, suggests that two of the three unsaturated linkings are adjacent in a side-chain.

Consequently, like myrcene, which has a similar structure and may be reduced to dihydromyrcene and readily transformed into cyclic terpenes, zingiberene (I) may be reduced to dihydrozingiberene and also converted into a dicyclic hydrocarbon. The latter is found to yield the above hydrochloride, from which it may be regenerated. It receives the name, *iso*zingiberene (II).



Finally, like other butadienes, zingiberene may be polymerised or condensed with isoprene.

The reduction of zingiberene (b. p. 128—129°/9 mm., D^{20} 0·8684, n_D 1·4956) by means of sodium and alcohol results in the formation of monocyclic *dihydrozingiberene*, $C_{15}H_{26}$, with b. p. 122—125°/7 mm., D^{20} 0·8557, n_D 1·4837, $[\alpha]_D$ −37°. The complete reduction with platinum and hydrogen yields monocyclic *hexahydrozingiberene*, $C_{15}H_{30}$, with b. p. 128—130°/11 mm., D^{20} 0·8264, n_D 1·4560, $[\alpha]_D$ −10°12′. The linking-up of the side-chain into a ring is effected by dissolving the zingiberene in glacial acetic acid containing a small amount of sulphuric acid, and agitating for some hours at 60—65°. iso*Zingiberene*, $C_{15}H_{24}$, yields the same chloride as zingiberene itself (Schreiner and Kremers, A., 1902, i, 108) and also a *dihydrobromide*, m. p. 175°, from which alcoholic potassium hydroxide regenerates the pure hydrocarbon, with b. p. 120—123°/8 mm., D^{20} 0·9150, n_D 1·5034, $[\alpha]_D$ −41°. Reduction with platinum and hydrogen converts the substance into *tetrahydro*iso*zingiberene*, $C_{15}H_{28}$, which is similar to other bicyclic tetrahydrosesquiterpenes, and has b. p. 123—123·5°/10 mm., D^{20} 0·8822, n_D 1·4791, and $[\alpha]_D$ +4°36′.

When heated with isoprene in a sealed tube, zingiberene gave a mixture which was fractionated, and found to contain *i*-limonene, a bicyclic, dextrorotatory, modified zingiberene, "meta-zingiberene," a diterpene from the condensation of isoprene with zingiberene, and dizingiberene. J. C. W.

[Essential Oils.] SCHIMMEL & Co. (*Semi-Annual Report*, April, 1913, pp. 20—153. Compare A., 1912, i, 880).—First runnings from the distillation waters of angelica contained methyl alcohol, ethyl alcohol, furfuraldehyde, diacetyl, and a base having an odour of pyridine.

Angostura bark (*Cusparia trifoliata*, Engl.) yielded 1·03% of oil, D_5^{15} 0·9285, α_D^{20} −7°32′, n_D^{20} 1·50744, of pale brown colour and having

acid number 1·8, ester number 5·5, acetyl ester number 35·7; the oil is not completely soluble even in 9 vols. of 90% alcohol.

Arnica root oil, D_{15}^{15} 0·984—1·00, α_D^{20} +0°25′—2°, n_D^{20} 1·507—1·508, had acid number 4 to 10, ester number 60 to 100, and gives a turbid solution with 7 to 12 vols. of 80% or 0·5 to 6·0 vols. of 90% alcohol. Arnica flower oil, D_{30}^{30} 0·8905 to 0·9029, acid number 62·6 to 127·3, ester number 22·7 to 32·2, is a buttery mass, m. p. 20—30° (approx.), and very sparingly soluble in alcohol.

Artemisia vulgaris, L., oil from India, had D_{15}^{15} 0·9219, α_D^{20} −8°52′, n_D^{20} 1·46201, acid number 1·2, ester number 22·1, acetyl ester number 55·5, and was soluble in 1 vol. of 80% alcohol, becoming turbid and depositing crystals of a solid paraffin on further dilution. The oil was of greenish-yellow colour and sage-like odour. It contains α-thujone, and possibly borneol.

Banana fruit oil according to Kleber (*Amer. Perf.*, 1912, **7**, 235) contains amyl acetate and traces of a phenol.

Borneo camphor oil, D_{15}^{15} 0·9180, α_D^{20} + 11°5′, n_D^{20} 1·48847, was of dark brown colour, soluble in 5 vols. or more of 90% alcohol, and had acid number 5·6, ester number 0, acetyl ester number 50·5. It contained *d*-α-pinene, β-pinene, dipentene, and camphene (35% of terpenes in all), borneol, and α-terpineol (10% together), sesquiterpenes 20%, and resin 35%.

The "Camphor leaf oil" (*Cinnamomum camphora*) described previously (A., 1905, i, 537) is now stated to be from the leaves of *Cinnamomum glanduliferum*, Meissn. It contains no camphor (compare Pickles, T., 1912, **101**, 1433). An oil from a hybrid between these two species deposited 58% camphor on freezing, and then had D_{15}^{15} 1·0465, α_D^{20} + 34°24′, acid number 1·0, ester number 23·3, acetyl ester number 46·2, and was soluble in 0·8 vol. of 80% alcohol. It still contained camphor, but no safrole could be detected.

Further investigation of Seychelles cinnamon bark oil (A., 1909, i, 112) shows that it contains the same constituents as Ceylon cinnamon bark oil.

The comparison of various methods for the estimation of geraniol and citronellal in citronella oils has been continued (A., 1912, i, 880). Kleber's phenylhydrazine process gives the following percentage values: *Java oil*, citronellal 35—41·3, geraniol 26·6—40·1; *Ceylon oil*, citronellal 7·5—11·6, and geraniol 29·6—34·4. Dupont and Labaune's method gives citronellal 35·4—46·3% and 6·5—8·0% for Java and Ceylon oils respectively. Kleber's phenylhydrazine process may also be used for cuminaldehyde, benzaldehyde, and methyl nonyl ketone; in the case of oil of bitter almonds only the free benzaldehyde reacts with phenylhydrazine. The process is being tried for the estimation of ketones in rue oil.

The two alcohols already noticed in cypress oil (A., 1904, i, 604) have been further examined: the chief constituent of the mixture is now shown to be 4-terpineol; the second alcohol, $C_{10}H_{18}O$, has D_{15}^{15} 0·9422, α_D^{20} +43°38′, n_D^{20} 1·46678, b. p. 76—77°/4—5 mm., and has a rose odour with a suggestion of borneol. The highest fractions of the oil contain in addition to cypress camphor and cadinene, a liquid

sesquiterpene *alcohol*, $C_{15}H_{26}O$, b. p. 136—138°/4—5 mm., which on treatment with formic acid yields a hydrocarbon.

Dipterocarpus turbinatus, Gaertn., oleo-resin yielded 46% of a pale yellow balsamic oil, D_{15}^{15} 0·9271, a_D^{20} $-37°$, n_D^{20} 1·50070, acid number 0, ester number 1·9, soluble in 7 vols. of 95% alcohol. *D. tuberculatus*, Roxb., oleo-resin gave 33% of a yellowish-brown oil, D_{15}^{15} 0·9001, a_D $-99°40'$, n_D^{20} 1·50070, soluble in 6 vols. of 95% alcohol. Both these oleo-resins and oils gave Turner's colour reaction.

Caryophyllene was detected in a French lavender oil.

Lemon-grass oils from Assam, Burma, Formosa, Celebes, and Mayotte are described: these are mostly of the "insoluble" type.

Mentha aquatica, L., herb yielded 0·8% of oil, D_{15}^{15} 0·9553, a_D^{20} $+64°56'$, n_D^{20} 1·48276, of pale yellow colour and having a faint odour of mint. *Mentha sylvestris*, L., herb gave 0·9% of similar oil, D_{15}^{15} 0·9852, a_D^{20} $-132°52'$, n_D^{20} 1·46856. *M. viridis* herb gave 0·17% of oil, D_{15}^{15} 0·9512, a_D^{20} $-52°5'$.

Mosla Japonica, Max., oil according to Nurayama and Nara (*J. pharm. Soc. Japan*, 1912) contains α-pinene (compare A., 1910, i, 328).

Ocotea pretiosa, Benth., bark gave 0·83% of a brown oil, D_{15}^{15} 1·1200, n_D^{20} 1·52712, soluble in 6·5 vols. of 88% alcohol, and having a cinnamon-like odour. The oil is nitrogenous, contains no cinnamaldehyde, but probably contains caryophyllene, phenols, and lactones.

d-Ethyl-*n*-amylcarbinol from Japanese peppermint oil (A., 1912, i, 370) yields a *benzoate*, D_{15}^{15} 0·9641, a_D^{20} $+5°58'$, n_D^{20} 1·48905, b. p. 126·5°/3 mm., which is viscous, colourless, and possesses a faint odour. The *acetate*, D_{15}^{15} 0·8693, a_D^{20} $-4°46'$, n_D^{20} 1·41535, b. p. 194—194·5°/760 mm., has a peculiar odour of fruit and roses. The inactive modification of the alcohol, D_{15}^{15} 0·8286, n_D^{20} 1·42785, b. p. 176—177·5°, has been synthesised by the action of magnesium ethyl iodide on *n*-hexaldehyde.

Rhus Cotinus, L., leaves and flowers yielded a very pale yellow oil, D_{15}^{15} 0·8710, a_D^{20} $+32°54'$, n_D^{20} 1·4887, acid number 0·9, ester number 20·4, soluble in 6 vols. 90% alcohol, and having an odour of terpenes, but slightly suggestive of neroli; it contained camphene, β-pinene (?), and limonene; no phellandrene or terpinene could be detected.

Amomum globosum fruits ("wild cardamoms") from Indo-China yielded 4% of a colourless oil, D_{15}^{15} 0·9455, a_D^{20} $+43°54'$, n_D^{20} 1·47141, acid number 0·8, ester number 128·4, insoluble in 10 vols. of 70% alcohol, but soluble in 1 vol. of 80% alcohol and having a strong odour of camphor.

Cherry stones when ground and left for several hours furnished, on steam distillation, 0·016% of an oil, D_{15}^{15} 1·0532, a_D^{20} 0°, n_D^{20} 1·53888, soluble in 2·5 vols. of 60% alcohol, having an odour similar to, but clearly different from, that of bitter almond oil, and containing 0·27% of hydrocyanic acid.

Fennel herb from Jersey yielded an oil, D_{15}^{15} 0·9561, a_D $+16°40'$, soluble in 5 vols. 80% alcohol. Its odour indicated that methylchavicole was the chief constituent, and that very little anethole was present.

Meum athamanticum, Jacq., herb from the Harz mountains yielded

0·88% of a deep reddish-brown oil, D_{15}^{15} 0·9053, n_D^{20} 1·50327, acid number 8·8, ester number 63·1, soluble in 3 vols. of 90% alcohol, which had a celery-like odour, and on keeping deposited crystals, m. p. 91° (guaiacol?)

The Report also contains a résumé of recent work on the chemistry, pharmacology, etc., of essential oils and their constituents.

T. A. H.

[Essential Oils.] Roure-Bertrand Fils (*Sci. Ind. Bull.*, 1912, [iii], **6**, 3—191; 1913, [iii], **7**, 3—147).—*Calamintha Nepeta*, Lk. and Hoff., grown in Sicily, yielded 0·1426% of a brown oil, D_{15}^{15} 0·9249, α_D +17°48′, acid number 1·4, saponification number 12·6, which has an odour of pennyroyal, is soluble in 0·5 or more vols. of 80% alcohol, contains 20% of pulegone and 14% of alcohols, with a considerable quantity of a second ketone (menthone?).

Lemon grass oils from Mayotte, distilled from *Cymbopogon citratus*, had D_{15}^{15} 0·8877—0·9072, α −0°4′—0°′6, aldehydes 75·5 to 78% and were insoluble in 90% alcohol.

Basil oils from Mayotte had D_{15}^{15} 0·9630—0·9677, α_D +0°56′—0°58′, acid number 0·7 to 1·4, saponification number 5·6 to 6·3, esters 1·9 to 2·2%, and were soluble in 3·0 to 3·2 or more vols. of 80% alcohol. These oils had an odour of anethole as well as of estragol.

[Justin Dupont and Louis Labaune.]—With a view to ascertaining the cause of the anomalous results obtained in estimating aldehydes in essential oils by means of sodium hydrogen sulphite solution, the authors have investigated the action of such solutions on a large number of common unsaturated constituents of essential oils and find that many of these are wholly or partly converted into hydrosulphonates when shaken for some time with aqueous solutions of sodium hydrogen sulphite. Among the unsaturated substances which do not react in this way are hydrocarbons (for example, *l*-pinene, limonene, and styrene), esters, ethers, *iso*eugenol, and ionones. The results with all the substances examined are tabulated in the original. The following were isolated, the *sodium hydrogen sulphite* compounds of *geraniol* $C_{10}H_{18}O,2NaHSO_3$; *linalool*, $C_{10}H_{18}O,2NaHSO_3$; *terpineol*, $C_{10}H_{18}O,NaHSO_3$; *methylheptenone*, $C_8H_{14}O,NaHSO_3$; they are all hygroscopic masses (compare Labbe, A., 1900, i, 149), and are stable, since they do not regenerate the original organic constituent on addition of alkali. In a second paper on the analysis of citronella oil the authors point out that in Boulez's method for the assay of this oil (A., 1912, ii, 1105; Schimmel & Co., A., 1912, i, 880), the results for citronellal are liable to be rendered inaccurate by the absorption of a larger or smaller portion of the geraniol in the hydrogen sulphite solution.

Both "Bulletins" contain summaries of work recently published on essential oils.

T. A. H.

Theory of the Vulcanisation of Caoutchouc. II. Gustav Bernstein (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 273—277. Compare A., 1912, ii, 1007).—A continuation of the discussion of the theory of vulcanisation. It is shown that before vulcanisation occurs

a depolymerisation of the caoutchouc must take place, and that at the same time a polymerisation of the sulphur occurs. These two changes are shown to take place under the same conditions, whether the vulcanisation is effected by heat or by ultra-violet light. It is stated that the absorption of sulphur begins only when it has been converted into the insoluble form. It is also stated that the physical properties of the vulcanised product depend on the condition of aggregation of the caoutchouc at the moment of the formation and absorption of the insoluble sulphur. J. F. S.

Biochemical Synthesis of Alkylglucosides (α-Glucosides) by means of a Ferment (α-Glucosidase) contained in Air-dried, Bottom Yeast: α-Propylglucoside and α-Allylglucoside. ÉMILE BOURQUELOT, HENRI HÉRISSEY, and MARC BRIDEL (*Compt. rend.*, 1913, **156**, 1493—1495; *J. Pharm. Chim.*, 1913, [vii], **7**, 525—529. Compare this vol., i, 323, 428).—*α-Propylglucoside*, crystallising in long needles, having a bitter taste, $[\alpha]_D$ $+140·8°$, and *α-allylglucoside*, colourless needles, m. p. 85—90°, $[\alpha]_D$ $+131·72°$, are obtained by the action of α-glucosidase on solutions of dextrose in water containing 15% of the respective alcohols. They are both very soluble in water, and are readily hydrolysed in aqueous solution by the above ferment. W. G.

Biochemical Synthesis, by means of Emulsin, of a Glucoside Isomeric with Salicin, β-Salicylglucoside. ÉMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1913, **156**, 1790—1792).—Emulsin acts on a solution of salicyl alcohol and dextrose in acetone, containing 20% water, giving *β-salicylglucoside*, which is finally obtained crystallising in long, colourless needles, $[\alpha]_D$ $-37·5°$, the melting point varying considerably with the rate of heating. It is odourless, but possesses a bitter taste and is soluble in water, crystallising with $4H_2O$. It reduces Fehling's solution and gives a violet colour with ferric chloride, which does not disappear on shaking with ether. The yield of glucoside varies with the dilution of the acetone and the amounts of alcohol and dextrose used, the presence of an excess of alcohol favouring the synthesis. The glucoside is readily hydrolysed in aqueous solution by emulsin. W. G.

Cerebrosides of the Brain. III. HANS THIERFELDER (*Zeitsch. physiol. Chem.*, 1913, **85**, 35—58. Compare Loening and Thierfelder A., 1911, i, 898; 1912, i, 372).—Prolonged treatment of cerebrone with barium hydroxide is shown not to produce any marked change. The cerebrone fraction is found to consist of a crystalline and an amorphous component which have the same composition and optical rotatory power, but differ in solubility. The name cerebrone is retained for the crystalline substance and that of phrenosin restricted to the amorphous form. In addition to the cerebrone fraction the use of a mixture of chloroform and methyl alcohol as solvent resolves the mixed cerebrosides into a very soluble fraction and a fraction of intermediate solubility to which the term kerasin is applied. Acid hydrolysis of

this fraction shows it to be broadly similar to cerebrone. It yields about 20% of galactose, some quantity of dimethylsphingosine as sulphate, and *kerasinic acid*, $C_{24}H_{48}O_2$, which crystallises in slender, long needles, m. p. 77—78°. E. F. A.

New Derivatives of Artemisin and Santonin. ENRICO RIMINI and TEMISTOCLE JONA (*Chem. Zentr.*, 1913, i, 1773; *from Rend. Soc. Chim. Ital.*, 1913, **5**, ii, 52—53. Compare Weinhaus and Oettingen, this vol., i, 474, and Wedekind and Beniers, this vol., i, 476).—These substances have been reduced by Paal's method. *Tetrahydroartemisin*, $C_{15}H_{22}O_4$, forms lustrous leaflets, m. p. 192—193°, and tetrahydrosantonin has m. p. 153—155°. Both compounds are stable towards permanganate. J. C. W.

"Tecomin." OTTO A. OESTERLE (*Arch. Pharm.*, 1913, **251**, 301—303).—The colouring matter described under this name by Lee (T., 1901, **79**, 284) as occurring in the wood of *Bignonia tecoma* (Ipé wood or Ipé-tabaco wood) is now shown to be lapachol. The latter also occurs in the timbers of *Tecoma Ipê*, Mart. (Ipé preto), and *Tecoma ochracea* (Ipé amarillo), but not in greenheart wood, derived from *Nectandra Rodiaei*. The usual source of lapachol is "Surinam greenheart" derived from *Bignonia leucoxylon* (compare Stein, *Jahresb.*, 1866, 651). T. A. H.

[Bibirubic Acid and Derived Substances.] HANS FISCHER (*Ber.*, 1913, **46**, 1574—1577. Compare Piloty, this vol., i, 500).—Polemical. In regard to disputed questions of nomenclature, the author's proposals are as follow: (1) the acid $C_{17}H_{24}O_8N_2$ (Fischer and Röse, A., 1912, i, 575) is bilirubic acid; (2) the acid $C_9H_{13}O_2N$ (Piloty and Thannhauser, A., 1912, i, 736) is *iso*phonopyrrolecarboxylic acid; (3) if, as is probable, xanthobilirubic acid is identical with Piloty's dehydrobilirubic acid (dehydrobilic acid, Piloty and Thannhauser, A., 1912, i, 925), then the latter name should be adopted. R. V. S.

Constitution of Lutein. CESARE SERONO (*Chem. Zentr.*, 1913, i, 1198; *from Arch. Farmacol. Sperim.*, 1912, **14**, 509—511. Compare A., 1911, ii, 1005).—The opinion expressed by Willstätter and Escher that lutein from the yolks of eggs is a xanthophyll (A., 1912, i, 125) cannot be reconciled with that of the author who believes it to be an ethereal combination of cholesterol with unsaturated fatty acids. J. C. W.

Angostura Alkaloids. Decomposition Experiments with Cusparine. JULIUS TRÖGER and W. BECK (*Arch. Pharm.*, 1913, **251**, 246—290. Compare A., 1912, i, 895).—Further analyses of cusparine and of its derivatives show that this alkaloid has the formula $C_{19}H_{17}O_3N$ (compare Körner and Böhringer, A., 1884, 341, and Tröger and Muller, A., 1910, i, 414). Further descriptions of the purification of this alkaloid and of the isolation of galipoidine and of a new alkaloid are given.

Cusparine, $C_{19}H_{17}O_3N$, appears to be trimorphic, since in addition

to the two forms already described (*loc. cit.*, and A., 1911, i, 482) a third crystallising in long, pale yellow needles, m. p. 91—92°, was obtained by slow crystallisation from light petroleum. The oxalate, $B,C_2H_2O_4,1\frac{1}{2}H_2O$, m. p. 140—150°, crystallises in sulphur-yellow needles from water and is efflorescent. The *succinate*, $B_2,C_4H_6O_4,4\frac{1}{2}H_2O$, m. p. 80°, crystallises in greenish-yellow needles, loses water on standing in a desiccator and becomes anhydrous and colourless when crystallised from alcohol and then melts at 113°. The *malate*, $B,C_4H_6O_5$, m. p. 152°, forms heavy, prismatic crystals from water. The *tartrate*, $B,C_4H_6O_6,1H_2O$, m. p. 161—162°, forms yellow, microscopic crystals from water. The *citrate*, $B,C_6H_8O_7$, m. p. 174° (decomp.), crystallises in long, sulphur-yellow, prismatic needles. All these organic salts on melting yield pyrocusparine, $C_{18}H_{15}O_3N$, m. p. 255°, which crystallises from alcohol in masses of slender, colourless needles (compare Beckurts and Frerichs, A., 1904, i, 84), and yields well-crystallised salts: *hydrochloride*, B,HCl, m. p. 207°, stellate groups of colourless needles; *platinichloride*, B_2,H_2PtCl_6, m. p. above 150° (decomp.), reddish-yellow, glancing needles. Cusparine methiodide, m. p. 190°, yellow prisms; *ethiodide*, m. p. 206—212°, yellowish-brown, prismatic crystals, and the n-*propyl iodide*, m. p. 187° (decomp.), yellow prisms, were prepared. These on treatment with silver hydroxide or potassium hydroxide do not yield as Beckurts supposed (A., 1896, i, 66) the corresponding alkylcusparines, but the same *isomeride* of cusparine, m. p. 194°, crystallising from alcohol in colourless, prismatic needles, containing water of crystallisation, which is lost at 105°. This substance yields a *platinichloride*, m. p. 185° (approx.), crystallising in microscopic needles and with nitric acid yields a *nitro*-compound, $C_{19}H_{16}O_5N_2$, m. p. 234—235°, which forms greenish-yellow crystals from alcohol. Cusparine is optically inactive, does not react with hydroxylamine, yields no definite products when treated with acids or alkalis in closed vessels at 100° and in common with pyrocusparine and "nitrocusparine" (Tröger and Runne, A., 1911, i, 482) contains no ·OH group. When heated for several days at 100° with nitric acid (D = 1·075), cusparine yields an *acid*, $C_{10}H_7O_3N,H_2O$, m. p. 271—272°, which is probably a hydroxyquinolinecarboxylic acid, since on heating at 300° it loses carbon dioxide and furnishes a *base* from which a *platinichloride*, $(C_9H_7ON)_2,H_2PtCl_6,2H_2O$, m. p. 220° (decomp.), forming yellowish-red crystals, was obtained. On distillation over zinc dust the acid yielded quinoline (identified by means of the platinichloride). On the basis of these results a skeleton-formula for cusparine is suggested.

When galipoidine is examined by Zeisel's method it yields less methyl iodide than is required for $\cdot OCH_3$ in the formula $C_{19}H_{15}O_4N$ (A., 1911, i, 482).

In the purification of cusparine a fourth *alkaloid*, $C_{16}H_{13}O_2N$ (?), m. p. 186°, crystallising from boiling alcohol in sulphur-yellow, rhombic crystals was obtained. T. A. H.

Carpiline or Pilosine. ÉMILE LÉGER and FERDINAND ROQUES (*Compt. rend.*, 1913, **156**, 1687—1689).—The two bases, one soluble and the other insoluble in water, obtained by heating carpiline with

water in a sealed tube at 140° for ten hours (compare this vol., i, 83), are shown to be identical with the pilosinine and anhydropilosine of Pyman (compare T., 1912, **101**, 2260). W. G.

Ephedrine. ERNST SCHMIDT (*Arch. Pharm.*, 1913, **251**, 320).—It is shown that the asymmetry of ephedrine and ψ-ephedrine cannot be solely dependent on the ·CH(OH)· group, since the conversion of this into a $\cdot CH_2\cdot$ group does not destroy the optical activity.

A *base*, $C_{10}H_{15}N$ (hydrochloride has $[\alpha]_D$ +19·14°), has been prepared by treating ephedrine hydrochloride with phosphorus pentabromide and reducing the *bromide*, $C_{10}H_{14}NBr,HBr$ (glistening leaflets), with zinc and hydrochloric acid. This bromide on treatment with silver nitrate does not regenerate ephedrine, but gives ψ-ephedrine, m. p. 117°, $[\alpha]_D$ +49·45° (compare A., 1912, i, 644). The optical activity of the base $C_{10}H_{15}N$ must be due to the ·CHNMe group (compare Emde, A., 1909, i, 77; Gadamer, *ibid.*, i, 49), which, moreover, cannot be situated at the end of the $\cdot C_3H_7$ chain. T. A. H.

The Homologues of Morphine, Codeine and Dionine, and Some of their Derivatives. FRIEDRICH FERREIN (*Chem. Zentr.*, 1913, i, 1696—1698).—Attempts have been made to prepare a hydroxycodeine by the elimination of the amino-group from amino-codeine and to obtain nitroethyl- and aminoethyl-morphine. Vongerichten and Weilinger (A., 1905, i, 542) obtained diacetylaminocodeine by the reduction of nitrocodeine with tin and acetic acid, whereas the *mono*-derivative, $C_{20}H_{24}O_4N_2$, has now been obtained by the same method. It yields a hydrochloride and a sulphate, and also *acetylamino-codeine methiodide*, $C_{21}H_{27}O_4N_2I$, as a white substance, m. p. 215—216°, which is converted into triacetylaminomethylmorphol (*ibid.*) on heating with acetic anhydride and silver acetate. When nitrocodeine is reduced by stannous chloride, however, the product is *aminocodeine*, $C_{18}H_{22}O_3N_2$, which forms pale yellow crystals, m. p. 224°, and gives what is probably a hydroxy-compound on diazotising and warming.

Ethylmorphine (dionine) has also been nitrated. *Nitroethylmorphine*, $C_{19}H_{22}O_5N_2$, forms yellow crystals, m. p. 166—167°; *aminoethyl-morphine*, obtained by reduction with stannous chloride, has m. p. 115—116°; *acetylaminoethylmorphine*, by reduction with tin and acetic acid, forms a pale yellow *hydrochloride*; and *diacetylaminoethyl-morphine*, $C_{23}H_{28}O_5N_2$, prepared by acetylating the amino-compound, has m. p. 156°.

All these substances give very similar reactions with formaldehyde-sulphuric acid, Froehde's and Erdmann's reagents. J. C. W.

Action of Acylamino-acid Chlorides on Ethyl and Methyl Sodiomalonate and Ethyl Sodiocyanoacetate. II. ERNST PFAEHLER (*Ber.*, 1913, **46**, 1702—1716. Compare this vol., i, 622).—A mixture of a benzene solution of phthalylglycyl chloride with ethyl sodiomalonate (compare Gabriel and Colman, A., 1909, i, 491) gives a clear liquid from which during several days there separates the sodium derivative of *ethyl* γ-*phthalimino*-β-*ketopropanedicarboxylate*,

$$C_6H_4{<}{\substack{CO\\CO}}{>}N\cdot CH_2\cdot CO\cdot CH(CO_2Et)_2,$$

prisms, m. p. 68—68·5°; this ester with an alcoholic solution of sodium ethoxide yields needles of the *sodium* derivative, whilst it dissolves in aqueous ammonia solution shortly depositing the *ammonium* derivative, decomp. at 210°, m. p. 255—260°; it has an acid reaction, and gives a deep red coloration with ferric chloride in alcoholic solution; in chloroform solution it reacts with bromine, forming a *bromo*-derivative, $C_{17}H_{16}O_7NBr$, needles, m. p. 122—122·5°, whilst the corresponding *chloro*-compound forms needles, m. p. 95—96°. The sodium derivative when boiled with water and the solution acidified yields phthalylglycine, whilst the ketonic acid is decomposed by boiling with concentrated hydrochloric acid with the production of aminoacetone hydrochloride. When heated for six hours at 185° with benzyl chloride, the sodium derivative is converted into *ethyl γ-phthalimino-β-keto-α-benzylpropanedicarboxylate*,

$$C_6H_4{<}{\substack{CO\\CO}}{>}N{\cdot}CH_2{\cdot}CO{\cdot}C(CH_2Ph)(CO_2Et)_2,$$

cubes, m. p. 98°. The free ester, ethyl phthalylglycylmalonate, when warmed with water at 100°, undergoes hydrolysis with subsequent loss of a molecule of carbon dioxide, giving rise to *ethyl γ-phthaliminoacetoacetate*, m. p. 110°; this gave a coloration with ferric chloride, but no metallic derivatives could be isolated; the *αα-dibromo*-derivative,

$$C_6H_4{<}{\substack{CO\\CO}}{>}N{\cdot}CH_2{\cdot}CO{\cdot}CBr_2{\cdot}CO_2Et,$$

m. p. 87—88°, was obtained by direct substitution in chloroform solution.

Phthalylglycyl chloride in benzene solution readily reacts with a bimolecular proportion of ethyl sodiocyanoacetate; the *sodium* derivative which separates, on treatment with hydrochloric acid, yields the free *ethyl γ-phthalimino-α-cyano-β-keto-*n*-butyrate*,

$$C_6H_4{<}{\substack{CO\\CO}}{>}NH{\cdot}CH_2{\cdot}CO{\cdot}CH(CN){\cdot}CO_2Et,$$

needles, m. p. 148—149°; on boiling with water, this substance undergoes considerable change, and after a few hours pure phthalic acid is obtained.

The clear liquid, obtained by mixing ethyl sodiomalonate and phthalyl-β-alanyl chloride in benzene slowly deposits the *sodium* derivative of *ethyl δ-phthalimino-β-ketobutanedicarboxylate*,

$$C_6H_4{<}{\substack{CO\\CO}}{>}NH{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH(CO_2Et)_2;$$

the free ester, needles, m. p. 68—69°, can be liberated by hydrochloric acid; it is a strongly acidic substance, which with ferric chloride gives a red coloration, and when boiled with water yields ethyl δ-phthalimino-β-keto-*n*-valerate, m. p. 121—122°.

Phthalylphenylglycyl chloride, m. p. 141—143°, was prepared by treating the acid with phosphorus pentachloride; its interaction with ethyl sodiomalonate yielded the *sodium* derivative of *ethyl γ-phthalimino-β-keto-γ-phenylpropanedicarboxylate*,

$$C_6H_4{<}{\substack{CO\\CO}}{>}N{\cdot}CHPh{\cdot}CO{\cdot}CH(CO_2Et)_2;$$

the free ester, leaflets and prisms, m. p. 104—105°, is acid in reaction,

and gives a red colour with ferric chloride; when boiled with a mixture of concentrated hydrochloric acid and acetic acid it undergoes scission, producing α-aminobenzyl methyl ketone.

α-Phthalimino-α-ethyl-n-butyryl chloride and ethyl sodiomalonate give as reaction product the yellow *sodium* salt of *ethyl γ-phthalimino-β-keto-γ-ethyl*-n-*pentanedicarboxylate*,

$$C_6H_4{<}^{CO}_{CO}{>}N\cdot CEt_2\cdot CO\cdot CH\cdot(CO_2Et)_2;$$

the free ester, prisms, m. p. 72—73°, gives the ferric chloride reaction, but is not appreciably acidic; unlike the esters described above, when warmed with sodium ethoxide, it undergoes rearrangement, yielding an acid *substance*, which from analogy with the corresponding *gem*-dimethyl compound (Pfaehler, *loc. cit.*) is probably a pyrrolidone derivative of the structure $CO_2Et\cdot C_6H_4\cdot CO\cdot N{<}^{CO-CH\cdot CO_2Et}_{CEt_2\cdot CO}$. In the original preparation, involving the acid chloride and ethyl sodiomalonate, the sodium derivative produced is accompanied by a substance, cubical crystals, m. p. 229—230°, insoluble in water, which proves to be *α-phthalimino-α-ethyl*-n-*butyric anhydride*, a remarkably stable substance, which is not affected by phosphorus pentachloride or boiling water or alcohol. Another by-product occurring in smaller quantity is *ethyl benzoylenediethylpyrrolonecarboxylate*, $\begin{matrix}C_6H_4\cdot C\colon C(CO_2Et)\\ CO-N\text{———}CEt_2\end{matrix}{>}CO$, a lemon-yellow substance, m. p. 85—85·5°, which is obtained in larger quantity if the reaction mixture is kept for a longer time under benzene containing an additional quantity of ethyl sodiomalonate. The normal ester, m. p. 72—73°, when boiled for thirty minutes with hydriodic acid (b. p. 127°) undergoes scission, yielding *methyl α-amino-α-ethyl*-n-*propyl ketone hydriodide*, short, columnar crystals, m. p. 184—186°; *hydrochloride*, silky needles, m. p. 236—236·5°; *platinichloride*, lemon-yellow needles, m. p. 188° (decomp.); *picrate*, yellow needles, m. p. 166°; *benzoyl* derivative, needles, m. p. 80—81°; the free base has an odour resembling that of turpentine.

Methyl sodiomalonate behaves like the corresponding ethyl compound towards phthaliminoethylbutyryl chloride, producing as by-product the same acid anhydride as mentioned above, together with the *sodium* derivative of *methyl γ-phthalimino-β-keto-γ-ethyl*-n-*pentanedicarboxylate* as main product; the free ester, prisms, m. p. 97—98°, is neutral, but gives the ferric chloride reaction; with sodium ethoxide it shows the same behaviour as the ethyl ester, whilst its sodium derivative when heated with methyl iodide in acetone solution is converted into *methyl δ-phthalimino-γ-keto-γ-ethyl*-n-*hexane-$\beta\beta$-dicarboxylate*,

$$C_6H_4{<}^{CO}_{CO}{>}N\cdot CEt_2\cdot CO\cdot CMe(CO_2Me)_2,$$

needles, m. p. 113—114°, which gives no ferric chloride reaction. Again, like the ethyl ester, the methyl ester in benzene solution is converted by the action of methyl sodiomalonate into *methyl benzoylenediethylpyrrolonecarboxylate*, lemon-yellow needles, m. p. 109—110°; this and also the corresponding ethyl ester are converted by hydrobromic acid into

diethylpyrrolonebenzo acid hydrobromide, yellow cubes, m. p. 214° (decomp.), which by the action of water or alkali yields *diethylpyrrolonebenzoic acid*, $\begin{matrix}CEt_2\cdot NH \\ | \\ CO\text{---}CH\end{matrix}\!\!>\!C\cdot C_6H_4\cdot CO_2H$, prisms and leaflets, m. p. 184·5—185° (decomp.); this on heating to 200° passes into the corresponding *lactam* (*benzoylenediethylpyrrolone*), $\begin{matrix}C_6H_4\cdot C{=}CH \\ | \quad\quad | \\ CO\text{---}N\text{-}CEt_2\end{matrix}\!\!>\!CO$, colourless needles, m. p. 71°.

α-Phthalimino-α-methyl-*n*-butyryl chloride in a similar manner with ethyl sodiomalonate gives the corresponding *phthaliminomethylbutyric anhydride*, cubes, m. p. 183°, insoluble in water, together with the expected sodium derivative, from which carbon dioxide liberates *ethyl γ-phthalimino-β-keto-γ-methyl*-n-*pentanedicarboxylate*,

$$C_6H_4{<}^{CO}_{CO}{>}N\cdot CMeEt\cdot CO\cdot CH\cdot(CO_2Et)_2\,;$$

this is a neutral oil which gives an intense coloration with ferric chloride. When this substance is heated in alcoholic solution with sodium ethoxide, or its sodium derivative heated in alcohol, a soluble sodium salt is produced, from which hydrochloric acid frees an isomeric *pyrrolidine derivative*, $\begin{matrix}CH(CO_2Et)\cdot CO \\ | \\ CO\text{------}CMeEt\end{matrix}\!\!>\!N\cdot CO\cdot C_6H_4\cdot CO_2Et$, m. p. 110°, which on heating with dilute acid is converted into *carbethoxybenzoylmethylethyltetramic acid* [*ethyl* 3 : 5-*diketo*-1-*benzoyl*-2-*methyl*-2-*ethylpyrrolidine*-o-*carboxylate*], $\begin{matrix}CH_2\text{---}CO \\ | \\ CO\cdot CMeEt\end{matrix}\!\!>\!N\cdot CO\cdot C_6H_4\cdot CO_2Et$, an acidic substance, m. p. 186—187°. The application of sodium methoxide to the same oily ethyl ester, or of methyl alcohol to its sodium derivative in a similar manner, causes a replacement of ethyl by methyl, the pyrrolidine *derivative*, prisms, m. p. 139—140°, produced being of the structure $\begin{matrix}CH(CO_2Et)\cdot CO \\ | \\ CO\text{------}CMeEt\end{matrix}\!\!>\!N\cdot CO\cdot C_6H_4\cdot CO_2Me$; the acidity of this substance is sufficient to cause its aqueous solution when heated to eliminate the carbethoxy-group with formation of *methyl* 3 : 5-*diketo*-1-*benzoyl*-2-*methyl*-2-*ethylpyrrolidine*-o-*carboxylate*,

$$\begin{matrix}CH_2\text{------}CO \\ | \\ CO\text{--}CMeEt\end{matrix}\!\!>\!N\cdot CO\cdot C_6H_4\cdot CO_2Me,$$

m. p. 209°, which reacts with bromine in chloroform solution, giving a neutral *dibromo*-derivative, m. p. 166—167°, by displacement of the methylene hydrogen atoms in the ring.

α-Phthalimino-α-methyl-*n*-butyryl chloride reacts with methyl sodiomalonate, yielding needles or prisms of *methyl γ-phthalimino-β-keto-γ-methyl*-n-*pentanedicarboxylate*, m. p. 98—99°, which colours ferric chloride blood-red. This substance with sodium ethoxide undergoes rearrangement into a pyrrolidine *compound*,

$$\begin{matrix}CH(CO_2Me)\cdot CO \\ | \\ CO\text{------}CMeEt\end{matrix}\!\!>\!N\cdot CO\cdot C_6H_4\cdot CO_2Et,$$

needles, m. p. 108—109° (of which an isomeride, m. p. 139—140°, has been described above), which when boiled with water yields the

pyrrolidine derivative, m. p. 186—187°, described earlier. Sodium methoxide on the other hand yields a *compound*,

$$\left.\begin{matrix}CH(CO_2Me)\cdot CO\\ CO\text{———}CMeEt\end{matrix}\right>N\cdot CO\cdot C_6H_4\cdot CO_2Me,$$

prisms, m. p. 146—147°, which is more acid in character than acetic acid, and which easily loses the carbomethoxy-group, producing the pyrrolidine derivative, m. p. 209°.

The action of ethyl sodiocyanoacetate on α-phthalimino-α-methyl-*n*-butyryl chloride gives a yellow *sodium* derivative, from which acetic acid liberates *ethyl γ-phthalimino-α-cyano-β-keto-γ-methyl*-n-*hexoate*,

$$C_6H_4{<}\substack{CO\\CO}{>}N\cdot CMeEt\cdot CO\cdot CH(CN)\cdot CO_2Et,$$

m. p. 140°; this loses carbon dioxide when boiled with water, but the decomposition is not a simple one.

The pyrrolone condensation observed with phthaliminoethyl-*n*-butyryl chloride and excess of ethyl or methyl sodiomalonate occurs under the same conditions with the phthaliminomethylbutyryl compounds. *Methyl benzoylenemethylethylpyrrolonecarboxylate*, $\left.\begin{matrix}C_6H_4\cdot C{=}C(CO_2Me)\\ CO\text{—}N\text{———}CMeEt\end{matrix}\right>CO$, forms yellow prisms, m. p. 130—131°; the corresponding yellow *ethyl* ester forms prisms, m. p. 112°. Both these esters react with hydrobromic acid, D 1·48, producing *methylethylpyrrolonebenzoic acid hydrobromide*, yellow needles, from which alkali in theoretical quantity separates the free *acid*, $\left.\begin{matrix}CO\text{———}CH\\ CMeEt\cdot NH\end{matrix}\right>C\cdot C_6H_4\cdot CO_2H$, prisms, m. p. 177° (decomp.), which above its m. p. passes into *benzoylenemethylethylpyrrolone*, $\left.\begin{matrix}C_6H_4\cdot C{=\!=}CH\\ CO\text{—}N\cdot CMeEt\end{matrix}\right>CO$, needles, m. p. 94—95°.

If methyl γ-phthalimino-β-keto-γ-methyl-*n*-pentanedicarboxylate is submitted to the action of methyl iodide in boiling acetone solution it is methylated to *methyl δ-phthalimino-γ-ketomethyl*-n-*hexane-ββ-dicarboxylate*, $C_6H_4{<}\substack{CO\\CO}{>}N\cdot CMeEt\cdot CO\cdot CMe(CO_2Me)_2$, prisms, m. p. 104°; this substance, which gives no ferric chloride reaction, is converted by boiling hydrochloric acid into oily *γ-amino-γ-methylhexan-δ-one*,

$$NH_2\cdot CMeEt\cdot COEt,$$

hydrochloride, crystalline; *picrate*, leaflets, m. p. 147—148°. D. F. T.

3-Nitropyridine and some of its Reduction Products. Franz Friedl (*Monatsh.*, 1913, **34**, 759—767).—The nitration of pyridine (A., 1912, i, 299) is most conveniently effected by the gradual addition of a solution of potassium nitrate in nitric acid (D 1·5) to a mixture of pyridine with an excess of sulphuric acid at 290—300°. It has already been shown that the product, 3-nitropyridine, is convertible by energetic reduction in acid solution into 3-aminopyridine, but it is now found that the analogy to nitrobenzene is still greater, extending to the successive formation of an azoxy-, azo-, and hydrazo-derivative when reduced in alkaline media.

3-Nitropyridine forms colourless needles, m. p. 41°, b. p. 216°;

hydrochloride, colourless leaflets, m. p. 154°; *sulphate*, hygroscopic crystals; *aurichloride*, yellow needles, m. p. 140°; *platinichloride*, broad, yellow needles, decomp. at 254°; *argentonitrate*,

$$(C_5H_4O_2N_2)_2,AgNO_3,$$

colourless needles, m. p. 175—176°.

When 3-nitropyridine is treated with a boiling solution of arsenious oxide in aqueous sodium hydroxide under reflux, it is reduced almost quantitatively to the corresponding *azoxypyridine*, silky needles, m. p. 130—131°, to a yellow liquid, which can be further reduced by zinc dust and alcoholic sodium hydroxide to *azopyridine*, orange-red needles, m. p. 142°, the yield again being almost the theoretical. The application of sodium methoxide as reducing agent for the production of the azoxy-compound and of iron filings for the azo-compound is unsatisfactory, yielding a complex mixture in each case and consequently an impure product.

If azopyridine is treated with zinc dust and boiling aqueous alcoholic sodium hydroxide in an atmosphere of hydrogen, reduction occurs with the formation of an 80% yield of *hydrazopyridine*, colourless needles, m. p. 202°; the pure substance is stable, but in alkaline alcoholic solution it undergoes atmospheric oxidation, especially readily on warming, with the production of azopyridine. It was not found possible to reduce hydrazobenzene further.

Partial nitration of pyridine occurs when nitric acid vapour is led into boiling pyridine nitrate, but there are formed simultaneously with 3-nitropyridine, also three other basic substances, m. p. 80°, 120, and 258° respectively; oxides of nitrogen in place of nitric acid lead to a similar result. Pyridine sulphate likewise gives a little 3-nitropyridine, but the main portion of the product consists of an oily mixture, b. p. 240—300°, of basic nature, from which could be isolated a *base*, woolly needles, m. p. 110°; *nitrate*, m. p. 245°; the base is very resistant to oxidising and reducing agents, and it is possibly related to the polymerised nitropyridine obtained by Spencer (P., 1903, **19**, 79).

D. F. T.

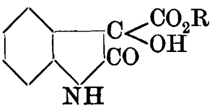
Syntheses of the Indole Group. IV. Basic Properties of Indoles, and Polymerides of Indoles. BERNARDO ODDO (*Gazzetta*, 1913, **43**, i, 385—394. Compare A., 1912, i, 649).—The publication of the author's results on polymeric indoles has been anticipated to some extent by that of Keller (this vol., i, 403). Di-indole hydrochloride (compare Keller, *loc. cit.*) is a microcrystalline powder, m. p. 180°, forming a yellow liquid. It can be prepared by the prolonged action of dilute aqueous hydrochloric acid on indole at the ordinary temperature, or by treating indole with concentrated hydrochloric acid for a few minutes, as well as by the action of hydrogen chloride on an anhydrous ethereal solution of indole.

a-Methylindole hydrochloride, C_9H_9N,HCl, may be obtained by the action of hydrogen chloride on an anhydrous ethereal solution of *a*-methylindole.

The author gives also the results of some preliminary experiments regarding the power of indoles to form simple or double salts.

R. V. S.

Condensation of Primary and Secondary Aromatic Amines with Mesoxalic Esters. Synthesis in the Indole Series. ALFRED GUYOT and J. MARTINET (*Compt. rend.*, 1913, **156**, 1625—1628).—Schmitt (A., 1905, i, 585) and Curtiss, Hill and Lewis (A., 1911, i, 366) obtained anilino-derivatives of the type $NHPh\cdot C(CO_2R)_2\cdot OH$; $NPh:C(CO_2R)_2$; $NHPh\cdot C(CO_2R)_2\cdot NHPh$ by the interaction of aromatic amines with mesoxalic esters. The authors have, however, obtained, as principal product of such reactions an ester of dioxindole-3-carboxylic acid (annexed formula), which is saponified by aqueous potassium hydroxide in the absence of air, giving the corresponding dioxindole, carbon dioxide being eliminated. In an open vessel oxygen is rapidly absorbed, and the product formed is the corresponding isatin. The amine is warmed with the mesoxalic ester in acetic acid solution at 60° for one hour, and then the acid and residual amine are removed by steam. From the product any phenyltartronic acid produced is extracted with hydrochloric acid, and the residual indole derivative is crystallised from ether.



From *p*-toluidine the authors have prepared *methyl* 5-*methyldioxindole*-3-*carboxylate*, m. p. 251°, the *ethyl* ester, m. p. 212°, 5-*methyldioxindole*, m. p. 210°, and the corresponding isatin.

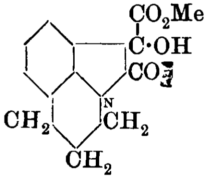
From β-naphthylamine, *methyl* 3-*hydroxy*-2-*ketodihydro*-ββ-*naphthindole*-3-*carboxylate*, m. p. above 300°, the *ethyl* ester, m. p. 210°, and the corresponding dioxindole and isatin.

From methylaniline, *methyl* 1-*methyldioxindole*-3-*carboxylate*, m. p. 217°, the *ethyl* ester, m. p. 130°, *methyl* p-*methylaminophenyltartronate*, m. p. 85°, and the dioxindole and isatin.

From ethylaniline, *ethyl* 1-*ethyldioxindole*-3-*carboxylate*, m. p. 141°, *ethyl* p-*ethylaminophenyltartronate*, m. p. 65°, the dioxindole, and isatin.

From ethyl-β-naphthylamine, *ethyl* 2-*hydroxy*-3-*keto*-1-*ethyldihydro*-ββ-*naphthindole*-3-*carboxylate*, m. p. 181°, the *dioxindole*, m. p. 172°, and the *isatin*, fine red needles, m. p. 173°.

From tetrahydroquinoline, *methyl* 1 : 7-*trimethylenedioxindole*-3-*carboxylate* (formula I), m. p. 188°, the *ethyl* ester, m. p. 174°, 1 : 7-*trimethylenedioxindole* (formula II), m. p. 160°, and 1 : 7-*trimethyleneisatin* (formula III), deep red prisms, m. p. 195°.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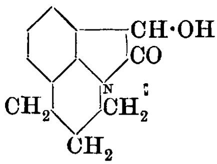
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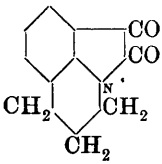
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W. G.

1-Methylisatins. MORITZ KOHN and ALFONS OSTERSETZER (*Monatsh.*, 1913, **34**, 787—794).—In the preparation of 1-methylisatin from isatin there is no necessity to isolate the intermediate

sodium derivative of isatin (compare Heller, A., 1907, i, 442), and the subsequent reaction with methyl iodide in a sealed tube can also be avoided. If isatin is treated with the calculated quantity of 25% methyl-alcoholic potassium hydroxide, the separation of the blue potassium derivative gives rise to a paste which on the addition of methyl sulphate (under reflux) enters into reaction so vigorously that the mixture boils; 1-methylisatin can be easily separated from the reaction mixture (compare Friedländer and Kielbasinski, A., 1911, i, 1021).

Following a similar course 5-bromoisatin can be converted into 5-*bromo*-1-*methylisatin*, red, microscopic needles, m. p. indistinct at 164°, and 5 : 7-dibromoisatin into 5 : 7-*dibromo*-1-*methylisatin*, red, microscopic needles, m. p. indistinct at 171°. In these cases the sodium compounds react less vigorously with methyl sulphate than does the sodium compound of the unsubstituted isatin.

If carefully dried methylisatin is treated in boiling acetic anhydride containing a little acetic acid, with small quantities of zinc dust until decolorisation is complete, diacetyl-1 : 1′-dimethylisatyd,

$$\mathrm{NMe}<\begin{matrix}\mathrm{C_6H_4}\\\mathrm{CO-}\end{matrix}>\mathrm{C(OAc)\cdot C(OAc)}<\begin{matrix}\mathrm{C_6H_4}\\\mathrm{CO-}\end{matrix}>\mathrm{NMe},$$

colourless, rhombohedral crystals, m. p. 218—220°, is obtained.

1-Methylisatin reacts with magnesium phenyl bromide in ethereal solution, giving a yellow, microcrystalline *substance*, $C_{21}H_{17}ON$, m. p. 145°; this is probably of the structure $\begin{matrix}\mathrm{C_6H_4\cdot CPh}\\ | \qquad\ \ | \\ \mathrm{NMe-CPh}\end{matrix}>\mathrm{O}$, produced by elimination of the elements of water from the ditertiary alcohol first formed by the action of the Grignard reagent on the two ketonic groups. D. F. T.

Some Derivatives of *cyclo*Hexanone and the Three Methyl-*cyclo*hexanones. VINCENZO SQUINTANI (*Atti R. Accad. Sci. Torino*, 1912–13, **48**, 675—686. Compare Guareschi, A., 1911, i, 792).—On warming a mixture of *cyclo*hexanone, ethyl cyanoacetate, and an alcoholic solution of methylamine, *aa′-dicyano*cyclo*hexane*-1 : 1-*diaceto-methylimide*, $\mathrm{CH_2}<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\\mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{C}<\begin{matrix}\mathrm{CH(CN)\cdot CO}\\\mathrm{CH(CN)\cdot CO}\end{matrix}>\mathrm{NMe}$, is produced; it has m. p. 175°. Its aqueous solution, when neutralised by ammonia, gives a blue precipitate with copper sulphate and a white, flocculent precipitate with silver nitrate. When treated with bromine it yields a white, flocculent compound, probably the *dibromide*, and when this is boiled with 10% alcoholic formic acid, *aβ-dicyano-aβ*-cyclo*hexane-succinomethylimide*, $\mathrm{CH_2}<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\\mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{C}<\begin{matrix}\mathrm{C(CN)\cdot CO}\\ | \\\mathrm{C(CN)\cdot CO}\end{matrix}>\mathrm{NMe}$, is formed; it is a white, crystalline substance, m. p. 222°.

When a mixture of 1-methyl*cyclo*hexan-4-one, ethyl cyanoacetate and alcoholic ammonia is kept for some hours, an ammoniacal salt is deposited; from this, by the action of dilute acid, the *imide* of *aa′-dicyano*-1-*methyl*cyclo*hexane*-4 : 4-*diacetic acid*,

$$\mathrm{CHMe}<\begin{matrix}\mathrm{CH_2\cdot CH_2}\\\mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{C}<\begin{matrix}\mathrm{CH(CN)\cdot CO}\\\mathrm{CH(CN)\cdot CO}\end{matrix}>\mathrm{NH},$$

m. p. 210—211°, is obtained. Its *copper* salt is a chestnut-coloured precipitate which becomes yellowish-green ; when it is made anhydrous and heated, it assumes at about 120° a red tint, which disappears on cooling. The imide of m. p. 210—211° yields a *dibromo*-derivative, from which *αβ-dicyano-αβ-1-methyl*cyclo*hexane*-4 : 4-*succinimide*,

$$CHMe<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}C(CN)\cdot CO\\|\\C(CN)\cdot CO\end{matrix}>NH,$$

m. p. 207—208°, can be prepared.

αα'-Dicyano-1-*methyl*cyclo*hexane*-4 : 4-*diacetomethylimide*,

$$CHMe<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}CH(CN)\cdot CO\\CH(CN)\cdot CO\end{matrix}>NMe,$$

has m. p. 181—182°. It yields a crystalline *bromo*-derivative, m. p. 137°, which on treatment with an aqueous solution of sulphurous acid gives *αβ-dicyano-αβ-1-methyl*cyclo*hexane*-4 : 4-*succinomethylimide*,

$$CHMe<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}C(CN)\cdot CO\\|\\C(CN)\cdot CO\end{matrix}>NMe,$$

m. p. 182—183°.

1-Methyl*cyclo*hexan-2-one yields similar products.

The *ammonium* salt, $C_{13}H_{18}O_2N_4$, obtained from 1-methyl*cyclo*hexan-2-one, ethyl cyanoacetate, and alcoholic ammonia has m. p. 165°. The corresponding *αα'-dicyano*-1-*methyl*cyclo*hexane*-2 : 2-*diacetimide*,

$$CH_2<\begin{matrix}CH_2\cdot CHMe\\CH_2—CH_2\end{matrix}>C<\begin{matrix}CH(CN)\cdot CO\\CH(CN)\cdot CO\end{matrix}>NH,$$

has m. p. 210°. Its *copper* salt is a rusty-red precipitate which turns bluish-green.

*αβ-Dicyano-αβ-1-methyl*cyclo*hexane*-2 : 2-*succinimide*,

$$CH_2<\begin{matrix}CH_2\cdot CHMe\\CH_2—CH_2\end{matrix}>C<\begin{matrix}C(CN)\cdot CO\\|\\C(CN)\cdot CO\end{matrix}>NH,$$

is a microcrystalline substance, m. p. 235—236°.

αα'-Dicyano-1-*methyl*cyclo*hexane*-2 : 2-*diacetomethylimide*,

$$CH_2<\begin{matrix}CH_2\cdot CHMe\\CH_2—CH_2\end{matrix}>C<\begin{matrix}CH(CN)\cdot CO\\CH(CN)\cdot CO\end{matrix}>NMe,$$

h s m. p. 181—182°.

αα'-Dicyano-1-*methyl*cyclo*hexane*-3 : 3-*diacetomethylimide*,

$$CH_2<\begin{matrix}CHMe\cdot CH_2\\CH_2—CH_2\end{matrix}>C<\begin{matrix}CH(CN)\cdot CO\\CH(CN)\cdot CO\end{matrix}>NMe,$$

has m. p. 154° ; in its preparation, a *substance* of m. p. 195—198° is also met with. R. V. S.

Preparation of Nitro-*N*-alkylcarbazoles. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 259504).—The nitration of *N*-alkylcarbazoles has previously given rise to a mixture of difficultly separable nitro-derivatives, but it is now found that if nitrous acid is employed definite compounds are obtained.

Nitro-9-ethylcarbazole, yellow crystals, m. p. 128°, is obtained when 9-ethylcarbazole (200 parts) in benzene (1000 parts) is mixed with a concentrated aqueous solution of sodium nitrite, and 600 parts of hydrochloric acid slowly added with efficient stirring at the ordinary temperature and the mixture subsequently boiled. *Nitro-9-methylcarbazole* forms small needles, m. p. 147—148°. F. M. G. M.

Preparation of Arylanthraquinone Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 259037. Compare this vol., i, 95—105).—4-p-*Toluidino*-1 : 2-*anthrathiazole*, dark bl e needles, is obtained by boiling 1-amino-4-*p*-toluidinoanthraquinone-2-mercaptan with benzaldehyde (3 parts) and nitrobenzene (3 parts); on sulphonation it furnishes a *compound* which dyes wool a fast violet colour.

The analogous *compound* from 2-amino-1-*p*-toluidino-3-thioanthraquinone and benzaldehyde is obtained in brownish-violet prisms.

F. M. G. M.

Syntheses of Alkyloxymalachite-greens by means of Magnesium Aryl Haloids. EMIL VOTOČEK and J. MATĚJKA (*Ber.*, 1913, **46**, 1755—1759).—The present work has been undertaken with the object of gaining insight into certain discrepancies observed in condensations with tetramethyldiaminobenzhydrol (Votoček and Jelínek, A., 1907, i, 245; Votoček and Krauz, A., 1909, i, 518). The use of Grignard's reagents presents the advantage that operations can be performed at a comparatively low temperature. A series of alkyloxymalachite-greens has been prepared from the magnesium derivatives of halogenated phenol ethers and Michler's ketone on the one hand, and from methyl anisate and the magnesium derivative of *p*-bromodimethylaniline on the other.

p-Methoxymalachite-green, obtained by the action of magnesium *p*-anisyl bromide on an ethereal suspension of Michler's ketone and subsequent decomposition of the product formed with hydrochloric acid and reduction with sodium hyposulphite, has m. p. 106°, and is identical with the compound prepared from anisaldehyde and dimethylaniline. The same substance is formed when ethereal solutions of magnesium *p*-dimethylaminophenyl bromide and methyl anisate (m. p. 46°, b. p. 255°) are mixed.

p-Ethoxymalachite-green is obtained in a similar manner from magnesium *p*-phenetole bromide and Michler's ketone, and is identical with the substance produced from *p*-ethoxybenzaldehyde and dimethylaniline.

m-Methoxymalachite-green is prepared by the gradual addition of an ethereal solution of magnesium *m*-methoxyphenyl iodide to a boiling solution of Michler's ketone in benzene and subsequent reduction to the leuco-base. It has m. p. 123°, and is identical with *m*-methoxytetramethyldiaminotriphenylmethane prepared from *m*-methoxybenzaldehyde and dimethylaniline.

o-Methoxymalachite-green, prepared from magnesium *o*-methoxyphenyl iodide and Michler's ketone, is identical with the product obtained from *o*-methoxybenzaldehyde and dimethylaniline. H. W

Further Investigations of Alkyloxy-derivatives of Malachite-Green. EMIL VOTOČEK and J. KÖHLER (*Ber.*, 1913, **46**, 1760—1769. Compare A., 1907, i, 245; 1909, i, 518; also previous abstract).—A difference has been previously noted between the leuco-bases obtained from alkyloxybenzaldehydes and dimethylaniline, and those prepared

from tetramethyl-*p*-diaminobenzhydrol and phenolic ethers. This is now attributed to the transformation of the methoxy- into the hydroxy-group under the conditions of the experiments. The work has been further extended to ethoxy-derivatives and to polyhydroxy-phenols.

Tetraethyldiaminobenzhydrol is prepared by reduction of tetraethyldiaminobenzophenone by sodium and alcohol or by oxidation of *tetraethyldiaminodiphenylmethane*, m. p. 41°, with lead peroxide. It condenses with phenol in the presence of hydrochloric acid, forming p′-*hydroxy*-p″ : p‴-*tetraethyldiaminotriphenylmethane*, m. p. 110—111°, which is also obtained by heating *p*-hydroxybenzaldehyde and diethylaniline with hydrochloric acid and a little alcohol at 125° for twelve hours. When oxidised with chloranil, it gives a green dye which becomes violet on addition of alkali.

Tetraethyldiaminobenzhydrol does not react readily with anisole in the presence of hydrochloric acid, and does not yield a uniform product. On the other hand, anisaldehyde readily condenses with diethylaniline, yielding p′-*methoxy*-p″ : p‴-*tetraethyldiaminotriphenylmethane*, m. p. 65°. In the hope of obtaining an abnormal base of betaine-like structure (A., 1909, i, 519), the substance was heated with hydrochloric acid at 120° during two hours. The products of the action consisted of methyl chloride and *p*′-hydroxy-*p*″ : *p*‴-tetraethyldiaminotriphenylmethane. Since hydrochloric acid was found to have a similar action in the methoxy-series, the supposed existence of a larger number of isomerides is disproved, and the supposition of a betaine-like structure is rendered unnecessary.

p′-Hydroxy-*p*″ : *p*‴-tetramethyldiaminotriphenylmethane, m. p. 165°, is obtained from *p*-hydroxybenzaldehyde and dimethylaniline, and also from phenol and Michler's hydrol. The same substance is isolated with difficulty from the product of the action of hot concentrated hydrochloric acid on a mixture of anisole and Michler's hydrol, the methyl group being partly eliminated during the reaction. That this is actually the case is proved by the isolation of the acetyl derivative of *p*′-hydroxy-*p*″:*p*‴-tetramethyldiaminotriphenylmethane, m. p. 145—146°, by the action of acetic anhydride on the above product, whereas, under the conditions employed, this reagent does not attack *p*′-methoxy-*p*″ : *p*‴-tetramethyldiaminotriphenylmethane. The latter substance evolves methyl chloride when heated with hydrochloric acid at 120°, and is converted into *p*′-hydroxy-*p*″ : *p*‴-tetramethyldiaminotriphenylmethane. When the last-named substance is acted on by methyl sulphate, an impure product is obtained from which the hydroxy-compound can be regained after repeated crystallisation (compare A., 1909, i, 519).

Similarly, the compound obtained from Michler's hydrol and phenetole, and that from *p*-ethoxyleucomalachite-green and hydrochloric acid are shown to be *p*-hydroxyleucomalachite-green.

The methyl group is also completely eliminated from *m*-methoxyleucomalachite-green by treatment with hydrochloric acid at 120° during two hours. *o*-Methoxyleucomalachite-green is not completely decomposed under these conditions.

p-*Dimethoxyleucomalachite-green*, m. p. 129—130°, is obtained by the addition of an ethereal solution of magnesium *p*-dimethoxyphenyl bromide to a solution of Michler's ketone in ether and benzene, and subsequent reduction of the dye formed by means of sodium hyposulphite, whilst the same substance can also be prepared by the condensation of Michler's hydrol and quinol dimethyl ether in the presence of hydrochloric acid and alcohol. When oxidised by chloranil, it yields a green dye, stable towards alkalis.

Michler's ketone may be condensed with catechol in the presence of phosphoryl chloride, and the dye produced is readily reduced to dihydroxytetramethyldiaminotriphenylmethane, m. p. 162—163°. The substance is identical with that obtained from protocatechualdehyde and dimethylaniline, or from catechol and Michler's hydrol. Under similar conditions, resorcinol yields a green *dye*, which becomes violet on addition of alkali; the corresponding leuco-base has not been obtained in the crystalline state. Quinol does not condense with Michler's ketone under these conditions.

The behaviour of these leuco-bases as photographic developers has been investigated. Reducing power is only observed in those cases in which the hydroxyl groups are in the ortho- or para-position.

H. W.

Influence of the Halogens on Phototropy in Hydrazones. II. FERDINANDO GRAZIANI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 623—629. Compare A., 1910, i, 777).—The paper describes the hydrazones derived from the three isomeric chlorophenylhydrazines.

None of the *o*-compounds is phototropic, all the *m*-derivatives are phototropic, whilst four of the eight *p*-derivatives prepared are phototropic.

Benzaldehyde-o-*chlorophenylhydrazone*, $C_6H_4Cl\cdot NH\cdot N{:}CHPh$, crystallises in minute, colourless needles, m. p. 73°.

Anisaldehyde-o-*chlorophenylhydrazone*, $C_6H_4Cl\cdot NH\cdot N{:}CH\cdot C_6H_4\cdot OMe$, is a white, crystalline powder, m. p. 67°.

Cuminaldehyde-o-*chlorophenylhydrazone*,

$$C_6H_4Cl\cdot NH\cdot N{:}CH\cdot C_6H_4\cdot CHMe_2,$$

forms slightly yellow needles, m. p. 67°.

Cinnamaldehyde-o-*chlorophenylhydrazone*,

$$C_6H_4Cl\cdot NH\cdot N{:}CH\cdot CH{:}CHPh,$$

crystallises in flat, sulphur-yellow needles, m. p. 99°.

Piperonaldehyde-o-*chlorophenylhydrazone*,

$$C_6H_4Cl\cdot NH\cdot N{:}CH\cdot C_6H_3{:}O_2{:}CH_2,$$

forms slightly yellow, flat needles, m. p. 96°.

Anisaldehyde-m-*chlorophenylhydrazone*,

$$C_6H_4Cl\cdot NH\cdot N{:}CH\cdot C_6H_4\cdot OMe,$$

crystallises in flat, colourless needles, m. p. 135°.

Cuminaldehyde-m-*chlorophenylhydrazone*,

$$C_6H_4Cl\cdot NH\cdot N{:}CH\cdot C_6H_4\cdot CHMe_2,$$

forms flat, colourless needles, m. p. 131°, and is very phototropic.

Cinnamaldehyde-m-*chlorophenylhydrazone*,

$$C_6H_4Cl\cdot NH\cdot N{:}CH\cdot CH{:}CHPh,$$

is a yellow, crystalline powder, m. p. 120°.

Piperonaldehyde-m-*chlorophenylhydrazone*,

$$C_6H_4Cl\cdot NH\cdot N:CH\cdot C_6H_3:O_2:CH_2,$$

forms minute, colourless needles, m. p. 95°; it is very strongly phototropic.

Salicylaldehyde-*m*-chlorophenylhydrazone is very feebly phototropic.

p-*Tolualdehyde*-m-*chlorophenylhydrazone*,

$$C_6H_4Cl\cdot NH\cdot N:CH\cdot C_6H_4\cdot Me,$$

is a white, crystalline powder, m. p. 112°.

Benzaldehyde-*p*-chlorophenylhydrazone has been prepared by Hewitt (T., 1893, **63**, 873), who gave m. p. 127°; the present author finds m. p. 132°. The substance is phototropic.

Anisaldehyde-p-*chlorophenylhydrazone*, $C_6H_4Cl\cdot NH\cdot N:CH\cdot C_6H_4\cdot OMe$, forms colourless leaflets, m. p. 150°, and is not phototropic.

Cuminaldehyde-p-*chlorophenylhydrazone*,

$$C_6H_4Cl\cdot NH\cdot N:CH\cdot C_6H_4\cdot CHMe_2,$$

forms slightly yellow needles, m. p. 131°, and is very phototropic.

Cinnamaldehyde-p-*chlorophenylhydrazone*,

$$C_6H_4Cl\cdot NH\cdot N:CH\cdot CH:CHPh,$$

crystallises in yellowish-green needles, m. p. 136°; it is phototropic.

Piperonaldehyde-p-*chlorophenylhydrazone*,

$$C_6H_4Cl\cdot NH\cdot N:CH\cdot C_6H_3:O_2:CH_2,$$

forms slightly yellow leaflets, m. p. 143°, and is not phototropic.

Salicylaldehyde-*p*-chlorophenylhydrazone has m. p. 173° (Auwers, A., 1909, i, 440, gave 169—170°). It is not phototropic.

p-*Tolualdehyde*-p-*chlorophenylhydrazone*,

$$C_6H_4Cl\cdot NH\cdot N:CH\cdot C_6H_4Me,$$

crystallises in slightly yellow needles, and is feebly phototropic.

Vanillin-p-*chlorophenylhydrazone*,

$$C_6H_4Cl\cdot NH\cdot N:CH\cdot C_6H_3(OH)\cdot OMe,$$

forms flat, slightly yellow needles, m. p. 135°. It is not phototropic.

R. V. S.

The Formation of Dipiperidyls in the Electrolytic Reduction of Pyridine. BRUNO EMMERT (*Ber.*, 1913, **46**, 1716—1719).—From the formation of azobenzene and pinacone respectively in the reduction of nitrobenzene and acetone, and of phenylmethylpyrrolidone (Emmert, A., 1907, i, 339) in the reduction of a mixture of nitrobenzene and lævulic acid, it would appear that the first stage of the reduction is the production of free radicles which subsequently couple together. The electrolytic reduction of pyridine (Ahrens, A., 1897, i, 368), which has been believed to yield only piperidine, might therefore be expected to give rise to at least a small quantity of some binuclear product.

The reduction of pyridine at lead cathodes with a current density of 17·1 amps. per sq. dm. in diluted sulphuric acid is found to give actually much piperidine accompanied by less volatile products including 4 : 4′-dipiperidyl, m. p. 158—160°, 2 : 2′-dipiperidyl, b. p. 258—260° (corr.), and a high boiling resinous substance the molecule of which probably includes a higher number of piperidine nuclei; these less volatile products amounted to more than 10% of the pyridine taken.

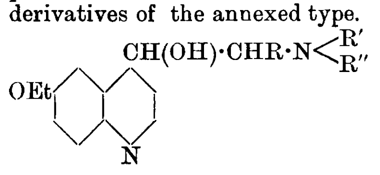
D. F. T.

[Preparation of a Condensation Product from 5 : 7-Dichloroisatin and 6-Chloroindoxyl.] Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 258258).—When a hot acetic acid solution of 5 : 7-dichloroisatin (220 parts) is treated with a similar solution of 6-chloroindoxyl (167 parts), some concentrated sulphuric acid added and the mixture warmed, it furnishes a *compound* crystallising in glistening, brown metallic needles. Differently substituted indoxyls and isatins can be employed for this reaction. F. M. G. M.

Preparation of New Condensation Products from Indigotin and its Halogen Derivatives. Gesellschaft für Chemische Industrie in Basel (D.R.-P. 259145).—When indigotin derivatives are treated with aromatic acid haloids in the presence of a condensing agent, they furnish compounds which dye wool in yellow shades.

The *compound* obtained by the action of benzoyl chloride on indigotin in the presence of copper powder forms yellowish-green needles, m. p. 275—276°. F. M. G. M.

Synthetic Bases Closely Related to the Cinchona Alkaloids. Adolf Kaufmann (*Ber.*, 1913, **46**, 1823—1837).—The difference in toxicity between quinine and quinotoxine is not due to the rearrangement of the nitrogen in the quinuclidine ring into a secondary amino-group with a free hydrogen atom, for methylcinchotoxine is just as active as cinchotoxine. Experiments by A. Warschawski have now shown that 4-quinolyl ketone (A., 1912, i, 1017), although it is chemically related to quinotoxine, is antipyretic, and only very slightly poisonous, from which it appears that the ketone group is not responsible for the toxicity. On the other hand, the ethyl ester of meroquinenine and especially the reduction product, ethyl cincholeuponate, are very powerful poisons. However, the author maintains his former hypothesis (*ibid.*) that the specific action of quinine is connected with the presence of an adrenaline-like grouping, and has now prepared derivatives of the annexed type.

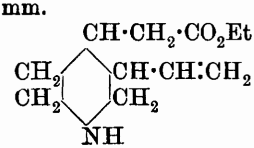


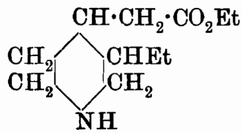
It was found that 6-alkyloxy-4-quinolyl ketones with methyl or methylene attached to the carbonyl group react with halogens, giving derivatives which condense with primary amines, and that the new substances could be reduced to hydroxy-compounds of the above type. They all have the same physiological effect as quinine, and give the same fluorescence and respond to the thalleoquinine test. The process is easily carried through, and it thus becomes possible to prepare numerous analogues of quinine.

I. [With Max Huber and A. Stettbacher.]—The cinchotoxine obtained by boiling 10 grams of cinchonine hydrochloride with 400 c.c. of 0·001% hydrochloric acid for fifty hours was extremely small in amount (compare Biddle, A., 1912, i, 296), but was characterised as the *phenylhydrazone-picrate*, which separated in microscropic, red needles, m. p. 200°, when phenylhydrazine and picric acid were added

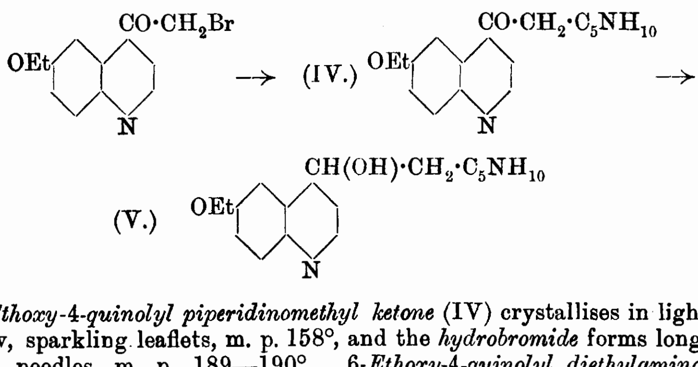
to the alkaline, ethereal extract. The reaction is sensitive in a dilution of 1 in 2500.

II. [With OTTO ZELLER and MAX HUBER.]—Meroquinenine was prepared by the hydrolysis of quinenine with 25% phosphoric acid at 180° (Koenigs, A., 1894, i, 392). The *p*-methoxylepidine *phosphate* separated on cooling in large, grey, lanceolate crystals, m. p. 208—210°, and the filtrate was fractionally precipitated with phosphotungstic acid. The meroquinenine obtained from the precipitate by means of baryta was esterified, and the hydrochloride of the ethyl ester (I) (Koenigs, A., 1906, i, 762), reduced by hydrogen and colloidal palladium to the hydrochloride of ethyl cincholeuponate, which formed beautiful white needles, m. p. 158°, $[\alpha]_D^{22}$ +5·71° (compare Skraup, A., 1895, i, 484). The free *ester* (II) is a colourless liquid, b. p. 140°/14 mm., $[\alpha]_D^{18}$ −17·2°, which reacts violently with methyl iodide, giving *ethyl* N-*methylcincholeuponate*, $C_{12}H_{23}O_2N$, as a colourless oil, b. p. 139°/21 mm.

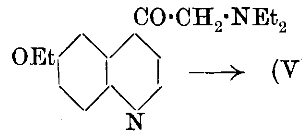
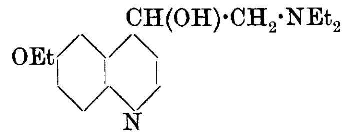
(I.) 

(II.) 

III. [With AUGUST POLL and HEINRICH PEYER.]—6-Ethoxy-4-quinolyl methyl ketone (this vol., i, 294) was warmed with bromine in hydrobromic acid, when the *hydrobromide* of 6-*ethoxy*-4-*quinolyl bromomethyl ketone* separated in lemon-yellow crystals, m. p. 207°. The *hydrochloride*, m. p. 190°, crystallised when hydrochloric acid was used. The free *base* (III) forms yellow needles, m. p. 104—105°, but is not so stable as the salts. When the hydrobromide is added to piperidine, diethylamine or dimethylamine in benzene or ether, the salt of the primary base is precipitated, and the new amino-ketone is obtained by evaporating the filtrate or by precipitation in the form of a salt.

(III.) 

6-*Ethoxy*-4-*quinolyl piperidinomethyl ketone* (IV) crystallises in light yellow, sparkling leaflets, m. p. 158°, and the *hydrobromide* forms long, white needles, m. p. 189—190°. 6-*Ethoxy*-4-*quinolyl diethylaminomethyl ketone* (VI) is a yellow, crystalline powder, m. p. 131°, which yields a neutral *monobromide* in white needles and a yellow *dibromide*, m. p. 193—194°, which reacts acidic. The *dimethylamino-ketone*, $C_{15}H_{18}O_2N_2$, forms yellow, prismatic columns, m. p. 132°.

(VI.)  ⟶ (VII.) 

The ketones are readily reduced by hydrogen in presence of palladium. 6-*Ethoxy*-4-β-*piperidino*-α-*hydroxyethylquinoline* (V) crystallises in white needles and plates, m. p. 85°, and the 6-*ethoxy*-4-β-*diethylamino*-α-*hydroxyethylquinoline* (VII) forms a very soluble *hydrochloride* in soft, white needles, m. p. 171°. J. C. W.

Hydantoins. XXII. History of 2-Thiohydantoin. TREAT B. JOHNSON (*J. Amer. Chem. Soc.*, 1913, **35**, 780—784).—2-Thiohydantoin was first synthesised by Klason (A., 1891, 179) by heating ethyl aminoacetate hydrochloride with potassium thiocyanate at 140—150°, but this work seems to have been overlooked by subsequent workers. Klason's observation has now been confirmed, but it has been found that the method gives too small a yield to be of practical value for preparing the compound. The reaction involves the intermediate formation of ethyl thiohydantoate. An attempt was therefore made to obtain 2-thiohydantoin by warming ethyl thiohydantoate with hydrochloric acid, but without success, hydrogen sulphide, ammonium chloride, and glycine hydrochloride being produced. E. G.

Preparation of ω-Methyl Sulphites [and ω-Alkyl Sulphites] of Substituted Aminoarylpyrazolones. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D. R.-P. 259503—259577).—An account of the preparation of compounds previously described (this vol., i, 401), by the action of formaldehyde and sodium hydrogen sulphite on substituted aminopyrazolones. The second patent states that the formaldehyde can be replaced by other aldehydes, and describes the *compounds* obtained from 4-amino-1-phenyl-2 : 3-dimethyl-5-pyrazolone with acetaldehyde, and with propaldehyde, both of which have m. p. 124—125°, the latter decomposing at 130°. F. M. G. M.

Reactions of αβ-Diketonic Esters. ANDRÉ WAHL and M. DOLL (*Bull. Soc. chim.*, 1913, [iv], **13**, 468—485. Compare A., 1905, i, 474; 1907, i, 217; 1911, i, 108; 1912, i, 536, 625; this vol., i, 473).—The interaction of these esters with various reagents is described, and a number of the compounds obtained have been characterised. Some of this work has been recorded already (*loc. cit.*). The following observations and compounds are new:

Action of o-*diamines* (A., 1912, i, 536, 625).—*Ethyl* 2-*methylquinoxaline*-3-*carboxylate*, m. p. 74°, forms colourless needles. *Ethyl* 2-*methyl*-1 : 4-*naphthaquinoxaline*-3-*carboxylate*, m. p. 113—114°, forms slender, colourless needles. *Ethyl* 2-*propyl*-1 : 4-*naphthaquinoxaline*-3-*carboxylate*, m. p. 83—84°, crystallises in long, colourless needles. *Ethyl* 2-n-*butylquinoxaline*-3-*carboxylate* is an oil, but the corresponding *acid*, m. p. 86°, is crystalline. *Ethyl* 2-*phenylquinoxaline*-3-*carboxylate*,

m. p. 62—63°, forms silky needles; the *propyl* ester, m. p. 72—73°, and the iso*butyl* ester, m. p. 71°, are both crystalline. *Ethyl 2-phenyl-1 : 4-naphthaquinoxaline-3-carboxylate*, m. p. 116°, forms colourless needles.

Action of cyclic amines (A., 1912, i, 536, 625).—The aromatic esters condense with 2 mols. of the cyclic amines with the loss of $1H_2O$. The resulting compounds are probably best represented by the general formula $R·CO·C(NHPh)_2·CO_2Ph$ or

$$R·C(:NPh)·C(NHPh)(OH)·CO_2Et.$$

Methyl benzoylglyoxalate yields a *dianilide*, m. p. 144—145°, crystallising in yellow needles from warm benzene, and a *di*-p-*toluidide*, m. p. 115—116°, forming lemon-yellow crystals. The propyl ester gives a *dianilide*, m. p. 88—89°, and the *iso*butyl ester a *dianilide*, m. p. 108—109°.

Action of hydroxylamine (A., 1907, i, 217; 1912, i, 536, 626).—With the exception of ethyl acetylglyoxalate, which yields a dioxime, all the esters yield monoximes when treated with hydroxylamine; thus methyl *p*-methoxybenzoylglyoxalate furnishes methyl oximinoanisoylacetate (this vol., i, 214, 532).

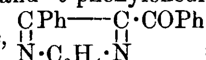
Action of phenylhydrazine (A., 1905, i, 474; 1912, i, 213, 536, 626; this vol., i, 532).—Ethyl *n*-valeroylglyoxalate yields *4-phenylhydrazino-1-phenyl-3-*n*-butyl-5-pyrazolone*, m. p. 119—120°, crystallising in orange needles. Methyl anisoylglyoxalate in addition to the two compounds already described (A., 1912, i, 626) when boiled in acetic acid with 2 mols. phenylhydrazine yields 4-phenylhydrazino-1-phenyl-3-*p*-methoxyphenyl-5-pyrazolone (A., 1912, i, 213). Methyl benzoylglyoxalate may yield (1) the *additive product*, $COPh·C(OH)(NH·NHPh)·CO_2Me$, m. p. 144—145°, or (2) a mixture of phenylhydrazinopyrazolone with the *monophenylhydrazone*, m. p. 76° (identical with methyl benzeneazobenzoylacetate) depending on the conditions of the reaction. iso*Butyl benzoylglyoxalatephenylhydrazone*, m. p. 62—63°, forms hexagonal tablets. Unlike phenylhydrazine, *p*-nitrophenylhydrazine does not give rise to additive products, but yields either α-mono-*p*-nitrophenylhydrazones or *p*-nitrophenylhydrazinopyrazolones (*loc. cit.*).

Action of semicarbazide (A., 1907, i, 217; 1912, i, 536, 626).—The acyclic esters yield normal disemicarbazones, whilst the cyclic esters furnish compounds which have the composition of disemicarbazones with 1 mol. H_2O in addition. Probably 1 mol. of semicarbazide is added to the α-carbonyl, whilst the second condenses normally with the β-carbonyl group. Methyl benzoylglyoxalate yields a *compound*, m. p. 215°, of this type, which on recrystallisation is partly converted into a yellow *compound*, m. p. 292°, which may be a true disemicarbazone.

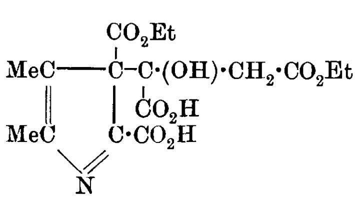
Action of hydrazine hydrate (A., 1912, i, 536, 626; this vol., i, 532). —Ethyl valeroylglyoxalate yields *dibutyl-3 : 3′-rubazonic acid*, and ethyl hexoylglyoxalate gives *dihexyl-3 : 3′-rubazonic acid*. With cyclic esters additive products are formed consisting of 2 mols. of the ester and one of hydrazine hydrate when the reaction takes place in acetic acid. Such a product has been described for methyl anisoylglyoxalate, $N_2H_2[C(OH)(CO·C_6H_4·OMe)·CO_2Me]_2$ (A., 1912, i, 626); that yielded by methyl benzoylglyoxalate has m. p. 137°, and crystallises in yellow

spangles. In alcoholic solution the benzoylglyoxalates yield 3 : 3′-diphenylrubazonic acid (*loc. cit.*).

The benzoylglyoxalates condense with the benzoylacetates in presence of piperidine, forming compounds in which condensation has probably been effected by interaction of the β-ketonic ester with the α-carbonyl. The following *products* of this kind are described; they crystallise in colourless needles: methyl benzoylacetate with methyl benzoylglyoxalate, $CO_2Me{\cdot}CBz(OH){\cdot}CHBz{\cdot}CO_2Me$ (?), m. p. 120°; ethyl benzoylacetate with methyl benzoylglyoxalate, m. p. 117—118°; methyl benzoylacetate with ethyl benzoylglyoxalate, m. p. 124—125°; methyl *o*-methoxybenzoylacetate with methyl benzoylglyoxalate, m. p. 136—137° (compare A., 1907, i, 217). T. A. H.

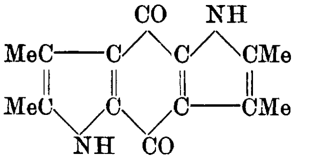
Behaviour of Diphenyltriketone with Amino-compounds. I. CARLO GASTALDI and F. CHERCHI (*Gazzetta*, 1913, **43**, i, 299—303).—When alcoholic solutions of diphenyltriketone and *o*-phenylenediamine are mixed and cooled, *benzoylphenylquinoxaline*, , separates in slightly yellow scales, m. p. 153°. Its constitution follows from the fact that it can also be obtained from bromodibenzoylcarbinyl acetate. When the solution from which the crystals of m. p. 153° separate is diluted with water, *diphenyltriketone-*o*-phenylenediamine*, $COPh{\cdot}C(OH)_2{\cdot}CPh{:}N{\cdot}C_6H_4{\cdot}NH_2$, is obtained in colourless rosettes, m. p. 155°. When this compound is heated on the water-bath for ten hours in aqueous-alcoholic solution with hydrochloric acid, phenylbenziminazole hydrochloride, m. p. 343°, is produced. The phenylbenziminazole liberated from it has m. p. 294° (compare Japp and Meldrum, T., 1890, **57**, 1043). R. V. S.

Tetramethylpyrrindoquinone and Some Other Derivatives of 2 : 3-Dimethylpyrrole. OSCAR PILOTY and K. WILKE (*Ber.*, 1913, **46**, 1597—1603. Compare Piloty, A., 1910, i, 277).—The paper deals with the preparation of a quinone, tetramethylpyrrindoquinone, from 2 : 3-dimethylpyrrole-4-carboxylic acid. The authors have also prepared 2 : 3-dimethyl-1-ethylpyrrole for comparison with their "hæmopyrrole-*e*," but have not yet been able to prepare "hæmopyrrole-*e*" picrate from it. They have found further that trisubstituted *C*-derivatives of pyrrole can yield bispyrrole picrates, so that the power to form bispyrrole derivatives and their picrates does not seem to follow any law.



The preparation of 4-ethyl hydrogen 2 : 3-dimethylpyrrole-4 : 5-dicarboxylate (A., 1912, i, 899) is simplified by using the tin double salt of β-aminobutan-γ-one, instead of that substance itself. The employment of ethyl hydrogen oxalacetate, instead of ethyl oxalacetate, presents no advantage, but it leads to the formation of a by-product, termed *aphaninester acid*, probably of the

annexed formula. This substance crystallises in hair-like needles, m. p. 156°. *Tetramethylpyrrindoquinone* (annexed formula) is obtained by boiling 2 : 3-dimethylpyrrole-4-carboxylic acid (*loc. cit.*) with acetic anhydride for several hours; it crystallises in rhombic tablets, which are yellow by transmitted, red by reflected, light; at a high temperature the substance sublimes.



2 : 3-*Dimethyl*-1-*ethylpyrrole*-4-*carboxylic acid*, $C_9H_{13}O_2N$, is obtained by acting on 4-ethyl potassium 2 : 3-dimethylpyrrole-4 : 5-dicarboxylate (*loc. cit.*) with ethyl sulphate in benzene solution, and saponifying the ester by means of boiling concentrated aqueous alkali; it forms thin rods, m. p. 156°. When compressed tablets of this acid are subjected to dry distillation, 2 : 3-*dimethyl*-1-*ethylpyrrole*, $C_8H_{13}N$, b. p. 59°/11 mm., is produced. If hydrogen chloride is passed into a dry ethereal solution of the substance, the bis-compound is obtained; it crystallises in a freezing mixture in long needles which melt at room-temperature.

Ethyl 1 : 2 : 3-*trimethylpyrrole*-4-*carboxylate*, $C_{10}H_{15}O_2N$ (prepared similarly, using methyl sulphate), forms flat, rhombic prisms, m. p. 52°. The *acid*, $C_8H_{11}O_2N$, forms stellar aggregates of small crystals, m. p. 229° (previously sintering and becoming slightly brown).

Ethyl 2 : 3-*dimethylpyrrole*-4 : 5-*dicarboxylate*, $C_{12}H_{17}O_4N$ (prepared by the action of ethyl sulphate on the potassium salt), forms rhombic leaflets, m. p. 110°. Its *picrate*, $C_{18}H_{20}O_{11}N_4$, crystallises in bright orange rods, m. p. 112—113°. The *picrate* of the methyl ethyl ester of the same acid (*loc. cit.*) forms straw-yellow needles, which sinter at 122°, and are completely melted at 140°; analysis gave the formula $C_{28}H_{33}O_{15}N_5$, indicating a bis-compound.

2 : 3-Dimethylpyrrole-4-carboxylic acid yields a *picrate*, $C_{20}H_{21}O_{11}N_5$, which forms compact, red rods, m. p. 143°. R. V. S.

Existence of Phenyldi-imide. STEFAN GOLDSCHMIDT (*Ber.*, 1913 **46**, 1529—1532. Compare Vaubel, A., 1900, i, 522; this vol., i, 519; Forster and Withers, T., 1913, **103**, 266).—Vaubel's supposed phenyldi-imide has been characterised by Forster and Withers as a mixture of aniline and phenylazoimide. The author has repeated Vaubel's experiments, and, employing conditions somewhat different from those used by Forster and Withers, finds that the product is pure phenylazoimide, b. p. 65—68°/12 mm., the identity of which is confirmed by the formation of a condensation product, m. p. 178—179°, with phenylacetonitrile (compare Dimroth, A., 1903, i, 129).

The author has further attempted to prepare di-imines by the oxidation of phenylhydrazine and *p*-bromophenylhydrazine. At the ordinary temperature, the action of oxidising agents, such as lead peroxide, silver oxide, or *p*-benzoquinone, etc., is accompanied by the evolution of nitrogen. Since the action of all these agents with the exception of *p*-benzoquinone ceases at 0°, the latter substance has alone been used.

When an ethereal solution of *p*-benzoquinone is gradually added to a

solution of *p*-bromophenylhydrazine in ether cooled to $-60°$ with careful exclusion of moisture and carbon dioxide, a copious separation of quinhydrone occurs and a yellow filtrate is obtained from which nitrogen is evolved on warming. Addition of a solution of stannous chloride in ether causes regeneration of *p*-bromophenylhydrazine. Attempts to isolate the di-imine in the pure state were, however, unsuccessful. It appears to possess no tendency to form salts or double salts, and does not react with substances such as anhydrous hydrocyanic acid, diphenylketen, etc., at the low temperature necessitated by the unstability of the substance. Tribromophenylhydrazine, which might be expected to yield a more stable oxidation product, is unaffected by *p*-benzoquinone. H. W.

Iminoindigotin. ARTHUR BINZ and K. R. LANGE (*Ber.*, 1913, **46**, 1691—1695).—When indigotin is shaken for two hours with alcoholic sodium ethoxide solution and the resultant additive product (compare Binz and Schädel, A., 1912, i, 317) shaken with a solution of zinc hydroxide in ammonia together with an excess of saturated alcoholic solution of ammonia, the resulting blue liquid after acidification with dilute hydrochloric acid deposits *iminoindigotin hydrochloride*; the *sulphate* is also sparingly soluble. The parent substance is evidently more reactive than indigotin, for the blue solution obtained before acidification can be completely oxidised by air to a brown *substance*, whilst hydrogen sulphide reduces the solution to a vat which on re-oxidation yields, not the imine, but a new *substance* which dissolves in alkali to a red, and in alcohol to a brown, solution. The iminoindigotin hydrochloride can be reduced by gentle warming with sodium hyposulphite, giving a greyish-white leuco-*compound*. The aqueous solution of the hydrochloride itself dyes wool and mordanted cotton, producing similar shades to indigotin.

If the blue solution obtained by the interaction of the additive compound of sodium ethoxide and indigotin with zinc hydroxide and ammonia is treated with much water instead of with acid, a *zinc* salt, $(C_{16}H_{10}ON_3)_2Zn$, a bluish-green, amorphous substance, soluble in chloroform and acetone, is obtained. This acid character of imino-indigotin is different from the power by which indigotin forms additive compounds because the colour is relatively unaffected.

The free *iminoindigotin*, $C_{16}H_{11}ON_3$ (compare Thiele and Pickard, A., 1898, i, 493), was obtained most satisfactorily by reducing the sulphate with aqueous sodium hydroxide and hyposulphite and re-oxidising the yellow solution; the deep blue product is obtained crystalline with difficulty, and decomposes without melting; it is probably not a pure substance, but possibly a mixture of isomerides, so that the formula $C_6H_4<\begin{matrix}C(:NH)\\NH\end{matrix}>C:C<\begin{matrix}CO\\NH\end{matrix}>C_6H_4$ must be accepted with reserve. The formation of the substance however, seems to supply further evidence in favour of the view that one-half of the indigotin molecule is more reactive than the second (compare Claasz, A., 1912, i, 513).

The halogen-indigotins, also indigo-red and "thioindigo," likewise form imino-derivatives, whilst by applying methylamine in the original

reaction a methylimino-product can be obtained. These substances also are possibly not homogeneous, and like iminoindigotin, exhibit both acidic and basic tendency. D. F. T.

Syntheses in the Fatty Aromatic Series. X. Derivatives of Diaryl Paraffins. JULIUS VON BRAUN, H. DEUTSCH, and O. KOSCIELSKI (*Ber.*, 1913, **46**, 1511—1526).—Attempts to prepare definite substitution products of diaryl paraffins by sulphonation, chlorination, or nitration have been only partly successful, the compounds obtained showing little tendency to crystallise or to distil without decomposition; 4 : 4′-dicarboxylic acids have been prepared by the use of oxalyl chloride, but the corresponding amides do not yield any considerable quantity of amines when subjected to Hofmann's reaction. Further attempts to prepare symmetrically substituted dinitro-derivatives have met with slight success, but well characterised tetranitro-derivatives, $C_6H_3(NO_2)_2\cdot[CH_2]_x\cdot C_6H_3(NO_2)_2$, have been obtained.

A method of obtaining mono-substituted derivatives of diaryl paraffins consists in the condensation of acyl derivatives of chlorinated bases with benzene in the presence of aluminium chloride (compare A., 1912, i, 688), a reaction which is remarkable, since the corresponding nitro-derivatives appear to be unsuitable for the Friedel-Crafts reaction. If, however, the chlorine atom is in the δ- or ε-position with respect to the benzene nucleus, hydrogen chloride is almost entirely eliminated from within the molecule.

4-*Benzoylaminodibenzyl*, m. p. 170—171°, is obtained in almost theoretical yield by the condensation of *p*-benzoylaminophenylethyl chloride with benzene in the presence of aluminium chloride, and is readily transformed into p-*aminodibenzyl*, colourless leaflets, which are stable to light, m. p. 48°. The latter forms a *hydrochloride*, leaflets, m. p. 210° after darkening at 205°, a *platinichloride*, m. p. 286—289° according to the rate of heating and after darkening from 200°, a *carbamide*,

$$CH_2Ph\cdot CH_2\cdot C_6H_4\cdot NH\cdot CO\cdot NH_2,$$

m. p. 155°, and a *phenylthiocarbamide*, m. p. 154°. The constitution of *p*-aminodibenzyl follows from its transformation into dibenzyl by the successive action of nitrous acid and stannous chloride. 4-*Iododibenzyl*, m. p. 44—45°, b. p. 210°/10 mm. (slight decomp.), reacts with sodium in much the same manner as does iodobenzene, but more slowly than the latter with copper powder or magnesium. 4-*Hydroxydibenzyl* forms yellow leaflets, m. p. 90°, and yields a yellow *sodium* salt with concentrated sodium hydroxide and a *benzoyl* derivative, m. p. 99°. *Dibenzyl*-4-*carboxylonitrile* is an oil which slowly solidifies when preserved, and is transformed by hydrochloric acid at 120° into *dibenzyl*-4-*carboxylic acid*, leaflets, m. p. 165°. The azo-dyes obtained from amino- and hydroxydibenzyl closely resemble those obtained from *p*-toluidine and *p*-cresol, so that the authors are led to the conclusion that the number of groups present is of greater importance for the alteration of colour than is the increase in weight of a group already present.

p-Nitrophenylethyl chloride, even after protracted treatment with benzene and aluminium chloride, yields oily products which still contain chlorine, and from which a uniform, chlorine-free nitro-

compound cannot be isolated. *p*-Nitrophenylpropyl chloride behaves in a similar manner.

p-Benzoylaminophenylpropyl chloride condenses with benzene in the presence of aluminium chloride to yield an oily *product*, which, when hydrolysed by hydrochloric acid at 150°, gives a colourless, mobile *base*, b. p. 95—110°/17 mm., which is probably aminohydrindene, $NH_2\cdot C_6H_3<\begin{matrix}CH_2\\CH_2\end{matrix}>CH_2$ (*benzoyl* derivative, m. p. 161°), and p-*amino-diphenylpropane*, b. p. 210—225°/18 mm. (slight decomp.). The latter does not solidify when preserved during several months. It forms a *picrate*, *benzoyl* and m-*nitrobenzoyl* derivative, all of which are oily. The hydrochloride has m. p. 195°. When heated with methyl iodide (about 4 mols.) and sodium hydroxide, *p*-aminodiphenylpropane yields the corresponding quaternary *iodide*, $Ph\cdot[CH_3]_2\cdot C_6H_4\cdot NMe_3I$, colourless needles, m. p. 179—180°, and p-*dimethylaminodiphenylpropane*, b. p. 221—222°/17 mm. The latter is best obtained in the pure state by decomposition of the quaternary iodide in a vacuum. p-*Hydroxy-diphenylpropane* has b. p. 215—220°/18 mm.

o-Aminodiphenylpropane, in contrast to the corresponding *p*-compound, yields a solid m-*nitrobenzoyl* derivative, m. p. 137°. Even with a large excess of methyl iodide it gives solely the tertiary *amine*, b. p. 177—183°/17 mm. (slight decomp.), which, although viscous, does not solidify.

p-*Benzoylaminophenylamyl chloride*, m. p. 210—212°, reacts with benzene and aluminium chloride to yield a *product*, the nitrogen content of which is too high for a normal condensation product (see above).

Only minimal amounts of substance could be obtained by the condensation of acyl derivatives of chloro-bases with thiophen.

The action of oxalyl chloride on a solution of $\alpha\zeta$-diphenylhexane in carbon disulphide in the presence of aluminium chloride results in the isolation of the *dicarboxylic acid*, $CO_2H\cdot C_6H_4\cdot[CH_2]_6\cdot C_6H_4\cdot CO_2H$, m. p. 303—304°, the *potassium* salt of which is sparingly soluble in water, whilst the *sodium* and *ammonium* salts are more soluble. The corresponding *amide*, m. p. 178°, like the diamide of diphenyloctane-dicarboxylic acid, is converted by bromine and alkali into a dark amorphous mass from which practically nothing can be extracted by acids.

Reduction of the oily product obtained by the nitration of diphenyl-hexane leads to a basic substance, which, when benzoylated, yields a *benzoyl* derivative of indefinite m. p. The latter may be resolved by alcohol into two isomeric portions, the less soluble of which, m. p. 212°, is probably mainly *pp'*-dibenzoylaminodiphenylhexane, and is converted by hydrochloric acid at 140° into a *hydrochloride*, $C_{18}H_{28}N_2Cl_2$, which melts indefinitely at about 205°. The more soluble portion has m. p. 174°.

It is noteworthy, that although the homologues of benzyl chloride readily condense in the presence of sodium with formation of diaryl paraffins, a similar reaction does not occur when the benzene nucleus contains a nitro- or benzoylamino-group.

The preparation of tetranitro-derivatives of diarylparaffins (compare Borsche and Wollemann, this vol., i, 171) is best effected by gradual addition of the hydrocarbon to nitric acid (D 1·52) at −15°. The

mixture is allowed to remain for half an hour in ice and then during two hours at the ordinary temperature, after which it is heated for a few minutes on the water-bath and then poured into water. In this manner diphenylhexane yields 2 : 4 : 2′ : 4′-*tetranitro-αζ-diphenylhexane,* colourless needles, m. p. 90°, which, on oxidation with chromic acid, is converted into 2 : 4-dinitrobenzoic acid. Similarly, *tetranitro-βη-diphenyloctane,* m. p. 145—146°, and *tetranitro-αζ-diphenyl-β : ε-dimethylhexane,* m. p. 112°, are obtained from the corresponding hydrocarbons. Reduction of 2 : 4 : 2′ : 4′-tetranitro-αζ-diphenylhexane in ammoniacal alcoholic solution by means of hydrogen sulphide yields mainly *dinitrodiaminodiphenylhexane,* in which the two amino-groups are probably in the para-position to the hexamethylene chain. (Its *hydrochloride* was also examined.) Smaller quantities of *trinitroaminodiphenylhexane,* m. p. 126—127°, and of an isomeric *dinitrodiaminodiphenylhexane,* m. p. 150—151°, in which the amino-groups are probably in the ortho-position to the hexamethylene chain, are also formed. 2 : 4 : 2′ : 4′-*Tetra-aminodiphenylhexane,* needles, m. p. 138°, is obtained by the reduction of 2 : 4 : 2′ : 4′-tetranitrodiphenylhexane by tin and hydrochloric acid. The *hydrochloride,* m. p. 275°, *picrate,* needles, m. p. 213—215°, *benzoyl* derivative, which is not melted at 280°, and *tetrabenzylidene* derivative, m. p. 151°, were investigated. The base is converted by an excess of boiling acetic anhydride into its *tetra-acetyl* derivative, m. p. 270°; acetylation by glacial acetic acid, in the presence of a few drops of water, gives a *diacetyl* compound, leaflets, m. p. 167°.

Tetra-amino-βη-diphenyloctane,

$$C_6H_3(NH_2)_2{\cdot}CHMe{\cdot}[CH_2]_4{\cdot}CHMe{\cdot}C_6H_3(NH_2)_2,$$

colourless leaflets, m. p. 131°, is obtained in a similar manner from the corresponding tetranitro-compound. H. W.

Syntheses in the Fatty-Aromatic Series. XI. Double Dyestuffs from Diarylparaffins. JULIUS VON BRAUN and O. KOSCIELSKI (*Ber.*, 1913, **46**, 1526—1529).—The authors have investigated the effect of the repetition of one and the same chromophore in an organic molecule on the intensity and nature of the colour [compare preceding abstract]. They have prepared double dyes in the azo-, triphenylmethane-, indamine, and azine series, and do not find any noticeable difference between them and the corresponding mono-dyes.

2 : 4 : 2′ : 4′-Tetra-amino-αζ-diphenylhexane and tetra-amino-βη-diphenyloctane when dissolved in dilute acid and treated with sodium nitrite yield reddish-brown colorations exactly similar to that given by 2 : 4-tolylenediamine under similar conditions. On keeping, or immediately in concentrated solution, the "Vesuvines" separate as amorphous, dark brown powders which were not further investigated. When 2 : 4 : 2′ : 4′-tetra-amino-αζ-diphenylhexane is treated with benzenediazonium chloride (2 mols.), the *bis-chrysoidine* separates as a red precipitate. The free *base,*

$$C_6H_{12}[C_6H_2(NH_2)_2{\cdot}N_2Ph]_2,$$

is a yellow, crystalline powder, m. p. 148—150°. The shades given by bis-chrysoidine and by the products derived from tolylenediamine

and tetra-aminodiphenyloctane are scarcely distinguishable from one another.

Tolylenediamine condenses with Michler's hydrol in acetic acid solution to yield the *base*, $CH(C_6H_4{\cdot}NMe_2)_2{\cdot}C_6H_2Me(NH_2)_2$, m. p. 156—158°. The corresponding *acetyl* derivative has m. p. 200°, and is oxidised by lead peroxide to a product which dyes cotton a pure green. The similar leuco-*base*, obtained from 2 : 4 : 2′ : 4′-tetra-amino-$\alpha\zeta$-diphenylhexane and Michler's hydrol (2 mols.),

$$C_6H_{12}[C_6H_2(NH_2)_2{\cdot}CH(C_6H_3{\cdot}NMe_2)_2]_2,$$

has m. p. 222°. With acetic anhydride it yields a *tetra-acetyl* derivative, m. p. 255—256°, which is oxidised by lead peroxide. The dye so obtained has precisely the same colour as that obtained from tolylenediamine in solutions of similar concentration, and yields precisely the same shades on cotton.

Amorphous *dyes* are obtained by the condensation of 2 : 4 : 2′ : 4′-tetra-amino-$\alpha\zeta$-diphenylhexane or tetra-aminodiphenyloctane with nitrosodimethylaniline hydrochloride. These give blue colours on the fibres indistinguishable from those obtained with tolylene-blue. When an aqueous solution of these dyes is boiled, the colour changes to red. The "double-reds" so obtained dye the fibres in practically the same shades as tolylene red. H. W.

Amines Derived from Proteins: The Peptamines Glycyl-*p*-hydroxyphenylethylamine, Alanyl-*p*-hydroxyphenylethylamine, and 4-Glycyl-β-aminoethylglyoxaline. MARKUS GUGGENHEIM (*Biochem. Zeitsch.*, 1913, **51**, 369—387).—It is known that by the scission of carbon dioxide from certain amino-acids, such as tyrosine and histidine, bases of pharmacological interest are obtained. The author has consequently undertaken the investigation of similar products from peptides, and with this object has prepared synthetically the substances named above. By the action of chloroacetyl chloride on *p*-hydroxyphenylethylamine, *chloroacetyl*-p-*hydroxyphenylethylamine*, $C_{10}H_{12}O_2NCl$, m. p. 109°, is obtained, which by the action of aqueous ammonia yields glycyl-*p*-hydroxyphenylethylamine, $C_{10}H_{14}O_2N_2$, m. p. 136°. By the action of bromopropionyl chloride on *p*-hydroxyphenylethylamine, dl-*bromopropionyl*-p-*hydroxyphenylethylamine*,

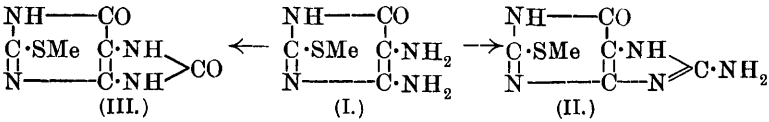
$$C_{11}H_{14}O_2NBr,$$

m. p. 98°, was obtained, which yields on treatment with ammonia dl-*alanyl*-p-*hydroxyphenylethylamine*, $C_{11}H_{16}O_2N_2$, m. p. 116°. By a similar series of reactions, 4-*glycyl*-β-*aminoethylglyoxaline*,

$$\begin{matrix} CH{=}N \\ | \\ NH{\cdot}CH \end{matrix}{>}C{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}NH_2,$$

was obtained, the hydrochloride of which melted with decomposition at 250°. The pharmacological action of these substances was investigated and compared with the actions of *p*-hydroxyphenylethylamine and 4-β-aminoethylglyoxaline. The conjugated products have a similar peripheral action on smooth muscle as the simple bases, but the effect is much weaker. The actions were investigated on the uterus, surviving small intestine, the frog's heart, etc., and on the blood-pressures, and the effects are illustrated by numerous tracings. S. B. S.

Purines. X. 6 : 8-Dioxy-2-methylthiolpurine and 8-Amino-6-oxy-2-methylthiolpurine. CARL O. JOHNS and EMIL J. BAUMANN (*J. Biol. Chem.*, 1913, **14**, 381—388).—The first orthodiaminoalkylthiolpyrimidine has been prepared and condensed to a purine. The presence of the methylthiol group instead of sulphur modified the properties of the new compound, 4 : 5-diamino-6-methylthiol-6-pyrimidone (I). Instead of combining with thiocarbamide to form a thiopurine, as 4 : 5-diamino-2-thio-6-pyrimidone does (this vol., i, 657), it gave an aminopurine (II), which is accounted for by assuming that the thiocarbamide is first transformed into guanidine thiocyanate. The latter substance is, indeed, the best reagent to use for the preparation of the aminopurine, which may even be obtained by employing ammonium thiocyanate. This is remarkable in view of the fact that a similar condensation between other diaminopyrimidines and guanidine salts could not be realised.



(III.) (I.) (II.)

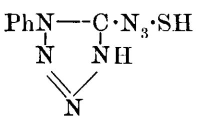
4-Amino-2-methylthiol-6-pyrimidone (A., 1905, i, 836) is best obtained by using methyl sulphate instead of methyl iodide. When it is dissolved in water with sodium nitrite and then acidified with acetic acid, *5-nitroso-4-amino-2-methylthiol-6-pyrimidone*, $C_5H_6O_2N_4S$, is precipitated as a white solid, which gives a blue solution in acids and a red in alkalis, and decomposes at 255°. It was reduced to 4 : 5-*diamino-2-methylthiol-6-pyrimidone* (I), by means of ammonium sulphide, only just sufficient to discharge the red colour due to the nitroso-compound being added. The substance was dried at 30—40°, and formed colourless crystals, m. p. 211°, which condense with carbamide to form 6 : 8-*dioxy-2-methylthiolpurine* (III) as a granular powder which gives the murexide reaction, is unaltered at 320°, and hydrolyses with difficulty to uric acid. *8-Amino-6-oxy-2-methylthiolpurine* (II) is also stable at 320°, gives the murexide reaction, and is hydrolysed by acids but not by alkalis, to uric acid. J. C. W.

Action of Azoimide on Thiocarbimides and Carbimides. Constitution of Azoimide. V. E. OLIVERI-MANDALÀ and F. NOTO (*Gazzetta*, 1913, **43**, i, 304—315).—By the action of azoimide on ethylcarbimide the authors have obtained ethylcarbamazide, and from phenylcarbimide, phenylcarbamazoimide, identical with that of Curtius and Hofmann (A., 1896, i, 648). From these results the authors consider it probable that azoimide and the azoimides should have the same structure, and they give reasons for preferring the cyclic formula $HN\!<\!\begin{smallmatrix}N\\ \|\\ N\end{smallmatrix}$, for azoimide to the chain formula which has been suggested.

By the action of azoimide on phenylthiocarbimide, one of two substances is obtained according to the temperature of reaction; at 40°, one molecule of azoimide reacts, yielding 4-phenyl-3-thiotetrazoline of Freund and Hempel (A., 1895, i, 193), whilst at 60—70° two molecules of azoimide are involved.

Ethylcarbamazoimide, $NHEt\cdot CO\cdot N_3$, prepared in ethereal solution, has b. p. 90°/28 mm., m. p. 10—14°; it forms large, tabular crystals. Its reactions are similar to those of other azoimides containing the group $\cdot NH\cdot CO\cdot N_3$. The action of water yields ethylamine azoimide, whilst alkalis yield ethylamine; the action of aniline on the substance leads to the formation of *s*-phenylethylcarbamide and aniline azoimide.

The action of azoimide on phenylthiocarbimide in ethereal solution is only complete at 40—50° (under pressure). When the phenylthiotetrazoline produced is dissolved in warm xylene, a decomposition occurs and triphenyl*iso*melamine, m. p. 190°, is obtained. Hofmann (A., 1886, 233) gave m. p. 185°. Triphenyl*iso*melamine platinichloride, $C_{21}H_{18}N_6,H_2PtCl_6$, was also prepared.



When an ethereal solution of azoimide and phenylthiocarbimide is heated under pressure at 60—70° for twenty-four hours, a *substance*, $C_7H_7N_7S$, is produced, which crystallises in soft, shining scales, m. p. 158—159°. When it is boiled with 50% potassium hydroxide, it yields azoimide and the thiocarbimide. Alcoholic sodium hydroxide eliminates 1 molecule of azoimide, yielding thiolphenyltetrazole, m. p. 150°. In view of these reactions the annexed structural formula is probable for the new substance. R. V. S.

Supposed Isomerism of Benzeneazoresorcinol. ARTHUR HANTZSCH (*Ber.*, 1913, **46**, 1556—1557).—Two isomeric forms of benzeneazoresorcinol have been described by Will and Pukall (A., 1887, 660). The product, m. p. 161°, is, in reality, a hydrate containing $\frac{1}{3}H_2O$, which can only be removed with difficulty. The dehydrated product has m. p. 169—170°, in agreement with that (170°) of the supposed isomeride. A very unstable *monohydrate* is obtained when acetic acid is added to a cooled alkaline solution of benzeneazoresorcinol. H. W.

[Preparation of Aminoazo-derivatives of Aromatic *m*-Diamines.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 258653).—It is found that 2 : 4-diaminophenetole, 2 : 4-diaminoanisole, or other ethers of 2 : 4-diaminophenols readily undergo bisdiazotisation by the ordinary methods, and when coupled with 2 mols. of a *m*-diamine-(substituted or otherwise) furnish brownish-red *compounds*. 2 : 4-*Diaminoanisole* and 2 : 4-*diaminophenetole* form colourless needles with m. p. 67—68°.

The nitro-ethers can be prepared as described by Willgerodt (A., 1879, ii, 716), and are readily reduced by the ordinary methods. F. M. G. M.

Nature of the Yellow and Red Helianthine Solutions and Chromoisomerism of Aminoazo-salts. ARTHUR HANTZSCH (*Ber.*, 1913, **46**, 1537—1556).—The solid, red helianthine is dissolved, not only by alkalis, but by all indifferent solvents in the form of yellow helianthine. Red helianthine solutions are only formed in the

presence of hydrogen ions. Yellow helianthine solutions are therefore obtained in the absence of hydrogen ions and not merely in the presence of hydroxyl ions.

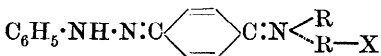
Yellow helianthines and red helianthines, as internal sulphonates, are optically very similar to the yellow and red chromoisomeric salts of aminoazobenzenes with acids. The generally very unstable, yellow acid salts are optically quite distinct from the yellow salts of the type $N_2Ph\cdot C_6H_4\cdot NMe_3X$, the absorption of which resembles that of azobenzene, and cannot therefore possess the analogous constitution

$$N_2Ph\cdot C_6H_4\cdot NMe_2,HX.$$

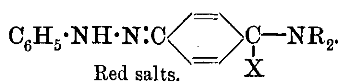
Since the quinonoid character of the red salts, $NHPh\cdot N:C_6H_4:NR_2X$, is established by the analogy of their absorption with that of magenta the yellow salts must have the formula

$$C_6H_5\cdot NHX:N\cdot C_6H_4\cdot NR_2$$

if structural isomerism is assumed. More probably, however, the yellow salts are themselves quinonoid, since they show a quinonoid band similar to that of the red salts and the aniline dyes, and hence must be regarded as valency isomerides of the red salts, thus:



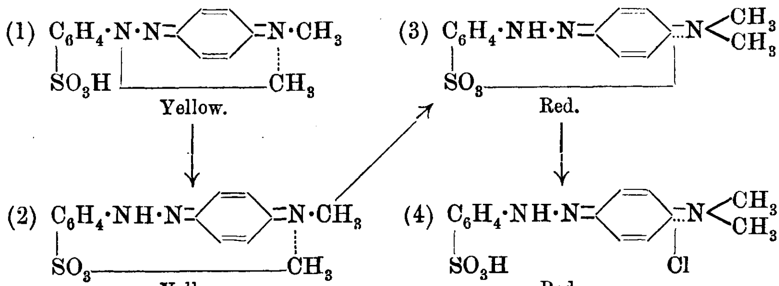
Yellow salts.



Red salts.

This conception leads to the adoption of a quinonoid structure for the corresponding aminoazobenzenes, $C_6H_5\cdot N\cdot N:C_6H_4:NR_2$, since the latter yield spectra closely analogous to those of the yellow acid salts.

In a similar manner, the transformation of yellow methyl-orange into red helianthine probably takes place in the following stages: The yellow sodium salt present in the alkaline solution is transformed by neutralisation of the alkali into the corresponding free acid (1) which immediately passes into the yellow internal salt (2) by wandering of the hydrogen atom; this yellow helianthine is converted by acid into the red valency isomeride (3), which, in the presence of a large excess of acid, passes into the analogously constituted red hydrochloride (4).



Whilst the dialkylaminobenzenes, including the halogenalkylates, which are incapable of isomerisation yield three series of salts, the

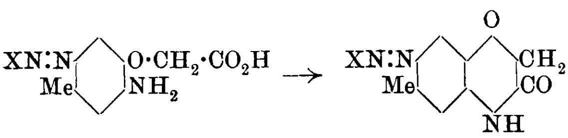
simple aminoazobenzenes can yield also a fourth graphite-black series which are possibly constituted according to the formula

$$C_6H_5\cdot NH(HX)\dot{:}N\dot{:}C_6H_4\dot{:}NH.$$

Red helianthines are best obtained in the pure condition by means of their *pyridine* salts, which, when dried at 100°, lose pyridine, leaving the pure helianthine.

Ethyl dimethylanilineazobenzoate, $NMe_2\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot CO_2Et$, forms leaflets of a reddish-golden colour, m. p. 160°. H. W.

[Preparation of Compounds Containing 3 : 4-Dihydro-1 : 4-oxazine-3-one Ring.] AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 259700).—When the azo-compounds obtained from 1-amino-2-naphthoxyacetic acids or 2-aminophenoxyacetic acids which contain an alkyl or alkyloxy-group in the meta-position are treated with acids, they lose water and furnish cyclic compounds according to the following scheme; and dyes in which X is represented by benzidine and other amino-compounds are described in the original. F. M. G. M.



Amount of *l*-Tyrosine in Proteins and the Accuracy of the Estimation of this Amino-acid. EMIL ABDERHALDEN (*Zeitsch. Physiol. Chem.*, 1913, **85**, 91. Compare this vol., i, 409).—*l*-Hydroxyproline, like tyrosine, shows a blue coloration with the Folin-Denis reagent. The preparation used had $[\alpha]_D^{20}$ $-72\cdot37°$. A synthetic product made by Leuchs has $[\alpha]_D^{20}$ $-76°$, whereas the value usually given is $[\alpha]_D^{20}$ $-81°$. Since tryptophan and hydroxytryptophan also react with the Folin-Denis reagent, their method for estimating tyrosine is of no value. E. F. A.

The Oxidative Degradation of the Proteins. OTTO EISLER (*Biochem. Zeitsch.*, 1913, **51**, 26—44).—On oxidation of proteins with calcium permanganate, "peroxyprotic" acids are produced, which, according to von Fürth, undergo hydrolysis with barium hydroxide with scission of oxalic acid, yielding deaminoprotic acids, which on further oxidation with permanganate yield "kyroprotic" acids. These, on treatment with barium hydroxide yield deaminokyroprotic acids. The deaminokyroprotic acid from caseinogen was prepared and described. The mercury salt contained 18·35% C, 2·62% H, 5·04% N, 0·4% S, 59·3% Hg, 1·7% amino-acid nitrogen (estimated by van Slyke's method), and 0·44% basic nitrogen. The probable constitution of this acid is discussed by the author. Sericoin was also prepared from silk-waste by Weyl's method. This also was submitted to oxidation by calcium permanganate, and the product hydrolysed by barium hydroxide. The substance thus obtained could not be oxidised further by permanganate in the cold. The mercury salt contained 8·02% C, 1·06% H, 3·40% N, 12·85% O, and 74·67% Hg. The amino-acid nitrogen was 2·21%, and the basic nitrogen 1·72%. The high

percentages of the latter and of the mercury are remarkable. They indicate that the simpler amino-acid groups are removed by oxidation, leaving the more basic groups intact, which seems to show that the protein is built up by branched chains from a more stable residue of diamino-acids. S. B. S.

The Amounts of Indole Produced by the Artificial Digestion or Putrefaction of Various Proteins. WACLAW VON MORACZEWSKI (*Biochem. Zeitsch.*, 1913, **51**, 340—354).—The amount of indole obtainable from various proteins by successive digestion with pepsin, trypsin, and putrefactive bacteria, both under the simplest conditions and in the presence of various foreign substances, such as fats, sugars, bile, etc., was estimated. The results are tabulated. S. B. S.

Hæmoglobin. The Magnesium Derivative of Mesoporphyrin. JEAN ZALESKI (*Ber.*, 1913, **46**, 1687—1691).—In order to introduce magnesium into mesoporphyrin (compare Willstätter and Forsén, this vol., i, 499), the substance is treated with magnesium, methyl or ethyl iodide, and a trace of iodine in ethereal solution; the product is a *compound*, $C_{38}H_{46}O_3N_4Mg$, or $C_{39}H_{48}O_3N_4Mg$, m. p. 335°, which in its absorption bands and easy scission of magnesium on treatment with dilute acid closely resembles rhodophyllin (Willstätter, A., 1908, i, 198); the *substance*, m. p. near 288°, obtained by elimination of magnesium, is distinct from the ethyl ester of mesoporphyrin originally taken. D. F. T.

Methæmoglobin. BÉLA VON REINBOLD (*Zeitsch. physiol. Chem.*, 1913, **85**, 250—285).—It is regarded as established that methæmoglobin takes a middle position between hydroxyhæmoglobin, $Hb{<}\overset{O}{\underset{O}{|}}$, and reduced hæmoglobin, Hb. It is uncertain whether it has Zeynek's formula $Hb(OH)_2$ or Küster's formula Hb–OH.

It is now proved by spectrophotometric and gasometric measurements that the reaction between potassium ferricyanide and hydroxyhæmoglobin is quantitative, one molecule of the cyanide being required to displace a molecule of oxygen as shown by the equation

$$Hb{<}\overset{O}{\underset{O}{|}} + K_3FeCy_6 + H_2O = Hb{\cdot}OH + K_3HFeCy_6 + O_2,$$

which is in agreement with Küster's formula. E. F. A.

Keratin of White Human Hair. HANS BUCHTALA (*Zeitsch. physiol. Chem.*, 1913, **85**, 246—249).—The result of hydrolysing white human hair is as follows: Glycine, 9·12; alanine, 6·88; leucine, 12·12; glutamic acid, 8·0; phenylalanine, 0·62; tyrosine, 3·3, and cystine, 11·55%. The amounts of cystine, glycine, and alanine are abnormally large. Hair keratin closely resembles that from sheep's wool.

E. F. A.

Keratin of the Scales of Manis japonica. HANS BUCHTALA (*Zeitsch. physiol. Chem.*, 1913, **85**, 241—245).—The keratin of *Manis japonica* yields amino-acids on hydrolysis, namely, glycine 1·33%,

alanine 12·0%, valine 4%, leucine 10·25%, proline 3·5%, glutamic acid, 3·5%, phenylalanine 2·67%, tyrosine 13%, and cystine 4·5%. The amount of alanine is abnormal, other keratins yielding 1·2%—1·8%. The proportion of tyrosine is likewise unusually large. E. F. A.

Keratin of Snake Skins (Boa Constrictor and Python). HANS BUCHTALA (*Zeitsch. physiol. Chem.*, 1913, **85**, 335—340).—The distribution of the nitrogen and the percentage of certain monoamino-acids is determined in the keratin of snake skins, and compared with that in other keratins. The distribution of the nitrogen is much the same in all keratins, but they differ widely in the proportions of the individual amino-acids which they contain. Snake-skin keratin contains a high proportion of tyrosine and leucine. E. F. A.

Action of Quinones on Wool and Other Protein Substances. WILHELM FAHRION (*Zeitsch. angew. Chem.*, 1913, **26**, 328. Compare *ibid.*, 1909, **22**, 2138).—A claim for priority against Scharvin (this vol., i, 661). H. W.

Reactions on Dyeing Animal Fibres. WILHELM SUIDA (*Zeitsch. physiol. Chem.*, 1913, **85**, 308—323).—Wool loses more of its substance in a faintly acid bath than in a neutral bath when heated under the conditions usual for dyeing. The difference is especially marked on subsequent treatment with an alkaline bath. Wool in both cases mainly gives up basic substances to the bath, so that, normally, during dyeing the wool itself becomes acid.

When wool is heated with phenols and acetic acid, the presence of the phenol on the fabric cannot be established, using ferric chloride. The substituted nitrophenols dye the wool, the intensity increasing with the acidity of the phenol. These colours are readily removed by faintly alkaline washes.

Wool fixes phenolcarboxylic acids, but no ferric chloride reaction is shown, indicating that the phenylhydroxyl group has combined with some constituent of the wool.

Whereas *p*-benzoquinone, toluquinone, *o*-3 : 6-xyloquinone, etc., in a weak acetic acid bath dye wool intensely, *p*-2 : 5- and *m*-2 : 5-xyloquinone, also thymoquinone, anthraquinone, and phenanthraquinone have no such action. The active para-quinones all contain the grouping $-CO\cdot CH\!:\!CH\cdot CO-$, which is absent from the inactive quinones.

Naphthazarin, a dihydroxy-α-naphthaquinone, dyes wool a deep violet-brown. The colour is not removed even by strong ammonia.

The quinones are supposed to give rise to quinoneanilide-like compounds with the amino-substances of the wool. Silk is not dyed so quickly by quinones as wool. E. F. A.

Precipitation of Enzymes from their Solutions by Moist Aluminium Hydroxide. WILLIAM H. WELKER and JOHN MARSHALL (*J. Amer. Chem. Soc.*, 1913, **35**, 822).—When solutions of the following enzymes were shaken with moist aluminium hydroxide, the enzymes were quantitatively removed: peroxydase and oxydase (aqueous extract of potato), pepsin (aqueous or 0·2% HCl solution), rennin

(aqueous solution), trypsin (0·5% Na_2CO_3 solution, 30% alcoholic extract of pancreas, or 30% alcoholic extract of pancreas containing an equal volume of 1% Na_2CO_3), and amylase and lipase (30% alcoholic extract of pancreas). The amylase of saliva was not completely removed by this treatment; the filtrate was capable of converting starch paste into soluble starch, but could not effect further hydrolysis. Pepsinogen could be precipitated quantitatively, but only with great difficulty. E. G.

Action of Hydrogen Chloride and Ammonia Gas on Invertase. VI. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1913, **85**, 225—230. Compare this vol., i, 113, 541, 662).—Invertase, when treated in turn with dry hydrogen chloride and dry ammonia, does not recover its hydrolytic activity. The groups destroyed by the acid are not restored when this is neutralised as is the case with diastase. This behaviour is regarded as further evidence in favour of the formation of anhydride by the action of the acid. E. F. A.

Action of Nitrous Oxide on Invertase. VIII. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1913, **85**, 392—398).—On subjecting invertase to the action of dry nitrous oxide, oxidation takes place, and subsequently a little nitrous oxide is fixed by the enzyme. The hydrolytic activity of the enzyme is not affected. The treatment increases the acidity of the enzyme, although in one instance the acidity decreased. The amount of amide and amino-nitrogen is less after treatment. The experiments again emphasise the difference between invertase and diastase. E. F. A.

Action of Hydrogen Chloride and Ammonia on Diastase. V. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1913, **85**, 97—111).—The action of dry hydrogen chloride and ammonia separately on diastase has already been studied (compare this vol., i, 113, 541). The enzyme has now been treated first with hydrogen chloride, and then with an excess of dry ammonia gas. The resulting increase in weight, acidity and nitrogen, shown by means of formaldehyde, was the same as when the enzyme was acted on by ammonia alone. The treatment with ammonia restores the hydrolytic activity of the diastase, whereas if the enzyme, after treatment with hydrogen chloride, is neutralised with aqueous ammonia, it remains inactive. E. F. A.

Action of Nitrous Oxide on Diastase. VII. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1913, **85**, 292—307).—Dry nitrous oxide gas was passed over diastase in the manner described for hydrogen chloride or ammonia. Whereas an enzyme preparation containing milk sugar absorbed about 3% of the gas, a purified enzyme material absorbed three times this amount. Only a small quantity of the gas can be pumped off in a vacuum. The nitrous oxide does not cause either hydrolytic decomposition or anhydride formation. The hydrolytic activity of the purified enzyme is largely destroyed by the treatment, but the presence of the milk sugar protects the enzyme from harm. E. F. A.

Action of Salts of Metals on the Saccharification of Starch by Amylolytic Ferments. C. GERBER (*Bied. Zentr.*, 1913, **42**, 265—268; from *Compt. Rend. Soc. Biol. Paris*, 1911, **70**, 139, 391, 547, 724, 726, 728).—Alkali salts of monobasic acids increase the rate of saccharification when present in small amounts, whilst large amounts have a retarding effect; acid salts act similarly to the corresponding acids. The salts of monobasic organic acids act similarly; the retarding effect increases with the mol. wt.

Magnesium salts in small amounts have no action, and larger amounts have a retarding effect. Manganese, ferric and aluminium salts have a quickening effect in small amounts, and a retarding effect when present in large quantities. Ferrous salts retard or inhibit saccharification according to the amount.

Cadmium and zinc in very small amounts have a retarding effect, whilst moderate amounts inhibit saccharification. Still larger amounts, up to a certain point, are, however, favourable. Similar results were obtained with copper and gold salts.

Salts of platinum and palladium in very small amounts are favourable; the action is very suddenly reversed as the amounts increase. N. H. J. M.

Synthesis of Glucosides of the Alcohols by means of Emulsin; Reversibility of Ferment Actions. ÉMILE BOURQUELOT and MARC BRIDEL (*Ann. Chim. Phys.*, 1913, [viii], **28**, 145—218).—A résumé and discussion of results already recorded in the following abstracts: 1906, ii, 386; 1911, i, 1053; 1912, i, 522, 592, 593, 672, 738, 790, 928, 946; this vol., i, 212, 303. T. A. H.

Behaviour of Emulsin in Presence of Pyridine. GÉZA ZEMPLÉN (*Zeitsch. physiol. Chem.*, 1913, **85**, 415—426).—β-Glucosides are hydrolysed by emulsin in presence of 12% of pyridine. When the proportion of pyridine is increased, hydrolysis is retarded, and ceases in 20% solution. In presence of pyridine, amygdalin is converted into *iso*amygdalin. E. F. A.

Use of Increasing Proportions of Dextrose in the Biochemical Synthesis of β-Methylglucoside. Influence of the Glucoside Formed on the Arrest of the Reaction. ÉMILE BOURQUELOT and ÉM. VERDON. (*Compt. rend.*, 1913, **156**, 1638—1640; *J. Pharm. Chim.*, 1913, [vii], **7**, 575—579).—In methyl alcohol (70%) the quantity of glucoside formed increases proportionately as the quantity of dextrose in solution increases up to 12%, above which the amount of glucoside formed diminishes slightly. The presence of methylglucoside in the solution has a marked inhibiting effect on the amount of glucoside synthesised. The quantity of glucoside necessary to check the reaction is proportional to the amount of dextrose in the solution. W. G.

Enzyme Action. XIX. Urease. II. Observations on Accelerative and Inhibitive Agents. HENRY E. ARMSTRONG, M. S. BENJAMIN, and EDWARD HORTON (*Proc. Roy. Soc.*, 1913, *B*, **86**, 328—343. Compare A., 1912, i, 594).—The manner in which the

activity of urease is affected by the presence of various substances together with the urea has been studied throughout the whole course of the change with considerable accuracy. The results are expressed graphically.

Both strong acids and carboxylic acids such as $M/50$ aspartic and salicylic acids prevent action. Boric acid in all strength retards action. Guaiacol and resorcinol at first retard and subsequently accelerate hydrolysis. *p*-Benzoquinone is poisonous, and quinol and quinol monomethyl ether, both of which are easily oxidised to *p*-benzoquinone, soon stop action. Glycine, asparagine, and carbonic acid all accelerate action.

It is emphasised that in presence of carbonic acid the rate of change approximates to a "linear" character.

Hydrogen cyanide accelerates action.

Saligenin, acetaldehyde, benzaldehyde and salicylaldehyde are moderately active depressants.

It is considered that enzymic changes would be found to take place at approximately constant rates were it not that they are subject directly and indirectly to considerable retardation by the products of change; probably the products of change have an affinity for the enzyme which is actually greater than that which obtains between the hydrolyte and the enzyme.

Enzyme action takes place entirely at the surfaces of colloid particles suspended in the solution of the hydrolyte, and not between substances which are all in true solution. E. F. A.

Fermentations with Yeast in the Absence of Sugar. XI. Carboxylase. CARL NEUBERG and P. ROSENTHAL (*Biochem. Zeitsch.*, 1913, **51**, 128—142).—The carboxylase from yeast, which causes the decomposition of pyruvic acid, can be distinguished from the sugar ferment (zymase) by various reactions. The latter does not act in the presence of chloroform, whilst the former retains its full activity, especially in the presence of "buffers," which prevent great changes in the reaction of the fermenting liquid. For this latter purpose, solutions of either alkali salts of pyruvic acid in the presence of free arsenious or boric acids or free pyruvic acid in the presence of borates or arsenites can be used. Similar results were obtained both with fresh and dried yeasts of pure culture. The carboxylase acts in a much shorter time than the zymase. Furthermore, if maceration juices are preserved at room temperature, the zymase activity is readily lost, whereas the carboxylase remains active over comparatively long periods. Furthermore, the zymase is readily destroyed by heating to 50°, whereas the carboxylase activity remains intact. There is a further difference in that the zymase loses its activity on dialysis, whereas the carboxylase does not, especially if the dialysed solution is kept for some time. Attention is called to the fact that the fermentation of sugar must precede in stages, the C_6-sugar being apparently broken down into C_3-substances, such as pyruvic acid. The ferment causing the evolution of carbon dioxide from the latter can remain intact, even after the zymase is destroyed. S. B. S.

Paralysis and Activation of Zymase and Catalase. HENRI VAN LAER (*Centr. Bakt. Par.*, 1913, ii, **37**, 529—534. Compare A., 1912, i, 1043).—In an earlier paper it was stated that the addition of papain depresses, and malt extract increases, the activity of zymase and catalase. The former is attributed to impurities in the juice of the *Carica papaya* which digest the two enzymes.

The activation of the enzymes by extract of malt may be due, firstly, to direct stimulation of the zymase and catalase by impurities in the extract of malt; secondly, by inhibition of the antagonistic enzyme (protease) by impurities, or else to the existence of pro-enzymes—prozymase and procatalase—combinations of the enzymes with a carbohydrate, such compounds being saccharifiable by amylase.

Experiments with a Munich bottom yeast and a Mons top yeast have been made, and again show a depressing action of the papain on the catalase and zymase in the yeast juice. Tests with extract of malt exhibit activation of the enzymes during the initial stages of the experiment with a pronounced depression later on. This action is ascribed to the presence of proenzymes in the yeast-juice. At the moment of fission a positive effect is produced, and this is followed by their digestion by impurities in the malt extract. H. B. H.

Arseno-compounds. AUGUST MICHAELIS and ARTHUR SCHÄFER (*Ber.*, 1913, **46**, 1742—1743).—Since arsenic compounds frequently have a higher molecular weight than the corresponding nitrogen compounds, the authors have determined the molecular weight of arsenobenzene and *p*-arsenotoluene respectively.

Arsenobenzene, slender, white needles, has m. p. 212°, not 196° as previously given (A., 1881, 722). It is readily oxidised in solution to phenylarsine oxide, which, even in small quantities, greatly depresses the m. p. A solution of arsenobenzene in benzene, when allowed to evaporate spontaneously in contact with air, leaves a resinous product consisting solely of phenylarsine oxide. In boiling benzene solution, arsenobenzene has mol. wt. at 399·8 (calc. 304).

p-Arsenotoluene separates from benzene in small plates, m. p. 202° (from chloroform, however, in needles, m. p. 184°; compare A., 1902, i, 411). In solution, it is readily oxidised to *p*-tolylarsine oxide. It has a normal molecular weight when dissolved in dry phenol. In the presence of a trace of moisture, on the other hand, a constant freezing point of the solution is not observed. H. W.

The Displacement of Metals from their Phenyl Compounds. SIEGFRIED HILPERT and GERHARD GRÜTTNER (*Ber.*, 1913, **46**, 1675—1691).—Although the action of various metals on the organo-metallic compounds has been fairly well investigated in the aliphatic series, the corresponding behaviour with the compounds of the phenyl series has been less well studied (compare Hilpert and Grüttner, A., 1912, i, 939). It is now discovered that at the temperature of the experiment (200—350°) the metals of comparatively low m. p. generally react with the organo-metallic compounds causing a displacement of the other metal, and that if the two metals do not affect one

another the reaction may proceed quantitatively. If the m. p. of the resulting mixture of metals lies below the temperature of the experiment the extent of the interaction appears to be dependant on the relative quantities of the two metals in the mixture.

Magnesium and aluminium react with mercury diphenyl so readily that no external heating is necessary; magnesium diphenyl (compare Fleck, A., 1893, i, 622) does not inflame in the air unless breathed upon; it forms feathery needles (from ether), which melt at the temperature of the hand, almost immediately afterwards passing into the ether-free, amorphous substance. For the reaction between zinc and mercury diphenyl (in a hydrogen atmosphere), heat has to be applied when the chemical change occurs with quantitative displacement of mercury; zinc diphenyl, needles, m. p. 105—106°, b. p. 280—285°, both in hydrogen, is very sensitive to air and moisture, the former converting it into zinc oxide and diphenyl, and the latter into zinc hydroxide and benzene; it is inflamed by fuming nitric acid, and reacts with chloroform, producing triphenylmethane; with iodine in benzene solution it produces zinc phenyl iodide, which is slowly converted further into zinc iodide; with mercury it reacts to a small extent, giving a trace of mercury diphenyl.

Contrary to expectation, aluminium reacts scarcely at all with zinc diphenyl, possibly on account of the protecting film of oxide; in order to determine the relative reactivity of these two metals towards the metallic phenyl compounds, the two metals were allowed to react simultaneously with the same quantity of mercury diphenyl under such conditions that the zinc if alone would form zinc diphenyl; it was found that the relative amounts of aluminium triphenyl and zinc diphenyl were 99 : 1. Magnesium decomposes completely the phenyl derivatives of aluminium and zinc, whilst mercury has no effect on them; the metals magnesium, aluminium, zinc, and mercury, therefore, stand in the same relative order of activity as in the ordinary potential series.

Cadmium exhibits but little tendency to form organo-metallic compounds and with the mercury alkyls gives rise only to hydrocarbons; with mercury diphenyl it is found that cadmium reacts, forming cadmium diphenyl, but the extent of the reaction depends on the composition of the liquid cadmium amalgam produced, and therefore on the relative amount of cadmium applied; by using an apparatus in which the liquid reaction product could be repeatedly treated in a hydrogen atmosphere with fresh cadmium until more than ten atomic proportions had been applied, a specimen of *cadmium diphenyl*, colourless prisms containing 25% of mercury diphenyl, was obtained; it is stable when dry, but in benzene solution it undergoes atmospheric oxidation. From the amount of cadmium necessary in the above experiment and the fact that the product when heated with excess of mercury quantitatively regenerates mercury diphenyl, it is evident that cadmium falls after mercury in the series, showing the relative activity of the metals towards the formation of phenyl compounds.

The behaviour of bismuth is somewhat analogous to that of cadmium; mercury diphenyl heated with an excess of bismuth and bismuth triphenyl heated with an excess of mercury both yield a mixture of

the phenyl derivatives of the two metals; the relative proportions in the mixed products indicate that bismuth falls before mercury in the series indicating relative activity in these compounds. With the six metals investigated above, therefore, cadmium alone falls into a position different from that occupied in the ordinary potential series.

The quadrivalent metals lead and tin appear to form a special class, for they fail to react with mercury diphenyl, whilst their tetraphenyl derivatives are entirely unaffected by magnesium.

The behaviour of the metallic haloids towards metallic phenyl compounds is very different from that of the corresponding free metal. Mercuric bromide reacts quantitatively with an ethereal solution of magnesium phenyl bromide producing *mercury phenyl bromide*, leaflets, m. p. 275°, if the original reagents are in approximately equimolecular proportions; with an excess of the organo-magnesium compound, mercury diphenyl is formed, but in only 40% yield. In a similar manner, mercury α-naphthyl bromide, m. p. 202°, can be produced, which even with a large excess of magnesium α-naphthyl bromide gives only a small quantity of the diphenyl compound. Cadmium chloride also reacts with magnesium phenyl bromide and magnesium α-naphthyl bromide, but the products were not isolated.

It is remarked that the sensitiveness of the phenyl compounds towards air and water diminishes with increasing atomic weight and electro-negative character of the metal.

The action of the alkali metals on mercury diphenyl or zinc diphenyl, with or without a solvent, was never found to yield a deposit of mercury until water was added (compare Acree, A., 1903, i, 724), and it is believed that an additive product is first produced.

In agreement with the earlier negative results (Smith, Barnett and Hall, A., 1900, i, 89) on the existence of a tungsten methyl iodide (Cahours, 1862), the authors were unable to isolate any compound of such nature. D. F. T.

Physiological Chemistry

Narcosis. I. The Relationship between Narcosis and Oxygen Respiration. HANS WINTERSTEIN (*Biochem. Zeitsch.*, 1913, **51**, 143—170).—The author gives a critical review of the various experiments which indicate a relationship between narcosis and diminution of oxygen respiration. He draws the conclusion that narcosis cannot be explained simply as a result of diminished oxidation, citing amongst other experiments the fact that certain ascarids, which are anoxybiotic, are particularly susceptible to narcosis. It seems more probable that narcosis and inhibition of oxidation are concomitant results of some more general action.

S. B. S.

The Chlorine Content of Blood and its Division between the Corpuscles and Serum. The Permeability of Corpuscles for Inorganic Substances. J. SNAPPER (*Biochem. Zeitsch.*, 1911, **51**, 53—61).—The chlorine was estimated in the total blood, and in the serum and corpuscles separately. It was found that the ratio of the chlorine in the corpuscles to that in the serum was approximately constant both in the dog and in man, being about 40%. As this is very nearly the ratio of the intraglobular fluid to the total volume of the erythrocytes as found by Hamburger, the conclusion is drawn that there is an even distribution of the inorganic contents of blood between the serum and the formed elements. S. B. S.

Formation of Methæmoglobin. WOLFGANG HEUBNER (*Arch. expt. Path. Pharm.*, 1913, **72**, 241—281).—Whereas the injection of phenacetin into the blood of carnivora causes the formation of methæmoglobin, dimethylphenacetin is without effect. Phenacetin outside the body has no action on blood, indicating that the active substance is formed from it in the organism.

Parallel experiments with derivatives of *o*-, *m*-, and *p*-aminophenols show the meta-derivatives to be barely poisonous, and, whereas the ortho- and para-derivatives are equally poisonous for dogs, the ortho-compound is the stronger in the case of cats, which are extremely sensitive to both aminophenols. Rabbits are resistant to these poisons.

Since each aminophenol molecule reacts several times with hæmoglobin molecules, the reaction is explained on the hypothesis that the *o*- and *p*-aminophenols are oxidised to *o*- or *p*-benzoquinone-imine, and that this actually reacts with hæmoglobin, 2(Hb⁚Fe), forming aminophenol and methæmoglobin, 2(Hb⁚Fe·OH). The change involves conversion of bivalent into tervalent iron, the active agent being the quinone. This is in agreement with the formation of hæmoglobin by the agency both of oxidising and reducing agents.

Quinol acts similarly, but has no effect in the absence of oxygen. *p*-Benzoquinone works energetically in the absence of oxygen.

Quinol and catechol readily produce methæmoglobin in test-tube experiments, whereas resorcinol is without effect. Similarly, pyrogallol is active, chloroglucinol inactive.

Aniline is active, dimethylaniline has no effect, although the isomeric *m*-xylidine is also active in producing methæmoglobin.

The substitution of the para- and of both ortho-positions in aniline by chlorine does not alter its activity. Apparently the aniline nitrogen is oxidisable without oxidation previously taking place at the ortho- or para-positions in the nucleus to form a quinone. Acetylation of the nitrogen in trichloroaniline has little effect; in dichloroaniline some lessening of the activity is brought about on acetylating.

Hæmoglobin is oxidised by hydroxylamine even in the absence of oxygen. The introduction into aniline derivatives of two methyl groups occupying the one the ortho-position to nitrogen, and the other either the ortho- or para-position lowers the oxidising

activity. Phenetidine, for example, has hardly any action in producing methæmoglobin.

Emphasis is laid on the difference between rabbits, dogs, and cats in the reactions between the blood and aromatic oxidising agents.

The spectrum of pure methæmoglobin does not show the two oxyhæmoglobin bands in the yellow and green. When these are seen, oxyhæmoglobin is present as impurity. E. F. A.

The Change in the Permeability of Blood Corpuscles on Addition of Acid. J. SNAPPER (*Biochem. Zeitsch.*, 1913, **51**, 62—88).—The results of Hamburger are confirmed, according to which the addition of acid causes a swelling of the corpuscles and a passage of chlorine from the serum into the corpuscles. The influence of the addition of acids to the blood both *in vivo* and *in vitro* was investigated. The diffusible and non-diffusible alkali was estimated. For this purpose, the total serum was titrated with *N*/25-tartaric acid, and also the filtrate after precipitation with alcohol, which throws down the proteins with the alkali combined with proteins (non-diffusible alkali). Congo-red paper was used as indicator. Both *in vivo* and *in vitro*, there was found to be a relative increase of the diffusible as compared with the non-diffusible alkali as a result of the action of acids. A possible explanation of the action of acids as regards the distribution of chlorine between serum and corpuscles seemed therefore to be the relative increase of $\cdot SO_4$ ions in the corpuscles when sulphuric acid was employed, as compared with the serum, due to the larger amount of alkali set free from proteins in a diffusible form and a subsequent interchange of $\cdot SO_4$ and Cl ions between serum and corpuscles. As, however, a change in distribution of chlorine could not be brought about by addition of neutral sulphates alone without addition of acids, this explanation is inadequate. It is assumed, therefore, that the acids act on the proteins and so alter the permeability of the cells to ions. A similar change of distribution could not be brought about by lipoid solvents, such as chloroform, even when the latter is present in sufficient quantities to cause a small amount of hæmolysis. S. B. S.

The Biological Significance and Metabolism of the Proteins. VII. The Amino-Nitrogen Titratable in the Presence of Formalin in the Blood Corpuscles of Various Animals. A. COSTANTINO (*Biochem. Zeitsch.*, 1913, **51**, 91—96).—The proteins were separated by barium salts by the method of Buglia and Costantino. In both the serum and corpuscles, nitrogenous substances titratable in the presence of formalin were found. The quantity found was small in the case of serum, but relatively large in that of corpuscles. In non-nucleated, the quantity is only about half that existing in nucleated corpuscles. In the case of mammals and turkey, the amount found in the serum is about the same. The author calls attention to the importance of examining chemically the corpuscles when investigating various problems of metabolism. S. B. S.

Hæmolysis by Chemical Agents. PHILIPP EISENBERG (*Centr. Bakt. Par.*, 1913, i, **69**, 173—225).—The author has carried out a long series of experiments on the action of salts, acids, alkalis, and various organic substances (including tetanolysin and vibriolysin) on blood corpuscles. He has investigated, amongst other factors, the influence of hypertonicity, synergism, and antagonism. He summarises his results, from which, however, no extensive generalisations can be made. S. B. S.

Blood Lipoids and Phagocytosis. B. STUBER (*Biochem. Zeitsch.*, 1913, **51**, 211—233).—A method is described by means of which the phagocytic index of leucocytes can be determined, thrush spores being employed as the foreign object, as they can be readily stained by Leishmann's method. For *in vitro* experiments human blood was employed, and for *in vivo* experiments cats and sometimes rabbits were used. It was found that cholesterol by itself greatly diminishes the phagocytic index, whereas lecithin has no action. On the other hand, lecithin greatly diminishes, and even obliterates when in sufficient quantity, the power of cholesterol to reduce the phagocytic index, provided that it has not been previously heated. If the cholesterol and lecithin are heated after mixing, they do not together diminish the phagocytic index. Similar results were obtained by both the *in vivo* and *in vitro* experiments. It appears, therefore, that cholesterol acts directly on the phagocytes, and destroys their phagocytic action, but in the presence of lecithin a lecithin-cholesterol compound is formed. This cannot, however, be produced if lecithin is heated before the two substances are mixed. S. B. S.

The Acetonitrile Reaction. FR. PORT (*Biochem. Zeitsch.*, 1913, **51**, 224—228. Compare Reid Hunt, A., 1905, ii, 847; 1910, ii, 736; Trendelenburg, A., 1911, ii, 50).—The author throws doubt on Reid Hunt's acetonitrile reaction with mice for detection of thyreogenic substances in the blood on the ground that the susceptibility of the animals to the poison is so very variable that it is impossible to determine the limiting dose. S. B. S.

Influence of Fatigue on the Amount of Dialysable Compounds, which React with Triketohydrindenhydrate, in the Serum. EMIL ABDERHALDEN and ARNO ED. LAMPÉ (*Zeitsch. physiol. Chem.*, 1913, **85**, 136—142).—After severe fatigue in the dog, the blood-serum contains less of the substances referred to in the title. Admixture of the serum either of normal or fatigued dogs with cooked muscle produced no change. A similar result was obtained with other tissues. W. D. H.

The Fermentative Properties of Blood. I. A Peptolytic Ferment of Normal Dog's Serum. LUDWIG PINCUSSOHN (*Biochem. Zeitsch.*, 1913, **51**, 107—115).—It is known that by injection of various proteins into animals, the blood acquires peptolytic properties. The author shows that normal dog's serum

possesses a ferment capable of hydrolysing the peptone of dog's muscle, prepared by treating the muscular tissue with 70% sulphuric acid in the cold, and precipitating by alcohol, after the removal of the sulphuric acid with barium hydroxide. The serum does not, however, digest a similar peptone prepared in the same way from cat's muscle, or other peptones from foreign substances.

S. B. S.

The Influence of Diet on the Activity of Ptyalin. H. VAN TRIGT (*Zeitsch. physiol. Chem.*, 1913, **85**, 156—160).—The author examined his saliva at frequent intervals; each meal increased its diastatic activity; the increased action was greatest after a carbohydrate meal, and least after a protein meal. W. D. H.

Fluorine in the Animal Organism. II. Skeleton, Cartilages, and Tendons. ARMAND GAUTIER and PAUL CLAUSMANN (*Compt. rend.*, 1913, **156**, 1425—1430. Compare this vol., i, 677).—An examination of bones, teeth, cartilage, and tendons for fluorine. Bones and teeth, either human or animal, are comparatively rich in fluorine, the content of the diaphyse portion of the bones being about four times as great as that of the epiphyse, in the case both of an elderly man and a new-born infant. The teeth approach the diaphyse in fluorine content. The skeleton of fish contains practically the same amount of fluorine as the scales, and a complete analysis of these organs shows a marked analogy. Cartilage and tendons are very low in fluorine content. W. G.

Is it Possible Artificially to Increase the Amount of Phosphatides in Brain? ERNST SALKOWSKI (*Biochem. Zeitsch.*, 1913, **51**, 407—422).—Commercial preparations of kephalin, when administered by the mouth, are well tolerated, and all but a small percentage is resorbed. Its ingestion causes an increased phosphoric acid output in the urine, both absolute and relative as compared with the nitrogen. In contrast to egg-yolk lecithin, kephalin does not accumulate in the liver, but appears to accumulate in the brain. Rabbits were used for the experiments, and the quantities of phosphatides in the organs were estimated by the following method. The organ (brain) was first extracted with hot alcohol, and the residue was then extracted with a mixture of equal volumes of absolute alcohol and benzene. The residues from both extracts were then dissolved in benzene, the extract thus made was filtered, and the phosphorus was estimated in the filtrate after the solvent had been evaporated off. S. B. S.

Normal and Pathological Alteration in the Lens of the Eye. ADOLF JESS (*Zeitsch. Biol.*, 1913, **61**, 93—142).—During life there is an increase in the weight, the protein, and the water of the crystalline lens, and to a smaller degree in the substances which are soluble in ether. The increase in protein is greater than that in water. Among the proteins, an "albumoid" is more abundant in old age than crystallin, which is the more important in youth.

In senile cataract, the weight, the water, and the protein all decrease, and the loss of water is greater than that of protein; among the proteins crystallin is most diminished; the amount of albumoid is high; the amount of fat, cholesterol, and lecithin are not increased. In traumatic cataract there is no decrease in weight, but both the proteins decrease in amount; fat, cholesterol, and lecithin do not increase, but the relative and occasionally the absolute amount of water usually rises. In senile cataract, the cystine reaction lessens owing to the disappearance of crystallin; the albumoid has no cystine group in its molecule. In old traumatic cataracts the cystine reaction is also negative, owing to the total absorption of crystallin. W. D. H.

Chemical Investigation of Calcified Aortæ. FRANZ AMESEDER (*Zeitsch. physiol. Chem.*, 1913, **85**, 324—334. Compare A., 1911, ii, 219).—A further series of analyses of calcified aortæ are given with full details of the experimental methods. E .F. A.

A Pigment in Melanosis of the Mucous Membrane of the Large Intestine. EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1913, **85**, 92—95).—A brown pigment was separated from a melanotic large intestine. An elementary analysis is given, which agreed closely with that of a pigment obtained from tryptophan (A., 1912, i, 521). W. D. H.

Ferments of the Pancreas. CESARE SERONO and ANTONIETTE PALOZZI (*Chem. Zentr.*, 1913, i, 1212—1213; from *Arch. Farmacol. sperim.*, 1913, **14**, 501—508).—All the ferments of the pancreas are contained in the glycerol extract, expressed under high pressure, and their activity remains for a long time unimpaired. The proteöclastic activity increases on keeping, that is, with the conversion of trypsinogen into trypsin. In addition to diastase, there is a ferment capable of acting on maltose. The tryptic power is not destroyed by digestion with pepsin. Only the proteoclastic ferment is precipitated by a mixture of sodium chloride and magnesium sulphate. S. B. S.

Autolysis of the Thymus. M. KASHIWABARA (*Zeitsch. physiol. Chem.*, 1913, **85**, 161—172).—Kutscher considered that during autolysis the thymus underwent characteristic changes, especially in the amount of lysine and ammonia formed; the present research does not support this view. The course of autolysis in this organ does not materially differ from that of the liver, and there is no increase in the amount of ammonia formed; in both organs its nitrogen is about 10% of that in the soluble nitrogenous substances. Among the decomposition products, lysine was found, also leucine and tyrosine in small quantities. There are certain differences between liver and thymus in the partition of nitrogen; the mono-amino-acids and proteoses are only about half as abundant in the thymus as in the liver, but the group diamino-acids + peptone + ammonia is twice as great, and the purine bases three times as great. W. D. H.

Extractive [Mytilitol] in the Valve Muscles of Mytilus edulis. BAREND C. P. JANSEN (*Zeitsch. physiol. Chem.*, 1913, **85**, 231—232).—On extraction of the valve muscles of *Mytilus edulis* with water and precipitation of certain impurities with colloidal ferric hydroxide, a substance, $C_6H_{12}O_5,2H_2O$, crystallises from the filtrate; the name *mytilitol* is applied to it. It forms an *acetate*, m. p. 182°, crystallising in microscopic needles, which gives up five acetyl groups on hydrolysis. Mytilitol contains a six-carbon ring, and is regarded as an isomeride of quercitol. The muscles also contain histidine, betaine, taurine, and about 1·5% of glycogen.

E. F. A.

The Influence of Nutrition on the Secretion of Indole and Indican by Healthy Individuals. WACLAW VON MORACZEWSKI and E. HERZFELD (*Biochem. Zeitsch.*, 1913, **51**, 314—339).—The amount of substance giving the indole reaction, which is obtained by the distillation of urine, was determined under different conditions of nutrition, and it was found that the amount increased on a diet of fats, of vegetables, and of gelatin, but diminished on a carbohydrate or sugar diet. The addition of proteins caused an increased output as compared with sugars, but a diminished output as compared with fats. No relationship could be found between the indole of the fæces and the indican of urine. The indole of the fæces was estimated both directly as excreted, and after submission to a secondary putrefaction. Fat was found to increase both the indole directly excreted and the amount obtained after secondary putrefaction. The same was found with proteins, whereas carbohydrates had the opposite effect. Vegetables protect proteins from putrefaction, so that the indole directly excreted is diminished, and that obtained by secondary putrefaction is increased to the same extent. The nitrogen and chloride of the fæces are affected in a similar way. At times a relationship between the indican of the urine and the indole of the fæces is to be found, the two rising and falling together; in the case of gelatin, sugar, and fat nutrition, the general metabolism exerts some influence on the amount of indole resorbed from the intestine; but the amount of indican of the urine is regulated by another factor in addition to its resorption from the alimentary tract, namely, the capacity of the organism to destroy the absorbed substance.

S. B. S.

Tryptic Digestion by the Urine. FILIP JOHANSSON (*Zeitsch. physiol. Chem.*, 1913, **85**, 72—90).—In the normal urine of man, ox, and horse, no proteolytic enzyme precipitable by caseinogen in an alkaline solution was obtained. In albuminous urine, it is sometimes present. From the urine of the ox, and to a small degree of the horse, the caseinogen precipitate contains an enzyme which favours the proteolytic action of fibrin prepared from ox blood, but has no such action on ox-serum. Trypsinogen is absent from the urine. The substance in question is possibly a kinase.

W. D. H.

Excretion of Glycuronic Acid Mistaken for Glycosuria. EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1913, **85**, 95—96).—A case of apparent glycosuria in a child turned out on further examination to have no sugar in the urine. The reducing properties were due to free and combined glycuronic acid. The urine also contained abundant phenol and indoxyl. W. D. H.

Changes in Voluntary Muscles in Disease. R. C. JEWESBURY and W. W. C. TOPLEY (*J. Path. Bact.*, 1913, **17**, 432—453).—In wasting diseases the voluntary muscles show varying degrees of wasting. In acute general diseases there is a hyaline or granular change, and in a few cases fatty degeneration. In cases of abnormal carbohydrate metabolism the interstitial fat is increased. Marked fatty degeneration occurs in diphtheritic toxæmia, certain blood disorders, and phosphorus poisoning. Glycogen was strikingly present in all the cases (three in number) of diabetes examined. Amyloid degeneration was not found at all. W. D. H.

Biochemistry of Growth. The Glycogen-content of the Liver of Rats Bearing Malignant New Growths. WILHELM CRAMER and JAMES LOCHHEAD (*Proc. Roy. Soc.*, 1913, *B*, **86**, 302—307).—Glycogen disappears more rapidly from the liver of tumour-bearing rats than from that of normal rats. There is no increased oxidation of carbohydrate material in tumour-bearing animals, so the result confirms the conclusion arrived at on pregnant animals, that in growth carbohydrate is used in the synthesis of protoplasm. W. D. H.

Nitrogen Content of Malignant Tumours in Man. ROBERT G. CHISHOLM (*J. Path. Bact.*, 1913, **17**, 606—608).—Ten tumours were investigated; in all cases the nitrogen percentage is lower in the fresh tumour than in the somatic tissues of the host, with the exception of the kidney. But reckoned for the dried tissue, the percentage was lower in four cases only. Cramer and Pringle found that the percentage of nitrogen coagulable by alcohol was low in tumour tissue; the variable results on this point obtained in the present research appear to be due to post-mortem changes. W. D. H.

Action of Diuretics in Experimental Nephritis. ARTHUR E. BOYCOTT and JOHN H. RYFFEL (*J. Path. Bact.*, 1913, **17**, 458—501). —After the convoluted tubules are put out of action by uranium nitrate, secretory diuretics, such as caffeine, fail to produce diuresis; so also do mechanical diuretics, such as Ringer's fluid. In the early stages of uranium nephritis, the urine produced is small in amount, and contains less chlorides than normal. Caffeine urine contains less chlorides than that produced by Ringer's solution or 5% sodium chloride solution. Uranium causes glycosuria. W. D. H.

Action of Radium Emanations on the Respiratory Exchange. J. VON BENCZÚR and DIONYS FUCHS (*Chem. Zentr.*, 1913 i, 1444; from *Zeitsch. exp. Path. Ther.*, 1913, **12**, 564—567).—Doses'

even one hundred times greater than the ordinary therapeutic dose of radium emanation, have only a slight effect in increasing the gaseous exchange, and do not affect the combustion processes taking place in the organism. S. B. S.

Behaviour of Lecithin towards Radium Emanation and Thorium-*X*. CARL NEUBERG and LÁSZLÓ KARCZAG (*Chem. Zentr.*, 1913, i, 1356; from *Radium in Biol. Heilkunde*, 1913, **2**, 116—122). —Different authors have assumed that the hæmolytic action of radium emanation and thorium-*X* is to be referred to a lecithin scission in the red corpuscles. It is found, however, that no hydrolysis takes place when solutions of the active substances are mixed with lecithin emulsions. The acidity does not rise, neither do the solutions differ in colour, odour, or consistence from the ordinary aqueous solutions. J. C. W.

Bürgi's Law of the Combined Action of Drugs. BÉLA VON ISSEKUTZ (*Pflüger's Archiv*, 1913, **151**, 456—478. Compare A., 1912, ii, 667).—When two narcotics are introduced into the organism at the same time, or within a short interval, the combined effect is often greater than the sum of the effects of each individual drug. This increased effect is, according to Bürgi, greatest when the drugs have different cell receptors. This theory is adversely criticised in some detail by the author, who illustrates his arguments by numerous examples, both from his own experience and by quotations from the results of other workers. He draws the conclusion that it is difficult, if not impossible, to formulate any law which will explain the combined action of two drugs administered simultaneously. S. B. S.

Action of Adrenalin on the Respiration. DIONYS FUCHS and NIKOLAUS RÓTH (*Chem. Zentr.*, 1913, i, 1443; from *Zeitsch. exp. Path. Ther.*, 1913, **12**, 568—571).—In experiments on men, similar results were obtained to those in the case of animals, namely, an increase in the volume in respiration. In man, however, there was no increase of frequency, as was observed in the case of animals. S. B. S.

Colchicine and its Derivatives. HERMANN FÜHNER (*Arch. expt. Path. Pharm.*, 1913, **72**, 228—238).—The activity of some of Windaus's derivatives of colchicine was compared with that of the parent substance. Colchiceine, in which only one of the enolic methoxy-groups of colchicine is saponified, is much less active than the methyl ether, colchicine. If the hydroxyl group is methylated, the original toxic value of colchicine is reached, or nearly so. Replacement of the acetyl group in this by benzoyl reduces the activity to one-tenth of that of colchicine. Oxycolchicine, obtained by oxidation with chromic acid, has on frogs an action resembling that of veratrine, but has no action when given to mammals.
W. D. H.

The Influence of Cholesterol on Hæmolysis. G. JAHNSON-BLOHM (*Zeitsch. physiol. Chem.*, 1913, **85**, 59—67).—The inhibitory

influence of cholesterol on the hæmolytic action of saponin, which was discovered by Ransom, was attributed by Windaus to the hydroxyl group of the former substance, and other views have been advanced to explain it. In the present experiments saponin and soaps were employed as hæmolytics, and the inhibiting action of cholesterol was confirmed; it is specially great if the temperature is raised, and increases with the time cholesterol is allowed to act. In saponin-hæmolysis an irreversible process between the red corpuscles and cholesterol occurs. In soap hæmolysis the action is less marked, and the explanation not so clear.

W. D. H.

The Influence of Cyanogen Gas on the Organism. JEAN LOUIS BURCKHARDT (*Arch. Hygienie*, 1913, **79**, 1—24).—When cyanogen, in concentrations much below 0·1 mg. per litre of air, is inhaled by cats, it has no ill effects; in concentrations of 0·1 mg. per litre, it can be inhaled for half an hour without danger. When the concentration reaches 0·2 mg. per litre, it acts toxically within a few hours. Rabbits are less susceptible, and can tolerate concentrations of 0·4 mg. per litre; for these animals the toxic concentration lies between 0·6 and 0·8 mg. per litre. The symptoms are irritation of the mucous membrane, difficulty in respiration, and convulsions; death results from paralysis of the respiratory centre. The symptoms are apparently those of hydrogen cyanide poisoning, the cyanogen reacting in the organism according to the equation $(CN)_2 + 2KOH = KCN + KCNO + H_2O$. If this takes place, 1 mg. cyanogen must have the same toxic action as 1 mg. hydrocyanic acid; the latter is, however, according to Lehmann and his pupils, much more toxic. It is probable, therefore, that other secondary reactions take place. S. B. S.

The Physiological Action of Fraxin and its Behaviour in the Organism. GIOVANNI B. ZANDA (*Chem. Zentr.*, 1913, i, 1779; from *Arch. Farmacol. sperim.*, 1913, **15**, 117—121).—Fraxin has small physiological action, and a dog can tolerate 2 grams per kilo. of body-weight without ill effects. It has no appreciable influence on blood-pressure or temperature, and the greater part is excreted unchanged within twenty-four hours. To the mouse, it is relatively non-toxic, but it shows a slight action on the activity of a frog's heart. S. B. S.

Anæmia Produced by the Hæmolysin from Streptococci. J. W. McLEOD and J. W. McNEE (*J. Path. Bact.*, 1913, **17**, 524—537). —Rabbits vary in their susceptibility to streptolysin. Hæmoglobinæmia and hæmoglobinuria are produced, and the hæmolytic property of the filtrate is closely related to its toxicity. Incubation at 37° destroys toxic and hæmolytic properties. The bone marrow hypertrophies in long experiments, and changes were also noted in liver, kidneys, and spleen. Repeated injections produce increased susceptibility and no immunity. The hæmolysis *in vivo* is much less than *in vitro*. W. D. H.

Degradation of β-Ketonic Acids in the Animal Organism. LEO HERMANNS (*Zeitsch. physiol. Chem.*, 1913, **85**, 233—240).—It is uncertain whether, on decomposition of aliphatic acids in the organism, ketonic or acid intermediate compounds are formed. It is shown that ethyl phenylacetoacetate is decomposed into benzyl methyl ketone and hippuric acid. The ketone at first formed is converted into benzoic acid. When the ketone is administered to dogs, hippuric acid is recovered.

On subcutaneous injection of ethyl benzylacetoacetate, hippuric acid is formed in quantity, and only traces of phenylethyl methyl ketone. This ketone, when administered alone, yields exclusively phenaceturic acid. In this case, therefore, there is acid decomposition in contrast with the ketonic decomposition in the case of the phenyl ester.

Ethyl phenylpropylacetoacetate under similar conditions gives a good deal of hippuric acid, and traces of phenylbutyl methyl ketone.

When phenylbutyl methyl ketone is administered, only phenaceturic acid is obtained in the urine. The ketone is decomposed between the carbonyl and the methylene carbon, and phenylbutyric acid is formed: $C_6H_5\cdot[CH_2]_4\cdot CO\cdot CH_3 \longrightarrow C_6H_5\cdot[CH_2]_3\cdot CO_2H$. The ester, on the contrary, forms phenylvaleric acid:

$$CH_3\cdot CO\cdot CH\cdot CH_2\cdot CH_2\cdot C_6H_4\cdot CO_2Et \longrightarrow C_6H_5\cdot[CH_2]_4\cdot CO_2H.$$

The phenyl group in ethyl phenylacetoacetate has thus an abnormal influence.

The normal formation of acetone in the body is due to similar secondary reactions. Normally, acetoacetic acid is degraded to acetic acid, but under pathological conditions the secondary reaction predominates and acetone is formed. The degradation of the fatty acids accordingly does not take place with the formation of ketones, but there is an elimination of two carbon atoms.

E. F. A.

The Influence of Salvarsan and Neosalvarsan on the Circulation and on the Kidneys of Healthy and Diseased Animals. ALWENS (*Arch. expt. Path. Pharm.*, 1913, **72**, 177—223).—Intravenous injection of salvarsan causes nephritis. Its toxicity increases not only with the dose given, but with the concentration; the histological appearances of the kidneys are described in detail; the nephritis is a vascular one, analogous to that produced by arsenic and cantharides. An immediate result of the injection, if made rapidly, is a fall in blood-pressure. Neosalvarsan produces clinically no nephritis, and in animals the nephritis produced by long-continued use of the drug is less marked; so also is the fall in blood-pressure. In animals which already have nephritis from other causes, the condition is intensified by very small doses of salvarsan, and in cases where the heart is diseased, the action of salvarsan on the circulation is most unfavourable. W. D. H.

The Relationship of Strophanthin Action and the Intensity of the Heart's Action. VIKTOR WEIZSÄCKER (*Arch. expt. Path.*, 1913, **72**, 282—294).—It was proved in experiments

on the frog's heart that the action of strophanthin takes place more rapidly the more quickly the heart is beating. In the resting heart, the drug is not completely inactive. The rate of beat being constant, rise of temperature increases the velocity of the action of strophanthin. W. D. H.

The Resistance of Different Animals Towards Arsenic. M. WILLBERG (*Biochem. Zeitsch.*, 1913, **51**, 231—252).—The following are the tolerated doses of potassium arsenite, expressed in mg. per kilo. of body-weight. For pigeons, less than 0·012 (subcutaneous); mice, 0·0156—0·0176 (subcutaneous); hedgehog, 0·01—0·014 (subcutaneous); rabbits, 0·008—0·01 (subcutaneous); dogs, 0·007 (subcutaneous or intravenous); guinea-pigs, 0·009 (subcutaneous); cats, 0·005—0·006 (subcutaneous); hares, more than 0·005 and less than 0·008 (subcutaneous); snakes, 0·012. The corresponding doses for arsenious acid are: For pigeons, 1·786 (per os); rabbits, 0·015 (per os); dogs, 0·03 (per os); hens, less than 0·06 (per os). It is noteworthy that the tolerance by man is less than by any of the above animals, which is probably due to the more highly developed nervous system. When arsenic is administered by the mouth, animals are to a large extent protected from the poisonous action by vomiting. S. B. S.

Lipoids which Resemble Lecithin in Forming Hæmolysins along with Cobra-venom. JOHN CRUICKSHANK (*J. Path. Bact.*, 1913, **17**, 619—622).—A number of substances were obtained from the alcoholic extracts of egg-yolk, heart, liver, and kidney, which differ from lecithin. They are all soluble in water, and with one exception in ether. They are precipitated from the ethereal solution by acetone. They all form hæmolysins along with cobra-venom. W. D. H.

Action of the Lecithins on the Processes of Poisoning in Higher Animals. E. HANSCHMIDT (*Biochem. Zeitsch.*, 1913, **51**, 171—192).—Lecithin by itself exerts no toxic action on animals, which can tolerate large doses, whatever method of administration is adopted. If injected together with curare, strychnine nitrate, ethyl alcohol, chloral hydrate, veronal, or morphine, it inhibited the action of these drugs. It increased, however, the toxic action of ricin. In the case of phosphorus poisoning, the effect of the lecithin appears to depend on the weight of the substance administered, smaller doses having apparently a beneficial, and larger doses a harmful, effect. The general condition of the animal and its body content in lipoids appears also to have some effect in this case. S. B. S.

Poisoning by Methyl Alcohol. FRANCESCO OLIVARI (*Chem. Zentr.*, 1913, i, 1780; from *Arch. Farmacol. sperim.*, 1913, **15**, 83—96).—The toxicity of crude and pure methyl alcohol for frogs, mice, and guinea-pigs was investigated. In the case of the pure products, the minimal lethal doses were: for frogs, 16·2$^0/_{00}$; for

mice, 11·5 $^0/_{00}$; and for guinea-pigs, 9·5 $^0/_{00}$ of the body weight; the corresponding numbers for the crude acid product were 10·0, 7·5, and 6 $^0/_{00}$; and for the crude basic product, 8·6, 6·8, and 5·5 $^0/_{00}$. A scheme is given for the forensic examination of drinks, and animal organs in which wood-spirit is suspected. The liquid is acidified with phosphoric acid, and the volatile acids, etc., are distilled off, whilst the bases, pyridine, amines, etc., remain in the residue. The distillate containing the acids is neutralised, and again distilled, the salts of the acids remaining behind, the aldehydes, etc., distilling over. These are fixed by *m*-phenylenediamine hydrochloride, and the mixture is distilled, when acetone and methyl alcohol distil over, and are estimated in the distillate. If the mixture is saponified before these treatments, a conception can be formed as to the quantity of esters present from the amount of alcohol in this distillate. Finally, ethereal oils can be extracted by mineral oils (b. p. 140—230°), and separated from the higher alcohols by fractional distillation. S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

Formation of γ-Aminobutyric Acid from α-Glutamic Acid by Micro-organisms. EMIL ABDERHALDEN, GEORG FROMME and PAUL HIRSCH (*Zeitsch. physiol. Chem.*, 1913, **85**, 131—135).—Whereas Ackermann (A., 1910, ii, 1089) identified γ-aminobutyric acid amongst the bacterial decomposition products of *d*-glutamic acid, Abderhalden and Kautzsch (A., 1912, i, 952) were unable to confirm this. It is now found that γ-aminobutyric acid is formed when a mixture of glutamic acid, dextrose, Witte's peptone, and inorganic salts is incubated with decomposing pancreatic tissue. Success depends on the presence of the proper micro-organism; the mixture contained various yeasts, together with Diplococci and Staphylococci. E. F. A.

Methods in Soil Bacteriology. VI. Ammonification in Soil and in Solution. FELIX LÖHNIS and HENRY HAMILTON GREEN (*Centr. Bakt. Par.*, 1913, ii, **37**, 534—562).—A critical study of the factors affecting ammonification and nitrification of blood meal, flesh meal, and horn meal under laboratory conditions. Where the tests are carried out in solution and under aerobic conditions, the quantity of material does not appear to influence the rate of ammonification. Under anaerobic conditions there is a marked retardation of the process, due possibly to an accumulation of bacterial metabolic products. It is suggested that in the initial decomposition of flesh meal and horn meal in shallow layers of liquid, aerobic and anaerobic organisms play perhaps an equally

important part, but that aerobic organisms are concerned more actively with the later stages of ammonification. Under aerobic conditions, and with larger quantities of material, considerable amounts of ammonia may volatilise from the cultures, or undergo assimilation by bacteria. The decomposition of horn meal and blood meal is much more rapid in soil than in solution. When, however, soil tests in deep layers at full saturation are compared with solution tests in shallow layers, ammonification is faster in solution than in soil, and this would seem to indicate aeration as being one of the chief factors in determining the rate of decomposition in soils. The three materials used show differences among themselves in the rate of decomposition, and this varies again according as to whether the tests are made in solution or in soil. The conclusion is drawn that solution tests seem to afford more information concerning the nature of the materials used as sources of nitrogen.

Nitrification is not registered in solution in the presence of any of the materials, but in soil tests it keeps pace with ammonification provided that aeration is liberal, and that the quantity of ammonia formed is not excessive. H. B. H.

The Oxidation of Thiosulphates on Bacterial Filters. WILLIAM T. LOCKETT (*J. Soc. Chem. Ind.*, 1913, **32**, 573—581).—It has already been observed that phenol and thiocyanate undergo oxidation on bacterial filters (Fowler, Ardern, and Lockett, A., 1911, ii, 139). In the present investigation, thiosulphate solutions were passed repeatedly through filters, consisting of stoneware pipes 24 in. long, cemented at one end and filled with clinkers. The amount of change in the solution was determined by an estimation of the oxygen absorbed from acid permanganate solution, and of the residual thiosulphate by *N*/80-iodine. It was found that solutions up to 0·5% concentration (expressed as $Na_2S_2O_3$) can be oxidised; the resulting solution is acid, and the addition of alkali accelerates the rate of oxidation. The thiosulphate is oxidised finally to sulphate, but tetrathionate and pentathionate, with occasional traces of trithionate, are intermediarily produced.

In an extension of the investigation to the thionic acids, it was first shown that the usual tests are applicable with but few exceptions to thionate solutions of 0·1 and 0·02% concentration. With the exception of the dithionates, all the thionates undergo oxidation in this manner; potassium trithionate is oxidised to sulphate with intermediate formation of a considerable quantity of tetrathionate; potassium tetrathionate gives sulphate with a little pentathionate, whilst potassium pentathionate is directly oxidised to sulphate.

The conclusion is drawn that the oxidation is due to bacterial agency assisted by the physical and chemical properties of the filtering medium. D. F. T.

The Products of the Putrefaction of *l*-Aspartic Acid. New Method of Detecting β-Alanine. EMIL ABDERHALDEN and ANDOR FODOR (*Zeitsch. physiol. Chem.*, 1913, **85**, 112—130).—On putrefactive

decomposition of *l*-aspartic acid, succinic, propionic, and formic acids are formed (compare Neuberg and Cappezzuoli, A., 1909, ii, 691). These acids are easily separated by the ester method, as the acid esters may be extracted with ether from the ester hydrochlorides of the amino-acids.

Emphasis is laid on the necessity of carrying out putrefactive decomposition experiments with a single known organism or a mixture of known organisms. β-Alanine obtained by Ackermann (A., 1911, ii, 757) from aspartic acid could not now be identified. It is recognisable in the very smallest quantity by conversion into ethyl acrylate, which has a characteristic odour, and when added to a putrefaction experiment it is easily identified in this manner. Pure cultures of the five micro-organisms present were incubated separately with aspartic acid. In no case was β-alanine formed.

E. F. A.

Reaction Phases of Alcoholic Fermentation. HANS VON EULER and DAVID JOHANSSON (*Zeitsch. physiol. Chem.*, 1913, **85**, 192—208).—It is shown generally that, when sugar is fermented in presence of phosphate, the relation between the amount of carbon dioxide liberated and the phosphate fixed throughout the whole course of the change is that expressed by Harden and Young's equation, namely, $2C_6H_{12}O_6 + 2PO_4HR_2 = 2CO_2 + 2C_2H_6O + 2H_2O + 2C_5H_{10}O_4(PO_4R_2)_2$. This expression by no means explains the mechanism of fermentation or the part played in it by the individual enzymes.

Fermentation begins with the conversion by means of an enzyme of the hexose sugars into a carbohydrate, which can be esterified with phosphate. The development of carbon dioxide which accompanies this esterification is checked by an excess of phosphate. The fermentation controlled by phosphate is accelerated by the presence of lævulose. Both hexose diphosphate and triosemonophosphate are formed. The enzymatic hydrolysis of the hexose phosphate ester studied by Harden and Young is materially retarded by the presence of toluene. All the foregoing facts must be taken into consideration in any explanation of the fermentative changes.

E. F. A.

Invertase Reaction of Mixed Yeast Cultures. ALBERT J. J. VANDEVELDE and A. VANDERSTRICHT (*Biochem. Zeitsch.*, 1913, **51**, 388—397).—The invertase action of mixed cultures lies generally between that of the varieties forming the mixture, which is in contrast to the effect observed with certain mixed cultures, on the alcoholic fermentation, where a mixture exerts a favouring action.

S. B. S.

Reduction of Acetaldehyde by Yeast Juice. S. KOSTYTSCHEV and ELISE HÜBBENET (*Zeitsch. physiol. Chem.*, 1913, **85**, 408—411. Compare A., 1912, ii, 860).—An extract of dried yeast (maceration juice) is proved to reduce methylene-blue to the colourless state, and also acetaldehyde to alcohol, both in the presence and in the

absence of sugar. The active hydrogen in this case is probably formed in the same way as during zymase fermentation. E. F. A.

Are Moulds Able to Form Volatile Substances from Antimony Compounds? ERICH VON KNAFFL-LENZ (*Arch. expt. Path. Pharm.*, 1913, **72**, 224—227).—The moulds investigated are not able to form volatile antimony compounds. In this there is a difference between antimony and the similar elements arsenic, selenium, and tellurium. The possibility that chronic antimony poisoning is due to the formation of volatile substances is excluded.
W. D. H.

Nature of the Osmotic Optimum in Biological Processes. ALFRED GUILLEMARD (*Compt. rend.*, 1913, **156**, 1552—1554).—A theoretical paper explaining results obtained in the culture of *Aspergillus niger* under various conditions. The living matter absorbs metallic compounds necessary for its physico-chemical constitution, the rate of formation of plant tissue following a curve which presents an optimum for a certain density with respect to the properties of the metal experimented with. The osmotic optimum occurs with most chemical substances in biological reactions. The amount of substance which favours it is the "excitation" dose, and precedes the "toxic" dose. W. G.

Replacement of Zinc by Copper in the Culture of Aspergillus niger. CHARLES LEPIERRE (*Compt. rend.*, 1913, **156**, 1489—1491. Compare this vol., i, 326, 327).—Like cadmium, glucinum, and uranium, copper can replace zinc in the culture of *Aspergillus niger*. Added in the form of its sulphate, the weight of crop is normal if the amount of copper does not exceed 1 in 500,000, but the growth is retarded. If the amount rises to 1 in 1000, growth ceases. Sporulation takes place only if the copper present does not exceed 1 in 10,000. W. G.

The Assimilation of Guanine and Guanidine by Moulds. ALEXANDER KOSSOWITZ (*Chem. Zentr.*, 1913, i, 1297; from *Zeitsch. Gährungsphysiologie allg. landw. techn. Mykologie*, 1912, **2**, 84—86).—Guanine could be used by a large number of moulds as a source both of carbon and nitrogen. These include *Botrytis bassiana*, *Penicillium glaucum*, *Mucor γ-Boidin*, *Cladosporium herbarum*, *Phytophthora infestans*, *Penicillium brevicaule*, *Aspergillus glaucus* and *A. niger*, and *Isaria farinosa*. Guanidine, as carbonate, chloride, nitrate, or thiocyanate, could be used as a nitrogen source by all moulds. S. B. S.

Enzymatic Hydrolysis of Hippuric Acid by Mould Fungi. ARTHUR W. DOX and RAY E. NEIDIG (*Zeitsch. physiol. Chem.*, 1913, **85**, 68—71. Compare A., 1909, i, 861; ii, 510).—Some characteristic mould fungi—three Aspergillus and three Penicillium species—were grown for periods of one, two, three, and four weeks in a nutrient solution consisting of sucrose, tartaric acid, and inorganic

salts. The mycelium was removed, ground with glass, the juice expressed, and its action on hippuric acid tested, the formation of glycine being detected by means of titration with formaldehyde. In most cases nearly complete hydrolysis was observed independently of the age of the culture. There is very little secondary action converting glycine into ammonia. Taka-diastase (made from *Aspergillus oryzae*) has a similar hydrolytic action on hippuric acid. E. F. A.

The Penetration of Different Forms of Nitrogen in Plants; Phenomena of Adsorption. D. Chouchak (*Compt. rend.*, 1913, **156**, 1696—1699. Compare Pouget and Chouchak, A., 1912, ii, 796, 975).—The roots of young wheat plants deprived of vitality by immersion in boiling water for thirty minutes retain the property of adsorbing and fixing nitrogen in diffeernt mineral and organic forms. This property is due to the presence of certain substances not removed by boiling water, but removed by boiling alcohol. This power of adsorbing different nitrogenous compounds, at the same molecular concentration, varies according to the nature of the compound, and for the same form of nitrogen, the amount of nitrogen adsorbed varies, within certain limits, directly with the concentration of the surrounding medium with respect to nitrogen. The ratio of the concentration of adsorbed nitrogen in the roots to that of the nitrogen remaining in the liquid is always greater than unity. W. G.

The Absorption of Different Forms of Nitrogen by the Plant; Influence of the Medium. D. Chouchak (*Compt. rend.*, 1913, **156**, 1784—1787. Compare preceding abstract).—The adsorbing power of the exterior layer of dead roots, and the rate of absorption or diffusion in the living plant, for the same concentration in nitrogen, is considerably modified by the presence of such salts as magnesium sulphate, sodium chloride, etc., and the effects produced by a number of these have been studied. They do not act in the same manner, but by their action on dead roots and on living plants they arrange themselves in the same order. In a mixture of two or more salts, they may help or be antagonistic to one another. In many cases the adsorption of nitrogen is very considerably increased, sodium chloride having a beneficial effect. W. G.

The Significance of Lipoids for the Formation of Bioelectrical Differences of Potential in Certain Plant Organs. Jacques Loeb and Reinhard Beutner (*Biochem. Zeitsch.*, 1913, **51**, 288—299).—The bio-electrical differences of potential already described by the authors at the undamaged surface of certain plant organs (apple, etc.) are qualitatively and quantitatively almost identical with that at the interface of an aqueous solution, and a solution of phosphatides in guaiacol, *m*-cresol, and amyl alcohol, and a guaiacol extract of apple behaves in this respect exactly like the undamaged organ itself. The solvents themselves without the

phosphatide have practically no action. Fatty acids which are insoluble in water, such as oleic and palmitic acids, show the same effect towards the varying concentrations of the aqueous salt solutions as the living organ. They behave, however, differently towards different concentrations of acids. The bio-electric action of the organs is not due therefore to fatty acids, neither is it due to cholesterol, the electromotor effects of which are quite different to those of the living organ. Solid proteins, such as coagulated egg-white or gelatin, also act in a different way. The bio-electric effects of the living organ are therefore ascribed to the presence of phosphatides or some similar insoluble substances. Cephalin and lecithin were used in the experiments in chains, which were constituted in the following way: Hg | HgCl*M*/1KCl | Guaiacol solution | KCl in varying concentrations | *M*/KClHgCl | Hg. S. B. S.

The Influence of Anæsthetics on the Potential Difference at the Surface of Living Animal and Vegetable Tissues. JACQUES LOEB and REINHARD BEUTNER (*Biochem. Zeitsch.*, 1913, **51**, 300—306).—The addition of alcohol or ether to the aqueous phase diminishes the difference of potential at the interface of a living organ and an aqueous solution. The action is a reversible one. The quantities necessary to produce an effect are considerably larger than those necessary for the production of narcosis. A similar diminution of difference of potential is produced by the addition of alcohol or ether to the aqueous phase at the interface of an aqueous solution and a solution of oleic acid or lecithin in guaiacol. The action is due to the entrance of some ether into the non-aqueous phase. A similar action was not observed on the addition of an indifferent non-electrolyte, such as dextrose, to the aqueous phase. S. B. S.

The Part Played by the Surface Tension and by Lipoids in the Living Cell. HORACE M. VERNON (*Biochem. Zeitsch.*, 1913, **51**, 1—25).—Exosmosis of tannin from vegetable cells, caused by various narcotics, is apparently not a mere surface-tension phenomenon, as Czapek assumes. According to this observer, the substances cause exosmosis in those concentrations which reduce the surface tension of water/air to 0·685. Out of the twenty-nine substances investigated by Czapek, seven produce exosmosis in concentrations in which the surface tension varies between 0·82 and 0·998. The concentrations, according to the author, more nearly correspond with those which produce narcosis in tadpoles and hæmolysis of blood-corpuscles. The narcotics appear therefore to exert their action owing to their solubility in lipoids, according to the Overton theory. The part played by the lipoids in animal cells can be investigated by determining the concentration of the various substances which inhibit the action of indophenoloxydase, an insoluble ferment which only acts, according to the author, when the lipoids are intact. It is now found that the concentrations of narcotics which are just sufficient to inhibit this ferment action

are about twice as strong as those which cause exosmosis of tannin from *Echeveria* cells. The actual ratios vary between 0·9 and 2·8 for the seventeen substances investigated. As the concentrations varied between 1 and 720, the closeness of these ratios is striking. Colloidal sodium oleate acts in the same concentrations on *Echeveria* as on oxydase, whereas saponin acts on the oxydase in 1/40 of this concentration. Acids act on oxydase in concentrations corresponding more or less with the electrical conductivity of this solution, and there is a crude parallelism between these values and their hæmolytic action. S. B. S.

Carbohydrates of Vegetables. ERNST BUSOLT (*J. Landw.*, 1913, **61**, 153—160).—The sap of French beans (3000 c.c.), when kept for a week, yielded 9·3 grams of pure mannitol. No mannitol was found in the sap when quite fresh, or in sap which was at once sterilised by boiling and then kept for a week.

Cauliflower (1300 grams), without the stalk, yielded 7·9 grams of pure mannitol, which is supposed to have been present originally. It is, however, possible that the mannitol was produced during the evaporation of the sap. N. H. J. M.

Simple Vegetable Bases. GEORG TRIER (*Zeitsch. physiol. Chem.*, 1913, **85**, 372—391).—Emphasis is laid on the fact that the plant betaines are to be regarded as the simplest alkaloids formed from the amino-acids by exhaustive methylation.

The presence of glycine betaine and of choline in the alcoholic extract of oat seeds is established. In the phosphatide from oats, colamine (aminoethyl alcohol) but no betaine is present.

Glycine betaine may be identified as platinichloride. This salt undergoes a characteristic change when left in contact with its mother liquors.

Aminoethyl alcohol reacts quantitatively with nitrous acid, and may be estimated in this way. Since choline does not react with nitrous acid, the presence in it of 1% of colamine may be detected. Colamine is incompletely precipitated by phosphortungstic acid.

An investigation of the bases in areca nuts leads to the following formulæ being suggested:

$$\text{Guvacine, } C_6H_9O_2N = CH_2<\begin{matrix} CH_2\cdot CH_2 \\ N{=\!=}CH \end{matrix}>CH\cdot CO_2H.$$

$$iso\text{Guvacine, } C_6H_9O_2N = CH_2<\begin{matrix} CH_2\cdot CH_2 \\ NH-CH \end{matrix}>C\cdot CO_2H.$$

$$\text{Arecaine, } C_7H_{11}O_2N = CH_2\begin{matrix} \diagup CH_2-CH\diagdown\!\!-\!\!-\!\!-CO \\ \qquad\qquad >CH \quad | \\ \diagdown CH_2\cdot NMe\diagup\!\!-\!\!-\!\!-O \end{matrix}.$$

These differ from the formulæ suggested by Jahns. E. F. A.

Formation of the Anthocyan Pigments of Plants. IV. The Chromogens. FREDERICK KEEBLE, E. FRANKLAND ARMSTRONG, and W. NEILSON JONES (*Proc. Roy. Soc.*, 1913, *B*, **86**, 308—317. Compare A., 1912, ii, 673; this vol., i, 325).—Flowers of any colour

variety of Brompton stocks, when treated with alcohol, lose their colour rapidly. The original colour is regained when the decolorised petals are placed in water, the recovery being rapid when the water is heated. The phenomenon is a general one, and it is also shown by the vegetative parts of plants. The brown wall-flower, which contains a mixture of purple anthocyan and yellow plastid colour, recovers purple. The power of recovering the original colour serves as a means of distinguishing anthocyan from plastid pigments. The recovery of the pigment is shown to be due to the oxidation of a chromogen.

The decolorisation is due to the activity of a reducing agent, which is extracted by alcohol. This is resistant to high temperatures, as the alcohol may be evaporated to dryness, and the residue taken up in water; it then contains an active reducing agent. This agent prevents the action of bran peroxydase on benzidine, whilst, when added to the blue solution resulting from the interaction of bran peroxydase, hydrogen peroxide, and benzidine, it brings about the decolorisation of the blue. Quinol has a similar effect, but not formaldehyde.

The flower petals contain a much larger quantity of chromogen than is used in the natural flower, as the colour may be removed and recovered several times. The amount of active water present in the cells determines the direction in which the pigment producing reaction shall go; as the amount of water decreases, the reducing agents become active and the oxydases inert.

The activity of α-glucase ceases in 60% ethyl alcohol and in 40% methyl alcohol. The activity of emulsin falls rapidly in alcohols up to 40% strength; in solutions with from 40 to 90% of alcohol the activity is proportional roughly to the amount of water present. Oxydase action ceases in about 70% alcohol, but in the plant cell the chromogens may undergo oxidation, even in 95% alcohol.

E. F. A.

Formation of the Anthocyan Pigments of Plants. V. Chromogens of White Flowers. W. NEILSON JONES (*Proc. Roy. Soc.*, 1913, *B*, **86**, 318—323. Compare Keeble and Armstrong, A., 1912, ii, 673).—Lack of colour in recessive white flowers may be the consequence, not of the absence of an essential constituent of the colour-producing mechanism, but of the failure of these constituents to come together and interact with one another. White flowers of *Lychnis coronaria* contain a chromogen which gives rise to a reddish-brown pigment on oxidation. The chromogen may be extracted by treatment with absolute alcohol; it reacts with the peroxydases in other plants in presence of hydrogen peroxide to form the brown pigment, and can thus be used in the same way as benzidine to demonstrate the distribution of oxydase. In *Lychnis* the natural conditions are never such as to allow any interaction between oxydase and chromogen. On treatment with alcohol or a similar hormone, the barrier is removed by the destruction of the plasmatic impermeability, and pigment is formed. The following types of white flowers have been demonstrated: (1) Those which contain

an oxydase and a chromogen, for example, *Lychnis coronaria*. (2) Those which contain a peroxydase and a chromogen, for example, *Dianthus*, sp. (3) Those which contain a peroxydase but no chromogen. These give no colour reaction after treatment with chloroform and hydrogen peroxide. (4) Those which contain no peroxydase. E. F. A.

Variation in the Composition of Water-Trefoil (Menyanthes trifoliata, L.) during a Season's Growth. MARC BRIDEL (*J. Pharm. Chim.*, 1913, [vii], **7**. 529—535. Compare A., 1911, i, 659).—This investigation was carried out on the same lines as were adopted in the case of gentian root (A., 1911, ii, 426), with the exceptions that (1) the carbohydrates hydrolysed by invertase in the water-trefoil are unknown, and (2) that meliatin, unlike gentiopicrin, cannot be isolated and weighed. The proportion of meliatin was therefore estimated by the change in rotation induced by emulsin in an aqueous solution of a dry alcoholic extract of the plant, in which (1) the initial reducing sugar, and (2) the carbohydrates hydrolysed by invertase had already been determined.

The results, tabulated in the original, show that the plant contains most meliatin (0·891%) towards the end of May, and least (0·655%) at the beginning of October. The carbohydrates hydrolysed by invertase are at a minimum (0·950%) at the middle of June, and increase steadily to 2·761% at the beginning of October. As in the case of gentian, it appears that the percentage of glucoside shows little variation, so that this substance cannot be regarded as a reserve material. On the other hand, the carbohydrates are accumulated as reserve materials up to the period at which the fruit ripens, to be used at the resumption of vegetative activity. T. A. H.

Husks of Buckwheat Seeds. KURT FESSLER (*Zeitsch. physiol. Chem.*, 1913, **85**, 148—155).—The brown husks of buckwheat seeds are reputed to contain a green pigment not identical with chlorophyll. The poisonous action of the husks towards animals is attributed to the photodynamic action of this pigment. The green pigment has now been studied more in detail and its absorption spectrum recorded; it shows red or brownish-red fluorescence in organic solvents. On keeping, the green colour changes to a yellow or brownish-green.

A yellow xanthophyll pigment is also present, which is closely related to phytosterol. The brown pigment of the husks is identified as a phlobaphen. E. F. A.

The Fruit of Crataegus macracantha. W. BRUCE ARMSTRONG (*Chem. News*, 1913, [iv], **13**, 280—281).—The fruits yielded 17·98% of sugars, 2·085% of ash, and contained 0·595% of nitrogen and 0·79% of oil. Protein was detected in all the fruits, and Wagner's reagent and the phenolphthalein test indicated that atropine may be present, although no other evidence of this could be obtained.

The ash had the following percentage composition: Al_2O_3 (trace of iron), 6·86; CaO, 13·93; MgO, 12·16; K_2O, 23·80; Na_2O, 37·63; SO_3, 3·09; Mn, 0·10; Cl, 0·15. The sugars present included dextrose and lævulose. Acetic and citric acids were also present, the former due to fermentation. T. A. H.

The Pharmacognosy of the Manna Ash. GIOVANNI B. ZANDA (*Chem. Zentr.*, 1913, i, 1779; from *Arch. Farmacol. sperim.*, 1913, **15**, 66—82).—Details are given for the preparation of the manna. To separate mannitol from fraxin, the aqueous extract of *Fraxinus* bark is treated with neutral lead acetate, the mixture is filtered, and then basic lead acetate is added. The mannitol in the filtrate can be estimated gravimetrically or polarimetrically. The fraxin is precipitated as a lead compound, which is decomposed by hydrogen sulphide. The product thus obtained is freed from tannic acid by treatment with a small quantity of water and recrystallised from alcohol. The fraxin can be estimated by titration with Fehling's solution after hydrolysis with dilute hydrochloric acid. The mannitol and fraxin contents of various species and of trees from different provinces and in different seasons were also investigated. When the quantity of mannitol is relatively large, that of fraxin is small and vice versa. S. B. S.

Presence of Gentiopicrin in the Leaf-bearing Stems of Gentiana spp. MARC BRIDEL (*J. Pharm. Chim.*, 1913, [vii], **7**, 486—492. Compare this vol., i, 434).—The leaf-bearing stems of *Gentiana cruciata*, L., *G. lutea*, L., and *G. asclepiadea*, L., were first examined by Bourquelot's biochemical method, and gave indications of the presence of gentiopicrin. The latter was then extracted from each of these materials. The first-named plant yielded very little, in which respect it resembles *G. pneumonanthe*, the stems of which also contain only a small amount of the glucoside (A., 1910, ii, 887). T. A. H.

Fruit of American Holly (Ilex opaca). F. F. CARHART and G. H. MILLER (*Chem. News*, 1913, **107**, 243—244).—The dry fruit contained 46·34% of reducing sugars, 8·31% of ash, 0·61% of nitrogen, and 1·5% of oil, as well as oxalic acid and proteins. The reducing sugars include dextrose and lævulose. The percentages of the constituents of the ash are as follows: SO_3, 4·59; Al_2O_3, 10·08; Fe_2O_3, 1·27; CaO, 15·91; MgO, 8·01; P_2O_5, 14·06; K_2O, 17·15; Na_2O, 24·32; MnO, 0·10; Cr, nil. The oil had D 0·9358 and saponification equivalent 303, and appeared to belong to the castor oil group. T. A. H.

Comparison of the Hydrolysing Diastases of the Latex of Maclura aurantiaca with those of Ficus carica and Broussonetia papyrifera. C. GERBER (*Compt. rend.*, 1913, **156**, 1573—1575).—The latex of *Maclura aurantiaca*, like those of *Broussonetia papyrifera* and *Ficus carica*, merits the name of "vegetable pancreatic juice." Like them, and in the same way as

animal pancreatic juice, it hydrolyses and renders soluble carbohydrates, fat and protein substances, and plays a primary part in the nutrition of the plant. These properties are due to the existence of certain enzymes, the characteristics of which are intermediate between those of the enzymes of the *Broussonetia* and *Ficus*, and place the latex of the *Maclura aurantiaca* between those of these two plants, and nearer to the first than the second.

W. G.

Migration of the Constituents of Maize Grain in Water and Aqueous Solutions. EDMOND POPPE (*Bull. Soc. chim. Belg.*, 1913, **27**, 103—109. Compare A., 1911, ii, 428).—Maize grains, when steeped in water or in dilute aqueous solutions of chlorides, nitrates, phosphates, or sulphates, or in saturated solutions of sucrose or sodium chloride, at the ordinary temperature for forty-eight hours, lose but very small amounts of their constituents. If, however, they are steeped in boiling solutions, a large amount of the nutritive substances is removed, and the grains diminish in alimentary value by 36·2%. Dilute solutions of the above-mentioned salts behave as distilled water with respect to the amount of nutrients removed. The ordinary temperature is not sufficiently high to kill the epidermic cells and so destroy their semi-permeability, but this occurs at the higher temperature, and the cell-walls become permeable to all the substances dissolved in the water. W. G.

Some Data on the Ripening of Florida Oranges. F. ALEX. MCDERMOTT (*J. Amer. Chem. Soc.*, 1913, **35**, 834—837).—A study has been made of the enzymes in the peel of Florida oranges with a view to ascertaining whether any change takes place in their nature or activity at the point at which the fruit becomes sufficiently ripe for consumption. The peel contains peroxydase, catalase, and invertase enzymes, but no oxydases. During ripening, the weight of the peel decreases in relation to the total weight, whilst that of the juice increases about equally in this relation. The total amount of acid in the juice decreases only slightly, but its concentration decreases considerably, whilst the sugar increases both in concentration and total amount. E. G.

Chemical Examination of the Roots of Phaseolus multiflorus, Lam. FREDERICK B. POWER and ARTHUR H. SALWAY (*Pharm. J.*, 1913, [iv], **36**, 550—552).—The statement having been made that the roots of this plant (scarlet runner bean) are poisonous, the authors have submitted the roots to a systematic chemical examination, and have isolated a number of definite constituents. Physiological tests of certain of these constituents, and of extracts of the roots, furnished no evidence that the roots are toxic.

An aqueous extract of the roots on precipitation with alcohol furnished a preparation which hydrolysed amygdalin and gave the biuret reaction. No hydrocyanic acid was formed on macerating the ground roots in water.

An alcoholic extract of the roots was mixed with water and

steam distilled, and thus separated into (*a*) a small amount of brown essential oil, (*b*) resinous matter, and (*c*) matter soluble in water. From the last-mentioned portion furan-3-carboxylic acid (compare Rogerson, T., 1912, **101**, 1044), allantoin (compare Ackroyd, A., 1911, ii, 308; Titherley and Coppin, A., 1912, ii, 289), an amorphous, glucosidic substance, and a reducing sugar which furnished *d*-phenylglucosazone were obtained.

The resinous matter was extracted successively with light petroleum, ether, chloroform, ethyl acetate, and alcohol. The material soluble in light petroleum was heated with alcoholic potassium hydroxide, and from the product of this reaction a *phytosterol*, $C_{27}H_{46}O$, m. p. 130°, pentatriacontane, and a *phytosterolin*, m. p. 275° (*acetyl* derivative, m. p. 162°), were isolated, as well as a mixture of solid fatty acids, which had m. p. 55°, and some liquid fatty acids, consisting of oleic, linoleic, and a third acid of lower molecular weight.

From the ether, ethyl acetate, and chloroform extracts nothing definite was isolated, but the second contained some glucosidic material.

The portion insoluble in the foregoing organic solvents, but soluble in alcohol, yielded a glucoside, *phaseosaponin*,

$$C_{50}H_{84}O_{20},7H_2O,$$

m. p. 238° (decomp.), crystallising in colourless leaflets, and having the properties of a saponin. On hydrolysis by hot dilute hydrochloric acid, this furnished rhamnose (4 mols.) and *phaseosapogenin*, $C_{26}H_{44}O_4$, m. p. 200° (dry, decomp.), which could not be obtained crystalline. A different saponin and sapogenin of the above empirical composition were found by van der Haar in *Polyscias nodosa*, Forst (A., 1912, i, 885). T. A. H.

Pine Nut Oil. MAXWELL ADAMS and AUGUST HOLMES (*J. Ind. Eng. Chem.*, 1913, **5**, 285—287).—The seeds obtained from the cones of the nut pine (*Pinus Monophylla* or *P. Fremontiana*), a tree growing on the Sierra Nevada Mountains, California, yield about 12% of oil having an aromatic odour and agreeable taste; it is light yellow in colour, but becomes colourless on exposure to light. The oil has m. p. −15°, b. p. 305°/60 mm., n_D^{40} 1·4543, saponification number 189·3, iodine number (Hübl) 108, and consists chiefly of olein, together with small quantities of stearin, palmitin, laurin, and linolein. W. P. S.

Fruit of the "Snowberry" (Symphocarpus racemosus). C. B. SMITH (*Chem. News*, 1913, **107**, 266).—The dried fruits contained 4·1% ash, 17·17% sugars, 1·1% of oil, 0·59% nitrogen (=3·68% protein) as well as tartaric and citric acids and a trace of malic acid. No alkaloids were found. The ash had the following percentage composition: SiO_2, 0·78; Fe_2O_3, 2·10; Al_2O_3, 3·15; CaO, 15·11; MgO, 6·30; Na_2O, 8·32; K_2O, 40·26; SO_3, 6·95; P_2O_5, 14·87; Mn, 0·94. The sugars probably included dextrose and lævulose. The oil had saponification value 212·3. T. A. H.

Imbibition of Strychnos Seed. EDUARD VERSCHAFFELT (*Pharm. Weekblad*, 1913, **50**, 697—706).—The seed of *Strychnos Nux vomica* has a cuticular layer permeated very slowly by water. The presence of this layer greatly retards the imbibition of the seed, but addition of chloroform, ethyl acetate, and certain other organic substances produces a marked augmentation in the permeability to water, and hence in the velocity of imbibition. A. J. W.

Occurrence of Barium in Tobacco and Other Plants. JAMES S. MCHARGUE (*J. Amer. Chem. Soc.*, 1913, **35**, 826—834).—Crawford (*Bull.* No. 129, *Bur. Plant Indust.*, *U.S. Dept. Agric.*) has shown that the poisonous effect of loco-weed (*Astragalus* spp.) on cattle is due to the presence of barium, and further work has shown that barium is of common occurrence in plant tissues and soils.

Barium has now been found in tobacco in amounts varying from 0·009% to 0·074% (calculated as $BaSO_4$). Some of the barium can be extracted from the leaves by means of water, and is probably present in combination with organic acids. It is suggested that the occurrence of barium in living cells of the higher plants may indicate that the metal has some metabolic function. E. G.

Constituents of the Leaves of Zygadenus intermedius. III. FREDERICK W. HEYL and F. E. HEPNER (*J. Amer. Chem. Soc.*, 1913, **35**, 803—811).—In an earlier paper (this vol., i, 386) an account has been given of zygadenine, a crystalline alkaloid obtained from the leaves of *Zygadenus intermedius.* Further investigation of the leaves has shown that in addition to the alkaloid, sucrose, reducing sugars, and dextrin (A., 1911, ii, 326), they also contain the following substances: Quercitin; cerotic acid; a *phytosterol*, m. p. 135°, $[\alpha]_D^{20}$ $-29·5°$, which yields an *acetyl* derivative, m. p. 122—123°; hentriacontane, m. p. 68°; a fat, composed of the glycerides of stearic, palmitic, linolic, oleic, and *iso*linolenic acids; a polyhydric *alcohol*, m. p. 285—288°, of the ipuranol class; and a crystalline substance, m. p. 112—114°, which has not been identified.

The ash from (1) the leaves and tops and (2) the bulbs had the following composition, the first figure in each case referring to (1) and the second to (2): Moisture, 3·79, 2·04; Cl, 0·30, 0·19; CO_2, 18·05, 16·61; sand, 8·31, 7·01; C, 0·71, 0·48; soluble SiO_2, 4·39, 3·55; SO_3, 2·89, 3·33; P_2O_5, 5·03, 8·73; Fe_2O_3, 1·03, 1·08; Al_2O_3, 2·55, 1·08; Mn, traces; CaO, 25·37, 26·48; MgO, 5·34, 5·02; Na_2O, 5·58, 4·68; K_2O, 20·64, 20·35. E. G.

Acidity in Silage: Method of Estimation. C. O. SWANSON, J. W. CALVIN, and EDWIN HUNGERFORD (*J. Amer. Chem. Soc.*, 1913, **35**, 476—483).—The estimation of acidity in silage is usually carried out on an aqueous extract (compare Hart and Willaman, A., 1912, ii, 1205; Dox and Neidig, this vol., i, 236). A comparison has now been made of the efficiency of water and alcohol as extracting agents, and it has been found that equally uniform results are obtained by means of either solvent, but that the alcoholic extracts always contain a higher percentage of acids than the aqueous. It

therefore follows that some of the acids in silage are soluble in alcohol, but insoluble in water. The quantities insoluble in water vary with different kinds of silage, but are greatest in maize silage.

E. G.

Occurrence of Methyl Alcohol in Fruit Wines. Hugo Bauer and R. Engler (*Pharm. Zentr.-h.*, 1913, **54**, 445—447. Compare Wolff, A., 1901, i, 110).—Methyl alcohol was found in currant wine; the amount was too small to be of practical importance.

N. H. J. M.

The Part Played by Oxydases in the Curly Top Disease of Sugar Beet. Herbert H. Bunzel (*Biochem. Zeitsch.*, 1913, **50**, 185—208).—Leaves of plants with this disease contain two to three times as much oxydase as those of normal plants. No differences could be detected in the roots. In beets in which the growth was impeded by other factors, no abnormally high content in oxydase could be detected. The difference in the oxydase content of leaves of different plants is not merely a function of their size, and young and healthy leaves are normal in this respect. Where a normal function of the plants is suppressed, such as the formation of seeds, there is a high oxydase content. The general conclusion is drawn that abnormal disturbances of growth lead to an increased oxydase content of the leaves. Attention is called to similar high oxydase contents in other plant diseases. The general distribution of the oxydases in the various juices of the plant was also investigated. The expressed juice of seeds is richest in oxydase; then follow the leaves and roots.

S. B. S.

Action of Flowers of Sulphur on the Growth of Sugar Beet. Josef Urban (*Zeitsch. Zuckerind. Böhm.*, 1913, **37**, 441—444). —Application of flowers of sulphur slightly increased the yield of sugar beet. The sulphur was without effect on the colour of the leaves, and also had no effect on the amount of sugar and the quality of the juice.

N. H. J. M.

The Acids in Honey. Alfred Heiduschka and G. Kaufmann (*Chem. Zentr.*, 1913, i, 1221; from *Südd. Apoth.-Zeit.*, 1913, **53**, 118—119).—About half of the volatile acids in honey is represented by formic acid, which was estimated in the steam-distillate and found to compose 0·0037 to 0·0072% of the substance. The non-volatile acids were estimated by the method of Heiduschka and Quincke (A., 1908, ii, 73) with the result: Lactic acid, 0·0225%; malic acid, 0·0019%; traces of tartaric acid; the merest traces of higher fatty or wax acids; no succinic acid; phosphoric acid, 0·0286% as P_2O_5. This accounts for about one-quarter of the total acidity as measured by 0·1*N*-potassium hydroxide. The remainder is largely due to carbon dioxide and to amphoteric substances.

J. C. W.

Behaviour of Nitrates in Soils. Ignaz Vogel (*Landw. Versuchs-Stat.*, 1913, **82**, 158—159. Compare A., 1912, ii, 1206).—The high

and irregular losses of nitrogen previously observed are now shown to be due to absorption of nitrates by the glazed dishes in which the soils were kept. Subsequent experiments showed, however, that light humous soils, kept in thin layers, may lose, in a few days, 10—12% of the nitrates present. The loss of nitrates is now attributed to denitrification, and not to a chemical decomposition of nitrates, or to assimilation. N. H. J. M.

The Behaviour of Acid Amides in the Soil. SAMUEL L. JODIDI (*J. Franklin Inst.*, 1913, **175**, 245—258. Compare A., 1910, ii, 339; 1911, ii, 820).—The author, having previously shown the different forms in which organic nitrogen exists in soils, now describes experiments on the ammonification of acetamide and propionamide when mixed with soil under different conditions; after varying intervals of time these mixtures were distilled with either magnesium oxide or barium carbonate, and the evolved ammonia carefully estimated.

It is found that acetamide and propionamide readily undergo ammonification when mixed with soil, that the rate of transformation is greatly influenced by the chemical structure of the amide, and that the maximum percentage of ammonia obtained from acetamide and propionamide is 83·43% and 75·14% respectively. F. M. G. M.

Fixation of Ammonia by Permutite and Clay Soils. Availability of Permutite Nitrogen for Plants. DAVID J. HISSINK (*Landw. Versuchs-Stat.*, 1913, **81**, 377—432).—The results of pot experiments showed that oats assimilate nitrogen as ammonium sulphate and as permutite nitrogen about equally well, 70% of both being utilised. The solubility of the two forms of nitrogen in water saturated with carbon dioxide is, however, totally different, permutite nitrogen requiring 1300 to 1400 times as much water as the nitrogen of ammonium sulphate held by a clay soil.

The very slow liberation of ammonia from permutite indicates that the ammonia is partly chemically combined, and not merely held by adsorption. N. H. J. M.

Evolution of Sulphur in Soil; Study of its Oxidation. CH. BRIOUX and MARCEL GUERBET (*Compt. rend.*, 1913, **156**, 1476—1479).—A study of the oxidation of sulphur when introduced into various kinds of soil, with or without the addition of certain other substances. The results show that the oxidation is almost entirely due to microbic action. With garden soil the oxidation is slow at first, but becomes very rapid after the tenth day, the introduction of carbohydrates, such as sucrose and starch, having a marked retarding influence on the rate of oxidation, whilst peptone produces very considerable increase in the oxidation after the fifteenth day. The addition of chalk to a soil poor in lime increases the rate of oxidation by fixing the sulphuric acid formed. The inoculation of sterilised soil by ordinary soil water increases the rate of oxidation by about twenty to sixty times. W. G.

Chemical Causes and Character of the Injurious Effect of Large Amounts of Lime on Peat Soil. GEORG A. RITTER (*Bied. Zentr.*, 1913, **42**, 239—242; from *Fühling's Landw. Zeit.*, 1912, 593).—The losses of nitrogen which take place when lime and nitrates are applied to peat are attributed to chemical and not to biological action. A very small part of the loss may be due to the production of nitro-compounds from humus; the main cause of the destruction of nitrates is the reducing action of the humus.

The injury to vegetation observed when lime alone is applied in large amounts to peat cannot be due to the destruction of nitrates, since no nitrates are present, but to the increased oxidation of the organic matter and the production of substances, such as oxalic, formic, and acetic acids, etc., which are injurious to plants.

N. H. J. M.

Influence of Humus on the Weathering of Silicates. H. NIKLAS (*Bied. Zentr.*, 1913, **42**, 231—232; from *Intern. Mitt. Bodenk.*, 1912, **2**, 214).—The results of experiments in which silicates were kept in contact with peat for seven years, showed that the silicates were only very slightly attacked. N. H. J. M.

Zeolitic Properties of Ground Phonolite and Lime Trass Manure Compared with some Soil Varieties. ERICH BUSSMANN (*J. Landw.*, 1913, **61**, 97—134).—The ammonia of ammonium chloride is very strongly and chemically absorbed by lime trass; it is strongly absorbed by marsh soil, and well absorbed by phonolite, whilst red soils and loam have respectively only moderate and slight absorptive properties. All the substances adsorb potassium in dilute solutions, and absorb it in strong solutions. Calcium is only notably absorbed by lime trass. Nitrogen as nitrates is not absorbed by any of the substances, and magnesium only by lime trass and marsh soil. Phosphoric acid is fixed chemically, most by lime trass, and least by lime.

Under certain conditions the addition of phonolite and lime trass is favourable to the activity of Azotobacter, and consequently induce increased fixation of nitrogen in the soil. The sum of factors which produce this result is, however, still unknown.

N. H. J. M.

Manure Analyses. EILHARD ALFRED MITSCHERLICH and WILH. SIMMERMACHER (*Landw. Jahrb.*, 1912, **43**, 405—435).—A continuation of the author's work on the law of minimum as a logarithmic function (compare A., 1911, ii, 760). Numerous analyses are described, and the results tabulated, from which the author deduces formulæ supporting his theory. F. M. G. M.

Organic Chemistry.

Formation of Pure Methane from Aluminium Carbide. ENRIQUE HAUSER (*Anal. Fis. Quim.*, 1913, **11**, 317—319).—The carbide may on treatment with water yield alkali hydroxides, which with metallic aluminium give hydrogen, which in one case amounted to 8% of the gas. G. D. L.

The Inflammability of Acetylene Mixed with Approximately 30% of Air. MARCEL DELEPINE (*Eighth Inter. Cong. App. Chem.*, 1912, **4**, 25—28).—In a series of experiments on the inflammability of mixtures of acetylene and air in approximately the proportion 70 : 30, an ovoid globe of one litre capacity was used. Electric sparks 2 mm. in length failed to ignite the gas even when the pressure was increased to $1\frac{1}{2}$ atmospheres. An electrically heated platinum wire is more effective than one of iron, for a wire of the latter metal, 2 cm. in length, caused ignition only when the additional pressure was 3·5 cm. and the wire was actually fused. The effect of the extent of the heated surface is indicated by the failure of a platinum wire 10 mm. long and 0·1 mm. in diameter to inflame a mixture under 11·3 cm. additional pressure although the wire fused, whilst a wire 0·2 mm. in diameter and 20—30 mm. long inflamed the gaseous mixture even when the pressure was slightly reduced; the latter wire failed to ignite a similar gaseous mixture enclosed in a lead tube 20 mm. in diameter and 1·4 mm. long. Mercury fulminate is very active in causing ignition, for although 0·005 gram failed to affect a mixture containing 29% of air, 0·01 gram caused inflammation in a mixture containing 28% of air under an additional pressure of 1 cm.; if the air is reduced to 23%, however, the pressure must be increased by more than 9 cms. before ignition is caused by this quantity of fulminate.

The initiation of the combustion is believed to be due to the primary decomposition of the acetylene giving hydrogen which forms a more combustible mixture with the air; the combustion of the new mixture then induces the inflammation of the remaining gas. It is suggested that the decrease in inflammability in the lead tube used above is due to the rapid mixing of the hydrogen and air being checked. D. F. T.

Action of Acetylene on Some Copper Compounds: New Cupro-Acetylene Compounds. FELIPE LAVILLA LLORENS (*Anal. Fis. Quim.*, 1913, **11**, 320—327).—When pure acetylene is allowed to act on a 10% solution of copper sulphate, to which is added 3 volumes of a 20% solution of sodium sulphite, there is first precipitated the compound $Cu_2SO_3{,}Cu_2C_2$ of a clear red colour. When an excess of acetylene is employed, the dark red $Cu_2SO_3{,}2Cu_2C_2$ is formed. When acetylene in excess acts for a long period on the well washed precipitates obtained from copper sulphate by means of sodium hydroxide or carbonate, or ammonium hydroxide, a black, explosive substance of the composition $C_6Cu_3{,}H_2O$ is obtained. G. D. L.

Action of Alkali Hydroxide and of Dry Silver Oxide on Trimethylene Bromide. B. F. FORTINSKI (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 568—580).—The author reviews the literature dealing with the formation of β-oxides, and describes attempts to prepare such an oxide from $\alpha\gamma$-dibromopropane.

The action of aqueous potassium hydroxide on $\alpha\gamma$-dibromopropane yields allyl alcohol and β-propylene glycol; the latter forms a *phenylurethane*, $C_{17}H_{18}O_4N_2$, m. p. 137—137·5°.

The reaction occurring between dry silver oxide and $\alpha\gamma$-dibromopropane is very energetic, but in presence of ether proceeds more smoothly, the products being β-propylene glycol and a compound of high boiling point which is converted into the same glycol by treatment with 10% sulphuric acid solution, and is hence probably a double β-oxide. T. H. P.

Oxidation of Alcohols under the Influence of Heat. JEAN B. SENDERENS (*Compt. rend.*, 1913, **156**, 1909—1912).—As a preliminary to the investigation of the oxidation of alcohols in presence of various metals and metallic oxides, the action of hot air on various alcohols has been examined, and it is shown that oxidation occurs at lower temperatures than has previously been supposed.

The experiments were made by passing a mixture of dry air and the vapour of the alcohol into a vacuous glass tube, heated to the required temperature. The air was passed in at the rate of 100 c.c. per minute. Under these conditions, the oxidation of ethyl alcohol begins at 405°, and the issuing gas contains no oxygen, when the temperature is raised to 450°. The corresponding temperatures for *iso*butyl alcohol are 400° and 435°, and for *iso*amyl alcohol, 380° and 410°. The principal product is carbon monoxide, but some dioxide is also formed, and at the lower temperatures some aldehyde and acid are produced. In the case of ethyl alcohol the issuing gas contains also some ethylene, methane, and hydrogen. Magnesium turnings, finely-granulated zinc, aluminium powder, molybdic anhydride, blue tungstic oxide, thoria and silica only feebly assist or accelerate these reactions, whereas vanadic anhydride lowers the temperature at which oxidation begins, and accelerates the absorption of oxygen, and is therefore a true catalyst (compare Naumann, Moeser and Lindenbaum, A., 1907, ii, 273).

T. A. H.

The Hydrogenation of Some Secondary *d*-Ethylenic Alcohols in the Presence of Nickel. ROGER DOURIS (*Compt. rend.*, 1913, **157**, 55—57).—By the passage of secondary ethylenic alcohols of the type CHR:CHR'·OH over reduced nickel at 200°, they are converted, by isomerisation, into the corresponding ketones, $CH_2R\cdot CH_2\cdot COR'$, some of the saturated hydrocarbon $CH_2R\cdot CH_2\cdot CH_2R'$ being formed at the same time. The secondary ethylenic alcohols are readily obtained by the condensation of magnesium alkyl haloids with acraldehyde or crotonaldehyde (compare Grignard, A., 1901, i, 679). Thus *iso*amylpropenylcarbinol is converted into *propyl* iso*amyl ketone*, $C_5H_{11}\cdot COPr$, b. p. 177—179°, D_4^0 0·8362, D_4^{21} 0·8205, giving a *semicarbazone*, m. p. 107°. This ketone is also obtained by oxidation of *propyl*iso*amyl*-

carbinol, $C_5H_{11}\cdot CHPr\cdot OH$, b. p. 184—186°/760 mm., D_4^0 0·8335, D_4^{16} 0·8199, prepared by the action of butaldehyde on magnesium *iso*amyl bromide.

*iso*Butylvinylcarbinol, when passed over reduced nickel at 200°, yields ethyl *iso*butyl ketone, b. p. 134—135°, giving an *oxime*, m. p. 129°. *cyclo*Hexylpropenylcarbinol yields cyclo*hexyl propyl ketone*, not yet obtained free from *butyl*cyclo*hexane*, b. p. 178—182°, D_4^0 0·8315 D_4^{20} 0·8178. The ketone gives a *semicarbazone*, m. p. 155°. W. G.

Action of Bromine on Ethyl Ether. ALEXANDER E. ARBUZOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 442—457).—In view of the divergent results obtained by McIntosh (T., 1905, **87**, 784; A., 1910, i, 808) and by Tschelinzev and Konovalov (A., 1909, i, 353; 1911, i, 415) the author has investigated the action of bromine on ethyl ether, with the following results.

At temperatures above 0°, this action yields no "oxonium dibromide," the sole product being Schutzenberger's perbromide (A., 1873, 487). If Tschelinzev's directions are followed closely, the same perbromide is obtained in an impure condition.

The value 9·13 Cal., given by Tschelinzev and Konovalov for the heat of formation of the dibromide, really represents the heat of formation of the perbromide, the value found by the author being 8·8 Cal. per gram-mol.

The interaction of ether and bromine in presence of solvents does not lend itself to calorimetric investigation, indefinite results being obtained.

At −80°, the action of bromine on ether yields the dibromide described by McIntosh (*loc. cit.*). T. H. P.

Vanadic Esters and Other Organic Vanadium Compounds WILHELM PRANDTL and LUDWIG HESS (*Zeitsch. anorg. Chem.*, 1913, **82**, 103—129).—The only previous preparation of vanadic esters is by Hall (T., 1887, **51**, 751). It is found that finely powdered vanadium pentoxide dissolves in many alcohols on boiling, and esters may be isolated from the solutions. Orthovanadic esters are readily prepared, with the exception of the methyl ester, and may be distilled without decomposition. Pyrovanadic esters have not been obtained. Metavanadic esters result from the action of small quantities of water on the ortho-esters, and form unstable solids, which decompose without melting. It is proposed to call the metavanadates, trivanadates. The further action of water gives the hexavanadates, which have not been obtained in a pure condition, as they are always mixed with trivanadates and colloidal vanadic acid.

The alcoholic solutions are of the colour of potassium dichromate when cold, but become lighter, and finally colourless, on heating, the colour change being completely reversible. This is due to the reaction in the case of the ethyl ester:

$$\underset{\text{Orange}}{Et_4V_6O_{17}} + 2Et\cdot OH \rightleftharpoons \underset{\text{Colourless.}}{2Et_3V_3O_9 + H_2O}$$

Any change tending to remove water should therefore cause a lightening of the colour. This is confirmed. The deeply coloured cold 1·5% solution of vanadium pentoxide in ethyl alcohol becomes colourless at 60—70°, but if diluted with an equal volume of absolute alcohol the change takes place at 50—60°, whilst the addition of a few drops of water raises the temperature of the change to above 70°. Anhydrous copper sulphate removes most of the colour at the ordinary temperature. An excess of alcohol in the cold does not alter the colour, but only affects the temperature at which the change takes place. The electrical conductivity diminishes at the same time as the colour, and only begins to increase with the temperature after decolorisation is complete. The conductivity also diminishes with increasing concentration of the alcohol. Pure ethyl orthovanadate has a very small conductivity. A solution of 1 mol. V_2O_5 in 1·09 mol. Na_2O exhibits similar colour changes to the ester.

The esters, especially *tert.*butyl orthovanadate, are very suitable for the preparation of clear colloidal solutions of vanadic acid, as the alcohol is easily removed by boiling.

Ethyl orthovanadate, Et_3VO_4, is a bright yellow liquid, b. p. 98·5°/16 mm., and 152°/145 mm., D^{15} 1·167, forming white crystals in liquid air. A greenish-black, crystalline *compound*, $V_4C_{16}H_{40}O_{13}$, is obtained by heating the ester at 160—170°, acetaldehyde and ether being evolved. Propyl orthovanadate, $Pr^{\alpha}{}_3VO_4$, has b. p. 143°/24 mm., D^{15} 1·088, and forms an amber-coloured glass in liquid air. *n*-Butyl orthovanadate, $(C_4H_9)_3VO_4$, has b. p. 175°/22 mm., and the *iso*-propyl ester, b. p. 149°/16 mm., and D^{15} 1·033.

tert.*Butyl orthovanadate*, b. p. 117°/15 mm., forms colourless crystals, m. p. 45—47°. *iso*-Amyl orthovanadate forms yellow crystals, m. p. about 70°, b. p. 185—187°/18 mm. The tert.*amyl ester*, $(C_5H_{11})_3VO_4$, is a colourless liquid, b. p. 161°/19 mm., D^{15} 0·993, and is stable towards air and water.

Ethyl trivanadate (*metavanadate*), $Et_3V_3O_9$, is a light yellow powder, which readily decomposes. The molecular weight determination in phenol gives figures corresponding with the above formula. The n-*propyl* and iso-*amyl* esters have similar properties.

Vanadium oxychloride and sodium ethoxide react in benzene, forming *diethyl chloro-orthovanadate*, $VOCl(OEt)_2$, a dark red liquid, b. p. 103°/33 mm., D^{15} 1·366. By using suitable proportions, *ethyl dichloro-orthovanadate*, $VOCl_2{\cdot}OEt$, is obtained as a red liquid, b. p. 102°/49·5 mm.

The methyl esters have not been isolated, and glycerol and benzyl alcohol are oxidised by vanadium pentoxide.

Aniline hexavanadate, $(NH_3Ph)_4V_6O_{17},2H_2O$, forms reddish-brown, monclinic prisms, $a:b:c = 0{\cdot}4912:1:0{\cdot}8511$, β 93°57′. Vanadium oxychloride forms an *additive product*, $VOCl_2,2Et_2O,2H_2O$.

C. H. D.

The Methods for the Synthesis of Glycerides. ADOLF GRÜN (*Ber.*, 1913, **46**, 2198—2200).—Polemical. A criticism of the results and conclusions of van Eldik Thieme (this vol., i, 701). J. C. W.

The Preparation, Crystalline Structure, and Physical Properties of the Two Forms of Solid Nitroglycerin [Glyceryl Trinitrate]. HAROLD HIBBERT (*Eighth Inter. Cong. App. Chem.*, 1912, **4**, 37—57).—The statement of Kast (A., 1906, i, 922) as to the existence of two isomeric forms of glyceryl trinitrate, m. p. 2·8° and 13·5° respectively, has been considerably discounted by the failure of Nauckhoff (A., 1912, i, 63) to isolate the more fusible isomeride.

It is now found that if a mixture of wood pulp or powdered glass wool with glyceryl trinitrate (preferably a fresh specimen which has not been previously solidified) is cooled to −40°, the latter crystallises in the new form described by Kast, for if glyceryl trinitrate at −40° is inoculated with it the whole crystallises to a *labile* form, m. p. 2·0°. This labile isomeride passes readily into the stable form, m. p. 13·1°, for although when fused and cooled again to −40° within one minute it spontaneously crystallises in the labile form, a longer period in the fused condition prevents any tendency to spontaneous crystallisation in any form. The solid labile form also passes rapidly into the stable one when inoculated with a trace of the latter or sometimes even on rubbing, the transformation being accompanied by a very appreciable development of heat; the labile form also appears to be the more sensitive towards shock.

If the wood pulp used for the initial freezing contains powdered sodium nitrate, inoculation with this mixture causes more rapid crystallisation of glyceryl trinitrate, but in the more stable modification. Potassium nitrate has no such effect on the nature of the solid which separates, and it is possible that the separation of the less fusible isomeride is not due merely to the presence of the sodium nitrate, but depends on other conjoint factors of which the presence of moisture is one.

Microphotographs are given of the crystals of the two forms, of which the labile belongs to the triclinic and the stable to the rhombic system. Attention is drawn to the remarkable analogy between the isomeric forms of glyceryl trinitrate and those of benzophenone (Zincke, this Journ., 1871, **24**, 832; Auwers and Meyer, A., 1889, 611).

D. F. T.

Boiling Points of Solutions of Glyceryl Trinitrate. A. L. HYDE (*Eighth Inter. Cong. App. Chem.*, 1912, **4**, 59—67).—Molecular-weight determinations have been effected by means of a modified form of the electrically heated Beckmann apparatus, with glyceryl trinitrate in various solvents; as the concentrations attained in some cases over 75 grams of the nitrate to 100 of solvent, the results calculated from the usual law for dilute solutions can hardly be very trustworthy. With ether, methyl alcohol or chloroform as solvent, the results indicate an association which increases with the concentration, whilst with acetone the results are below the theoretical. Ethyl acetate gave, over a fairly wide range of concentrations, concordant results, which agreed well with the theoretical molecular weight and its application for such determinations should be useful, for example, in the estimation of diglycerol tetranitrate admixed with glyceryl trinitrate.

In a mathematical discussion of the results obtained with the three

solvents which give indications of association, it is shown that the rise in boiling point can be expressed by the equation $a = ch^n$, where a is the rise in b. p., h the percentage composition of the solution, whilst c and n are constants. D. F. T.

Separation of Glyceryl Trinitrate from Nitro-substitution Compounds. A. L. HYDE (*Eighth Inter. Cong. App. Chem.*, 1912, **4**, 69—76).—On shaking 1—3 grams of a mixture of glyceryl trinitrate and a nitro-derivative of toluene with 75 c.c. of carbon disulphide, four times with fresh portions (30 c.c.) of diluted acetic acid (65 acid : 35 water by volume), it is found that a fairly constant percentage of the nitrotoluene originally present in the mixture is left in the carbon disulphide, whilst the glyceryl nitrate is almost entirely to be found in the acetic acid. The quantity of nitrotoluene in the carbon disulphide is determined by careful evaporation after first washing the solution with water.

The following nitro-compounds were tried: *o*- and *p*-nitrotoluenes, liquid dinitrotoluene and its isomerides, m. p. 48° and 68° respectively, also liquid trinitrotoluene. Knowing the proportion of each of these to be found in the carbon disulphide after the above procedure, it is possible to apply this process to the rough estimation of any one of these nitro-compounds in a binary mixture with glyceryl trinitrate. D. F. T.

Phytic Acid in Cottonseed Meal and Wheat Bran. J. B. RATHER (*J. Amer. Chem. Soc.*, 1913, **35**, 890—895).—The Patten and Hart modification of Posternak's method for the separation of inositol-phosphoric acid, or so-called phytic acid, from wheat bran gives a product containing at least 5% of inorganic impurity mainly iron and aluminium phosphates, so that the formula $C_2H_8O_9P_2$ based on such results is probably erroneous (compare Posternak, A., 1903, ii, 679). Examination of the phosphorus compounds of wheat bran which are soluble in 0·2% hydrochloric acid and of cottonseed meal which are soluble in similar acid and also extracted by subsequent treatment with 0·2% ammonium hydroxide, indicates that by purification they yield an identical acid $C_{12}H_{41}O_{42}P_9$; this on heating with sulphuric acid undergoes scission into inositol and phosphoric acid and it is free from pentosans. D. F. T.

Trimethylene Trisulphide and Its Oxidation Products. OSCAR HINSBERG (*J. pr. Chem.*, 1913, [ii], **88**, 49—58. Compare A., 1912, i, 546).—Trimethylene trisulphoxide dissolves in concentrated hydrochloric acid, yielding a compound which is resolved into its components on the addition of alcohol, and is considered to be a basic salt containing the group $CH_2·SCl·OH$; when kept the solution deposits a colourless oil. In view of these results, the author is undertaking a study of the action of the halogen acids on the trisulphoxide, the present paper dealing particularly with the action of hydriodic acid.

Trimethylene trisulphoxide dissolves in warm dilute hydriodic acid and crystallises out again unchanged. When dissolved in concentrated

hydriodic acid (1 gram in 20—25 c.c., D = 1·96) and the solution maintained for twenty-four hours at the ordinary temperature, the trisulphoxide is reduced to a new labile (β) *trimethylene trisulphide*, which is obtained as yellow, crystalline precipitate on diluting the solution with water. The new trisulphide has m. p. 247° (decomp.), and passes into the stable (α) trisulphide of m. p. 216° on crystallisation from chloroform, acetic acid, benzene or alcohol. Attempts to effect the reverse transformation by the action of acetyl chloride, ethyl iodide or iodine proved successful.

The β-trisulphide may also be prepared by dissolving the α-compound in concentrated hydriodic acid, and maintaining the solution for several days at the ordinary temperature.

A solution of trimethylene trisulphoxide in seven times its weight of hydriodic acid (D 1·96) deposits after twelve hours stout, brown plates or prisms of *β-trimethylene trisulphide tri-iodide*, $CH_2<{SI\cdot CH_2 \atop SI\cdot CH_2}>SI$, which melts indefinitely at 118—123° (decomp.), and loses its iodine completely when exposed to the air for eight days, or when heated at 60°, yielding β-trimethylene trisulphide. If the tri-iodide is crystallised from chloroform and then heated at 60° until the iodine is removed, either the pure α-trisulphide or a mixture of the α- and β- forms is obtained.

The tri-iodide combines with iodine in chloroform solution, yielding a *tetraiodide*, $C_3H_6S_3I_4$, which is derived from the α-trisulphide, and crystallises in elongated prisms, resembling iodine, m. p. 100° (decomp.), with previous sintering. The tetraiodide is more stable than the tri-iodide, but loses its iodine completely when heated for several hours at 60°, or when exposed to the air for several weeks yielding α-trimethylene trisulphide. If kept for several weeks in contact with aqueous sodium hydrogen carbonate, the tetraiodide loses only part of the iodine, with the formation of a brown substance which is probably the tri-iodide of α-trimethylene trisulphide.

The author has also investigated the action of hydrogen peroxide on the isomeric trisulphides, in the hope of obtaining the corresponding trisulphoxides, but no evidence of the existence of such isomerides was obtained.

When heated for two hours with 10—15% hydrogen peroxide on the water-bath, the trisulphides are converted into trimethylene trisulphoxide, which is accompanied by *trimethylenedisulphonesulphoxide*, $CH_2<{SO_2\cdot CH_2 \atop SO_2\cdot CH_2}>SO$.

The latter compound is separated from the trisulphoxide by taking advantage of its sparing solubility in water and organic solvents. It crystallises in colourless needles, which become brown at 270° without melting.

The action of hydrogen peroxide on the trisulphide also leads to the formation of *trimethylenedisulphoxidesulphide*, $CH_2<{SO\cdot CH_2 \atop SO\cdot CH_2}>S$, which is readily soluble in water and crystallises in slender, colourless needles; m. p. about 210° (decomp.).

With respect to the isomerism of the trimethylene trisulphides, it is

pointed out that the existence of the two forms cannot be explained by a *cis-trans*-isomerism as in the case of the trithiobenzaldehydes, for, owing to the symmetrical structure of the molecule, stereoisomerism of this kind is excluded. The author inclines to the view that the isomerism is of a new type determined by spatial configuration of the sulphur atom, and suggests that the two modifications of trithiobenzaldehyde and of other substituted trithioformaldehydes may be sulphur isomerides of this type and not *cis-trans*-isomerides is usually imagined. F. B.

Uranyl Formate. Reply to Courtois. WILLIAM ŒCHSNER DE CONINCK and ALBERT RAYNAUD (*Bull. Soc. chim.*, 1913, [iv], **13**, 665—666. Compare this vol., i, 333).—A reply to Courtois (this vol., i, 585), in which the authors suggest that the salts used were different and that the experiments were conducted under different conditions. W. G.

The Mechanism of the Hell-Volhard Reaction. II. OSSIAN ASCHAN [With (Frl.) ELLA EUROPAEUS] (*Ber.*, 1913, **46**, 2162—2171. Compare A., 1912, i, 599).—Meyer (A., 1912, i, 941) expressed the opinion that the formation of a mixture of α-bromo-acid chloride and α-bromo-acid bromide by the action of bromine on acid chlorides is due, in the first place, to direct α-substitution, followed by a reaction between the liberated hydrogen bromide and the bromo-acid chloride, as in the equation : $CH_2Br{\cdot}COCl + HBr = CH_2Br{\cdot}COBr + HCl$.

The author now shows that anhydrous sulphuric acid does not react with acetyl chloride in the cold, and also describes the action of hydrogen chloride and bromide on the acid haloids. He finds that hydrogen bromide will convert acetyl chloride into acetyl bromide (compare Staudinger and Anthes, this vol., i, 616), but that, conversely, hydrogen chloride will transform acetyl bromide into acetyl chloride. Such changes cannot both be due to direct substitution, but are best explained by assuming the formation of the intermediate compound, $CH_3{\cdot}C{\lessgtr}\begin{smallmatrix}Br\\OH\\Cl\end{smallmatrix}$, which can part with either hydrogen chloride or bromide, according to the conditions. Thus, whether it is assumed that direct α-substitution is the first step in the action of bromine on acid chlorides, or that enolisation of the carboxyl group takes place, the fom ation of the same intermediate product must be assumed.

$$1.\ CH_3{\cdot}COCl + Br_2 = CH_2Br{\cdot}COCl + HBr = CH_2Br{\cdot}C{\lessgtr}\begin{smallmatrix}Br\\OH\\Cl\end{smallmatrix}.$$

$$2.\ CH_3{\cdot}COCl \rightarrow CH_2{:}C(OH)Cl + Br_2 = CH_2Br{\cdot}C{\lessgtr}\begin{smallmatrix}Br\\OH\\Cl\end{smallmatrix}.$$

The following cases have been studied, and the amount of transformation that takes place during definite intervals of time, calculated from halogen estimations which were controlled by density determinations : the action of hydrogen bromide on acetyl chloride, chloroacetyl chloride and bromoacetyl chloride, and the action of hydrogen chloride on acetyl bromide, chloroacetyl bromide and bromoacetyl bromide. J. C. W.

Trichloroacrylic Acid and Certain of its Derivatives. JACOB BÖESEKEN and P. DUJARDIN (*Rec. trav. chim.*, 1913, **32**, 97—111).—Heptachloropropane, b. p. 115°/12 mm., obtained according to Prins' method (A., 1911, i, 173) by the action of chloroform on pentachloroethane in the presence of aluminium chloride, is converted by alcoholic potassium hydroxide into hexachloropropylene, b. p. 209—210°/760 mm., 99°/15 mm. (compare Fritsch, A., 1898, i, 63). The latter is conveniently converted into trichloroacrylic acid, m. p. 76°, by the action of slightly diluted sulphuric acid at 135° or by a boiling aqueous suspension of barium carbonate. The *sodium*, *potassium*, and *magnesium* salts of this acid are readily soluble, whilst the *lead* salt crystallises in leaflets sparingly soluble in water. From measurement of the conductivity, the acid appears to be dissociated to about the same extent as oxalic acid, whilst it has approximately the same influence on the rate of inversion of sucrose as hydrochloric acid in $\frac{1}{8}N$-solution.

Trichloroacrylyl chloride, prepared by the action of an excess of thionyl chloride on the acid, has b. p. 158°/760 mm., $n_D^{18\cdot5}$ 1·52709, and when treated with ammonia in benzene solution is converted into the corresponding amide, m. p. 96° (compare Fritsch, *loc. cit.*). The latter is transformed by phosphoric oxide into trichloroacrylonitrile,

$$CCl_2\!:\!CCl\cdot CN,$$

m. p. 20°, $n_D^{20\cdot5}$ 1·5100.

A series of mixed aromatic ketones of the general formula

$$CCl_2\!:\!CCl\cdot CO\cdot R,$$

has been prepared either by gradual addition of the benzenoid derivatives to the stable molecular compound, $CCl_2\!:\!CCl\cdot COCl\cdot AlCl_3$ (compare Böeseken and Hasselbach, this vol., i, 335), or by addition of the acid chloride to a mixture of benzenoid derivative and catalyst, reaction being continued only until one molecule of hydrogen chloride had been evolved. In this manner, the following ketones have been obtained: (i) *phenyl trichlorovinyl ketone*, b. p. 138°/2 mm., D_{25}^{4} 1·3902, n_D^{25} 1·5798, which unites with chlorine in sunlight to form pentachloropropiophenone, m. p. 82·5° (compare Böeseken and Hasselbach, *loc. cit.*); (ii) p-*chlorophenyl trichlorovinyl ketone*, $C_6H_4Cl\cdot CO\cdot CCl\!:\!CCl_2$, b. p. 159°/17 mm., m. p. 19°, from trichloroacrylyl chloride and chlorobenzene. The isomeric *o*-chloro-derivative could not be isolated from the product. When acted on by chlorine in sunlight, *p*-chlorophenyl trichlorovinyl ketone yields p-*chlorophenyl pentachloroethyl ketone*, white crystals, m. p. 116°; (iii) p-*tolyl trichlorovinyl ketone*, $C_6H_4Me\cdot CO\cdot CCl\!:\!CCl_2$, b. p. 147·5°/10 mm.; (iv) m-*xylyl trichlorovinyl ketone*, b. p. 165°/14 mm.; (v) p-*xylyl trichlorovinyl ketone*, b. p. 161°/13 mm.; (vi) sec.-*propylphenyl trichlorovinyl ketone*,

$$CHMe_2\cdot C_6H_4\cdot CO\cdot CCl\!:\!CCl_2,$$

b. p. 173°/12 mm. In the three latter cases, reaction is very vigorous, but seems also to proceed in another direction, since evolution of hydrogen chloride continues after the quantity corresponding to one molecule has been evolved. (vii) ψ-*Cumyl trichlorovinyl ketone*, $C_6H_2Me_3\cdot CO\cdot CCl\!:\!CCl_2$, m. p. 57°. (viii) p-*Anisyl trichlorovinyl ketone*, m. p. 26·5°. In this case, the action is far less rapid than with toluene. Reaction was carried out in carbon disulphide solution when

a certain amount of the ketone was simultaneously decomposed with formation of *p*-hydroxybenzoic acid. (ix) *Phenetyl trichlorovinyl ketone*, m. p. 58°, D_4^{58} 1·3202, n_D^{58} 1·5726.

The position of the substituents in the above ketones is deduced from a study of their decomposition by alkali. When mixed with potassium alkoxides they are immediately decomposed with separation of the potassium salt of the aromatic acid according to the equation: $X\cdot C_6H_4\cdot CO\cdot CCl{:}CCl_2 + KOH = X\cdot C_6H_4\cdot CO_2K + HCCl{:}CCl_2$. In this manner, benzoic, *p*-toluic, anisic, *p*-ethoxybenzoic, and *p*-chlorobenzoic acids were obtained from phenyl trichlorovinyl ketone, *p*-tolyl trichlorovinyl ketone, *p*-anisyl trichlorovinyl ketone, *p*-phenetyl trichlorovinyl ketone, and *p*-chlorophenyl trichlorovinyl ketone respectively.

H. W.

Methylation of Aliphatic Compounds by means of Methyl Sulphate. EUGÈNE GRANDMOUGIN, EM. HAVAS and G. GUYOT (*Chem. Zeit.*, 1913, **37**, 812—813).—Although methyl sulphate has been extensively used in the methylation of aromatic substances, very few instances have been recorded of its use with aliphatic compounds. The authors have therefore investigated its applicability to the latter class and find that, in a series of typical methylations, this reagent can advantageously replace the customary methyl iodide under definite conditions of experiment.

Ethyl methylacetoacetate is obtained in 85% yield by the gradual addition of methyl sulphate to a solution of ethyl sodioacetoacetate in methyl alcohol under definite conditions of temperature which are fully described in the original, and, when again methylated under similar conditions, gives an 87% yield of ethyl dimethylacetoacetate.

In an analogous manner, ethyl methylmalonate and ethyl dimethylmalonate may be prepared, the yield of the former being 80—85%. The latter substance can also be obtained directly from ethyl malonate, the most favourable proportions being ester (1 mol.), sodium (3 atoms) and methyl sulphate (3 mols.). Employment of the theoretical quantities leads to the formation of a mixture of monomethyl- and dimethyl-malonic esters.

Phenylmethylpyrazolone can also be readily methylated by means of methyl sulphate. When methyl sulphate is slowly added to a solution of sodium methoxide and phenylmethylpyrazolone in methyl alcohol, 5-methoxy-1-phenyl-3-methylpyrazole, $\begin{matrix} N\text{—}NPh \\ \| \\ CMe\cdot CH \end{matrix}\!\!>\!C\cdot OMe$, is obtained (compare Knorr, A., 1895, i, 397; von Pechmann, A., 1895, i, 494). When, on the other hand, methylation is accomplished by the addition of methyl sulphate to a boiling solution of sodium hydroxide in the minimum quantity of water and methylphenylpyrazolone in methyl alcohol, antipyrine is obtained in 80% yield.

The conversion of aminoantipyrine into pyramidone can also be readily effected by means of methyl sulphate. H. W.

Aliphatic Nitrosocarboxylic Esters. JULIUS SCHMIDT and EMIL AECKERLE (*Annalen*, 1913, **398**, 251—256).—*Ethyl chloromethylacetoacetate*, $CH_3\cdot CO\cdot CMeCl\cdot CO_2Et$, b. p. 116—117°/75 mm, D_4^{18} 1·157,

n_D^{18} 1·4382, obtained from ethyl methylacetoacetate and sulphuryl chloride, is not attacked by nitrous fumes at 0°. Ethyl α-benzoylpropionate is converted by careful treatment with nitrous fumes at 0° into *ethyl α-nitroso-α-benzoylpropionate*, $C_6H_5 \cdot CO \cdot CMe(NO) \cdot CO_2Et$, a dark blue liquid, n_D^{18} 1·4902, which exhibits oxidising properties, and gradually decomposes into benzoic acid and ethyl α-nitrosopropionate.

These two experiments indicate that the formation of nitrosocarboxylic esters by the action of nitrous fumes on the esters of alkylated ketonic acids is represented by the scheme:

$$R \cdot CO \cdot CHR' \cdot CO_2Et \longrightarrow R \cdot CO \cdot CR'(NO) \cdot CO_2Et \xrightarrow{H_2O} R \cdot CO_2H + NO \cdot CHR' \cdot CO_2Et.$$

C. S.

Ricinstearolic Acid. GEORG MÜHLE (*Ber.*, 1913, **46**, 2091—2098).—The presence of the triple linking in ricinstearolic acid is confirmed by the addition of iodine which occurs when the acid is treated with the calculated quantity of iodine and a trace of dried ferrous iodide in carbon disulphide or warmed with an acetic acid solution of iodine, the temperature being kept, however, below 40°; the resultant *ricinstearolic acid di-iodide*, $CH_2Me \cdot [CH_2]_4 \cdot CH(OH) \cdot CH_2 \cdot CI{:}CI \cdot [CH_2]_7 \cdot CO_2H$, forms colourless needles, m. p. 62°, decomp. at 175°; *sodium* and *barium* salts, colourless needles; *mercury* salt, yellow powder; *methyl* ester, pale yellow oil, decomp. at 150°.

Recinstearolic acid, needles, m. p. 51°, b. p. 260°/10 mm. without decomposition, obtained by successive treatment of castor oil with bromine and potassium hydroxide solution, is accompanied by a small quantity of *θιλ-trihydroxystearic acid*, m. p. 110—111°,

$$CH_2Me \cdot [CH_2]_4 \cdot CH(OH) \cdot CH_2 \cdot CH(OH) \cdot CH(OH) \cdot [CH_2]_7 \cdot CO_2H,$$

identical with the α-*iso*trihydroxystearic acid obtained earlier by oxidation of castor oil. A specimen of ricinstearolic acid kept for twenty years without any precautions for the exclusion of atmospheric moisture gave a deposit of a *dihydroxystearic acid*, leaflets, m. p. 140—141°. The author was unable to reproduce the results of earlier workers, who state that on distillation of ricinelaidic acid and of ricinoleic acid under reduced pressure, an acid, $C_{18}H_{32}O_2$, is produced.

Acetylricinelaidic acid, obtained by acetylation of ricinelaidic acid with acetic anhydride, is a bright yellow, viscid oil; *acetylricinstearolic acid* is very similar.

Methyl ricinstearolate, obtained by esterification with a methyl alcoholic solution of hydrogen chloride, or in alkaline solution with methyl sulphate, is a colourless oil, b. p. 225°/12 mm., D 0·9389; *ethyl* ester, b. p. 230°/12 mm., D 0·9371.

Glyceryl monoricinstearolate, obtained from α-monochlorohydrin and dried sodium ricinstearolate at 150°, is a pale yellow, viscid oil; *glyceryl triricinstearolate*, from trichlorohydrin and sodium ricinstearolate at 190—200° under pressure, is of similar appearance.

The action of phosphorus pentachloride on ricinstearolic acid in the cold, yields a chlorostearolic acid, $C_{18}H_{31}O_2Cl$, a pale yellow, viscid oil, which cannot be distilled without decomposition. D. F. T.

Thorium Chloro-oxalate. A. COLANI (*Compt. rend.*, 1913, **156**, 1907—1909. Compare A., 1913, i, 444; Hauser and Wirth, A., 1912, i, 827).—Hauser and Wirth's method is the most convenient for

the preparation of this salt, which has the composition assigned to it by Wyrouboff and Verneuil (A., 1899, ii, 598; compare Kohlschütter, A., 1902, i, 11). The behaviour of thorium oxalate with hydrochloric acid of various strengths at various temperatures is shown by lists of analytical results in the original. The chloro-oxalate loses from 0·5 to 1·00% of thorium by volatilisation of the chloride when heated rapidly, but no loss takes place when heat is gradually applied and the thoria, produced under the latter conditions, contains only 0·1 to 0·2% of chlorine. Similarly, thorium oxalate precipitated in solutions of moderately concentrated hydrochloric acid contains very little chlorine. In these two respects, thorium behaves differently from the rare earths. Determinations of the solubility of thorium chloro-oxalate in hydrochloric acid are given in the original, and show that the solubility is much diminished in presence of oxalic acid, but that in the absence of the latter and with liquids containing 21·2% or less of hydrogen chloride, decomposition is rapid and complete into oxalate and chloride. T. A. H.

Barium Malonate Jellies and their Micro-structure. FRIEDRICH FLADE (*Zeitsch. anorg. Chem.*, 1913, **82**, 173—191).—The transformation of barium malonate jellies into powders takes place more slowly than with other barium salts (compare Neuberg and Neimann, A., 1906, ii, 753; Neuberg and Rewald, A., 1908, ii 39).

Equivalent quantities of solutions of malonic acid and barium hydroxide in methyl alcohol and glycerol are freed from air-bubbles by placing under an exhausted bell-jar and mixed. The greater the proportion of glycerol, the slower the formation of the jelly. If the glycerol is removed by means of methyl alcohol, it may be replaced by other liquids, such as chloroform or benzene, without destruction of the jelly, and with a great increase in its transparency. Much of the liquid may be removed by pressure between filter-paper, or by evaporation. The residue is barium malonate with $2H_2O$. Warming does does not liquefy the jelly.

Microscopical observations show that the jelly is made up of a network of fibres of barium malonate, in which the liquid is held as in a sponge. These fibres are stained deeply by methyl violet. The fibres are about 0·5 mm. long and 0 0001—0·0003 mm. thick, and are shown to be crystalline by their behaviour in polarised light. C. H. D.

Stereochemistry of the Halogen Substituted Succinic Acids. BROR HOLMBERG (*J. pr. Chem.*, 1913, [ii], **87**, 456—479).—The author has shown previously (A., 1912, i, 603) that during the hydrolysis of the sodium salt of *l*-bromosuccinic acid, the elimination of bromine proceeds at a greater rate than the increase in the acidity of the solution, and from these results has drawn the conclusion that the formation of malic acid from the bromo-acid is preceded by the formation of propiolactonecarboxylic acid.

The present paper deals with conditions favourable to the formation of the lactone and also with the hydrolysis of the sodium salts of *l*-chlorosuccinic, *l*-iodosuccinic and *l*-bromosuccinamic acids. In the case of bromosuccinic acid, the addition of neutral salts of weak acids

(formate, acetate, succinate and malate) increases the velocity of bromine ion formation, but diminishes the rate of hydrolysis of the lactone. Further, the formation of the lactone proceeds less readily with chlorosuccinic and bromosuccinamic acid than with bromosuccinic acid.

It is also found that the hydrolysis of the lactone yields either a *l*- or *d*-malic acid accordingly as it is carried out in acid or alkaline solution. Thus, a solution of *l*-bromosuccinic acid after being exactly neutralised with sodium hydroxide was maintained for twenty-four days at 25°, and then contained 10% of unchanged bromo-acid, 25% of lactone and 65% of malic and fumaric acids; after the bromo-acid and lactone had been completely hydrolysed by heating the solution on the water-bath, the malic acid obtained from the product was lævorotatory. On the other hand, when the hydrolysis was effected by excess of sodium hydroxide, the resulting malic acid contained a preponderance of the dextrorotatory form.

Similar results were obtained in the case of silver oxide; the action of excess of the oxide on *l*-bromosuccinic acid yields a dextrorotatory malic acid, whilst the theoretical amount necessary to form the neutral silver salt gives rise to a lævorotatory acid. F. B.

Symmetric and Asymmetric Acid Dichlorides. II. ERWIN OTT (*Ber.*, 1913, **46**, 2172—2175. Compare A., 1912, i, 828).—A further difference in reactivity between symmetric and asymmetric chlorides is in their behaviour on treatment with hydrogen and platinum black. Whereas fumaryl and chlorofumaryl chlorides immediately "poison" the catalyst so that not even limonene can be reduced in their presence, chloromaleyl chloride may easily be reduced to *n*-butyric acid. The hydrogen chloride which is formed gradually impedes the reduction, but if it is removed from time to time by evacuation, the absorption of hydrogen can be carried almost to the theoretical value. The reduction of dibromomaleyl chloride, however, could only be carried to one-fifth before "poisoning" of the platinum took place, whilst *as*-*o*-phthalyl chloride and phthalyl tetrachloride could not be reduced at all. J. C. W.

Ethyl Cyanotartronate and its Reactions with Amines. RICHARD SYDNEY CURTISS and LLOYD F. NICKELL (*J. Amer. Chem. Soc.*, 1913, **35**, 885—890. Compare Curtiss and others, A., 1911, i, 353, 366; A., 1909, i, 763).—The reaction between anhydrous hydrogen. cyanide and ethyl oxomalonate is greatly influenced by small variations in temperature; at 30° it is complete in twenty-four hours, the product being *ethyl cyanotartronate*, $OH\cdot C(CN)(CO_2Et)_2$, an undistillable oily liquid, D_{30}^{30} 1·16; it is soluble in alkaline solutions to a yellow solution, and if treated in ether with sodium, deliquescent, colourless crystals of an unstable *substance* slowly separate.

Ethyl cyanotartronate in cooled ethereal solution reacts with many amines, producing compounds which in all probability have an amidine structure; thus dipropylamine yields a crystalline *substance*,

$$NPr^{\alpha}_2\cdot C(:NH)\cdot C(CO_2Et)_2\cdot OH,$$

m. p. 72·5—73°. With diethylamine an analogous *compound*, m. p. 56°, was obtained, whilst benzylamine gave in a similar manner a

substance, m. p. 55—56°. These three substances on exposure to the atmosphere or when kept at 25°, undergo decomposition with formation of a tarry mass. Ethylamine, *iso*butylamine and benzylethylamine gave rise to uncrystallisable syrups, triethylamine slowly produced a red, tarry mass, whilst ammonia formed a very unstable, crystalline *substance*. With aromatic amines there was apparently no reaction.

D. F. T.

Catalytic Decomposition of Aldehydes. M. I. KUZNECOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 557—568).—In his earlier experiments on the oxidation of methyl alcohol by means of atmospheric oxygen with a view to preparing formaldehyde, the author found that the aldehyde was always accompanied by carbon monoxide and hydrogen in proportions depending on the temperature conditions and on the nature of the catalyst employed (*Bull. Charkov Technol. Inst.*, 1909). These two products result from the decomposition of aldehyde previously formed: $CH_2O = CO + H_2$.

Further experiments show that resolution of the aldehydic group with formation of carbon monoxide is a general reaction for all aldehydes.

The first series comprises measurements of the degree of decomposition of formaldehyde at various temperatures and under the influence of a number of different metals and of wood charcoal, asbestos and powdered Jena glass. The results show that the action depends not only on the chemical character of the catalyst but also on its physical condition. For instance, with copper turnings at 500° there is no decomposition, and at 600° only 4% of the aldehyde is attacked; with copper reduced from the oxide by the action of hydrogen, 9·2% of the aldehyde is decomposed at 500°; and with copper obtained by reduction of copper sulphate solution by means of alkaline formaldehyde, the action proceeds to the extent of 35·3, 84·2, 94·8 and 95·8% at 200°, 300°, 400° and 500° respectively. With different forms of other metals smaller variations are observed.

In the second series the products obtained by the decomposition of the following aldehydes by palladium black were investigated: formaldehyde, acetaldehyde, paracetaldehyde, propaldehyde, *n*-butaldehyde, *iso*butaldehyde, benzaldehyde and *p*-tolualdehyde. The results show that the aldehyde group is decomposed by palladium into carbon monoxide and hydrogen, the latter combining with the hydrocarbon radicle: $R\cdot CHO = RH + CO$. In the cases of propaldehyde and the butaldehydes, free hydrogen and unsaturated hydrocarbons are also obtained owing to the partial decomposition of the saturated hydrocarbons originally formed.

T. H. P.

Stability of Paracetaldehyde. R. RICHTER (*Pharm. Zeit.*, 1913, **58**, 482—483).—A series of experiments has been performed on the stability of paracetaldehyde alone, in aqueous solution and in the presence of various pharmaceutical preparations. The author is led to the following conclusions: (1) pure paracetaldehyde, free from acid and acetaldehyde, can be kept for sixteen months without alteration; the presence of these substances even in small quantity,

however, induces a gradual decomposition of the paracetaldehyde; (2) in the presence of pure raspberry juice without addition of water, paraldehyde remains unchanged during two months; (3) when mixed with water and a syrup composed of sugar and citric acid, paracetaldehyde speedily undergoes conversion into acetaldehyde; after two months, 7·8% of the paracetaldehyde had undergone such conversion; (4) in aqueous solution, without addition of juice, formation of acetaldehyde occurs slowly but continuously. H. W.

Catalytic Actions. VII. Polymerisation of Chloral. JACOB BÖESEKEN and A. SCHIMMEL (*Rec. trav. chim.*, 1913, **32**, 112—127).—The authors have studied the polymerisation of chloral in the presence of pyridine. For this purpose, known weights of dry chloral and pyridine have been preserved for a month at the ordinary temperature, at the end of which time a quasi-stable state had been reached. The contents of the flask were then treated with a large quantity of dilute hydrochloric acid, which combined with the pyridine and dissolved unchanged chloral. The metachloral which is insoluble in this reagent was estimated by decomposition with potassium hydroxide.

As the quantity of pyridine employed relatively to the amount of chloral increases, the latter becomes more completely transformed into metachloral, until, in the presence of about $\frac{1}{12}$ mol. pyridine, transformation is practically quantitative. Beyond this point, the amount of metachloral formed diminishes with increasing quantities of pyridine. The separation of metachloral is incomplete, whatever the quantity of catalyst employed. From determinations of the vapour tension of metachloral, obtained from chloral either by means of pyridine or fuming sulphuric acid, it appears that the true equilibrium of the system, chloral $\rightleftarrows$ metachloral, is situate practically entirely on the side of metachloral, and thus, that starting from chloral, this equilibrium is not obtained after a month even in the presence of considerable quantities of catalyst. This result is probably due to the absorption of pyridine by the polymeride which separates in the colloidal state.

When pyridine (4—5 mols.) is added to chloral (100 mols.) a rapid separation of a gelatinous mass occurs. After several weeks, a second change is observable in that the metachloral in contact with the walls of the vessel again becomes transparent, forming a membrane greatly resembling a collodion pellicle. This *transparent metachloral* does not appear to retain pyridine and has a vapour tension below that of the equilibrium mixture.

When pure metachloral is placed in an atmosphere of pyridine, it almost immediately becomes opaque, and then has the same vapour tension as the pseudo-binary system. Subsequently, it becomes gelatinous and then completely liquid.

In the presence of larger quantities of catalyst, less chloral is transformed into the polymeride, although equilibrium is more certain to be obtained in this case since a portion of the metachloral dissolves in the pyridine. The catalyst here exerts a marked influence on the

equilibrium, although it has not been found possible to isolate an additive compound of pyridine and chloral.

The phenomena here observed are analogous to those encountered in the polymerisation of chloral by means of fuming sulphuric acid (Böeseken, *Rec. trav. chim.*, 1910, **29**, 104) or aluminium chloride.

H. W.

Modifications of Metachloral and Decomposition of Chloral by Aluminium Chloride. Perchlorobutanal, $CCl_3\cdot CCl_2\cdot CCl_2\cdot CHO$. JACOB BÖESEKEN and A. SCHIMMEL (*Rec. trav. chim.*, 1913, **32**, 128—133).—Metachloral is known in a gelatinous modification immediately obtained by the addition of pyridine to anhydrous chloral, an opaque modification formed by the action of different catalyats on chloral, and representing the equilibrium mixture of the system chloral$\rightleftarrows$metachloral and as a transparent modification which is slowly produced when pyridine remains in contact with chloral. The latter is probably the only pure metachloral, the others being mixtures of it with unchanged chloral and catalyst. Attempts have been made to obtain the polymeride of chloral described by Combes (A., 1887, 127) as the product of the action of aluminium chloride on chloral. The authors have repeated his experiments, and have also somewhat modified the conditions, and find that the products are tetrachloroethylene, pentachloroethane and relatively very small amounts of perchlorobutanal, b. p. 145·5—147°/20—26 mm., m. p. 46·5—48°, molecular weight in benzene solution, 334. The latter is quantitatively decomposed by alkali according to the equation :

$$CCl_3\cdot CCl_2\cdot CCl_2\cdot CHO + 2KOH = C_3Cl_6 + KCl + HCO_2K + H_2O.$$

When heated with excess of aluminium chloride, it is decomposed with evolution of carbon monoxide. H. W.

The Catalytic Preparation of Ketones. ALPHONSE MAILHE (*Bull. Soc. chim.*, 1913, [iv], **13**, 666—671).—A reply to Senderens (A., 1911, i, 134, 302 ; this vol., i, 342) in which the author maintains the utility of his method using zinc oxide, and more especially cadmium oxide, as a catalyst in the preparation of ketones from acids. W. G.

Cerium Acetylacetonates. ANDRÉ JOB and PAUL GOISSEDET (*Compt. rend.*, 1913, **157**, 50—52).—Urbain (compare A., 1897, i, 236) prepared a basic cerous acetylacetonate by the action of cerous hydroxide on acetylacetone, and Biltz (compare A., 1904, i, 715) obtained the crystalline, neutral cerous salt by the action of cerous nitrate on an ammoniacal solution of ammonium acetylacetonate. Adopting Urbain's method the author has now prepared the ceric compound in a crystalline state. An excess of acetylacetone is added to a suspension of ceric hydroxide in water and the mixture agitated, when it slowly turns brown, and at the end of several days deep red needles of *ceric acetylacetonate* separate, having the composition $Ce(CHAc_2)_4,11H_2O$. On drying this salt in a vacuum and crystallising it from carbon tetrachloride, it is obtained in the anhydrous state as black crystals, m. p. 171—172°, having a metallic lustre. It is slightly soluble in water, and in solution is readily hydrolysed except

in the presence of excess of acetylacetone. The anhydrous salt is soluble in most organic solvents to a deep red solution, the colour rapidly disappearing in sunlight in the case of oxidisable solvents.

W. G.

Syntheses by means of Sodamide. II. Alkylation of Aliphatic Ketones. ALBIN HALLER and EDOUARD BAUER (*Ann. Chim. Phys.*, 1913, [viii], **29**, 313—349).—The authors' work (A., 1909, i, 108) on the alkylation of acetophenone and analogous substances by the successive action of sodamide and alkyl haloids has been extended to aliphatic ketones.

When an ethereal solution of pinacoline is treated successively with sodamide (1 mol.) and methyl iodide (1·1 mol.), a mixture of unchanged material, methyl- and dimethyl-pinacoline is obtained from which ββ-dimethylpentan-γ-one, $CMe_3 \cdot CO \cdot CH_2 \cdot CH_3$, b. p. 124—126°, can be isolated by repeated fractional distillation. This substance has already been described by Wischnegradsky (A., 1875, 878). The *oxime* has m. p. 79—80°. When the methylation is repeated until no further action occurs in ethereal solution, ββδ-trimethylpentan-γ-one, $CMe_3 \cdot CO \cdot CHMe_2$, b. p. 133—135° (compare Nef, A., 1900, i, 349), is obtained. It has D_4^{25} 0·80536, n_α^{25} 1·40304, n_D^{25} 1·40513, n_β^{25} 1·41020, n_γ^{25} 1·41429. The oxime has m. p. 141°. When reduced by sodium and alcohol, the ketone yields *ββδ-trimethylpentan-γ-ol*,

$$CMe_3 \cdot CH(OH) \cdot CHMe_2,$$

b. p. 145—148°, the *phenylurethane* of which has m. p. 79°. ββδ-Trimethylpentan-γ-one can be further methylated by means of sodamide and methyl iodide in benzene solution, when *ββδδ-tetramethylpentan-γ-one*, $CMe_3 \cdot CO \cdot CMe_3$, is obtained. It has b. p. 150—151°, D_4^{25} 0·81992, n_α^{25} 1·41485, n_D^{25} 1·41702, n_β^{25} 1·42224, n_γ^{25} 1·42643. It does not appear to form an oxime, a semicarbazone or a hydrazone. Its ketonic nature is, however, established by reducing it to *ββδδ-tetramethylpentan-γ-ol*, b. p. 165—166°, m. p. 50°, the *phenylurethane* of which has m. p. 118—119°, whilst the *formate* has b. p. 185°. In a similar manner, pentamethylacetone can be converted into *ββδδ-tetramethylhexan-γ-one*, $CMe_3 \cdot CO \cdot CMe_2Et$, b. p. 172—174°, by the successive action of sodamide and ethyl bromide or iodide in benzene solution. Like its lower homologue, this substance forms neither oxime, semicarbazone or hydrazone. Reduction converts it into *ββδδ-tetramethylhexan-γ-ol*, $CMe_3 \cdot CH(OH) \cdot CMe_2Et$, b. p. 187—188°, the *phenylurethane* of which forms slender needles, m. p. 94—95°.

The ethylation of pinacoline can be effected in a precisely similar manner. The successive action of sodamide and ethyl bromide or iodide on an ethereal solution of pinacoline leads to the isolation of *ββ-dimethylhexan-γ-one*, $CMe_3 \cdot CO \cdot CH_2 \cdot CH_2Me$, b. p. 146—148°, D_4^{25} 0·81055, n_α^{25} 1·40740, n_D^{25} 1·40952, n_β^{25} 1·41465, n_γ^{25} 1·41888, and *ββ-dimethyl-δ-ethylhexan-γ-one*, $CMe_3 \cdot CO \cdot CHEt_2$, b. p. 174—176°, D_4^{25} 0·82521, n_α^{25} 1·42007, n_D^{25} 1·42227, n_β^{25} 1·42738, n_γ^{25} 1·43173. The former yields an *oxime*, needles, m. p. 76—77°, and on reduction gives *ββ-dimethylhexan-γ-ol*, b. p. 155—157° (*phenylurethane*, m. p. 70—71°). The latter does not combine with hydroxylamine or with semicarbazide, but, when reduced with sodium and absolute alcohol, forms

ββ-dimethyl-δ-ethylhexan-γ-ol, b. p. 187°, the *phenylurethane* of which crystallises with $\frac{1}{2}H_2O$ and has m. p. 107°. In benzene, or better in toluene solution, complete ethylation of pinacoline can be effected, whereby *ββ-dimethyl-δδ-diethylhexan-γ-one*, b. p. 214—216°, is produced. It does not yield an oxime or a semicarbazone. Reduction converts it into *ββ-dimethyl-δδ-diethylhexan-γ-ol*, $CMe_3·CH(OH)·CEt_3$, b. p. 226—228°, the *phenylurethane* of which has m. p. 110°.

ββδ-Trimethylhexan-γ-one, $CMe_3·CO·CHMeEt$, b. p. 155—156°, is obtained mixed with unchanged starting material by the methylation of ethylpinacoline in ethereal solution. Since a separation of the two could not be effected by distillation, the product was treated with an alcoholic solution of hydroxylamine hydrochloride with which only the latter reacted to form an oxime. The mother liquors, separated as completely as possible from the crystalline oxime, were acted on by phenylcarbimide, whereby the dissolved oxime was converted into carbanilidoxime, which remained on distilling the mixture under diminished pressure. The distillate was treated with water to decompose the excess of phenylcarbimide, and the ketone extracted with ether and distilled. When reduced, it is converted into *ββδ-trimethylhexan-γ-ol*, $CMe_3·CH(OH)·CHMeEt$, b. p. 169°, the *phenylurethane* of which has m. p. 78°.

ββε-Trimethylhexan-γ-one, $CMe_3·CO·CH_2·CHMe_2$ (compare Nef, A., 1902, i, 6), is obtained in the usual manner as a liquid, b. p. 157·5—158·5°. Its oxime has m. p. 77—78°, whereas Nef gives 66—70°.

Although the action of allyl iodide on the sodium derivative of acetophenone yields only complex resinous products, allylpinacolines can be readily obtained by the successive action of sodamide and allyl iodide on an ethereal solution of pinacoline. In this manner, *allylpinacoline*, $CMe_3·CO·CH_2·CH_2·CH:CH_2$, b. p. 61—64°/14 mm., and *diallylpinacoline*, $CMe_2·CO·CH(CH_2·CH:CH_2)_2$, b. p. 83—86°/14 mm., are readily prepared.

δ-Benzyl-ββ-dimethyl-δ-ethylhexane-γ-one, $CMe_3·CO·CEt_2·CH_2Ph$, is obtained by the action of benzyl chloride on a boiling solution of the sodium derivative of diethylpinacoline in toluene. It has b. p. 152—154°/15 mm., and does not yield an oxime or a semicarbazone.

In the cases of pinacoline and of acetophenone, a tertiary carbon atom is attached to the carbonyl group. The authors have therefore extended their investigations to such ketones in which this is not the case, and find that alkylation can be similarly effected, substitution occurring at either of the secondary carbon atoms attached to the keto-group (compare Haller, A., 1905, i, 214; Haller and Bauer, A., 1912, i, 269).

An ethereal solution of diethyl ketone reacts vigorously with sodamide, and, after addition of methyl iodide, yields, on fractionation, *ethyl* iso*propyl ketone*, $COEt·CHMe_2$, b. p. 115—119°, di-*iso*propyl ketone, $CO(CHMe_2)_2$, b. p. 123—124·5° (*semicarbazone*, m. p. 143—144°), and a *fraction*, b. p. 148—152°/18 mm., which is probably δζ-dimethyl-γη-diethyl-$\Delta^{\gamma\zeta}$-nonadien-ε-one,

$$CEt_2:CMe·CO·CMe:CEt_2.$$

βδδ-Trimethylhexan-γ-one, b. p. 158—161°, is prepared by the

ethylation of di-*iso*propyl ketone in ethereal solution. It does not yield an oxime or a semicarbazone. On reduction it gives *βδδ-trimethylhexan-γ-ol*, $CMe_2\cdot CH(OH)\cdot CMe_2Et$, b. p. 170—171°, the *phenylurethane* of which has m. p. 64°. *γγεε-Tetramethylheptan-δ-one*,

$$CMe_2Et\cdot CO\cdot CMe_2Et,$$

prepared by the ethylation of *iso*propyl *tert.*-amyl ketone in benzene solution, has b. p. 196—198°, and does not give an oxime or a semicarbazone. Sodium and absolute alcohol convert it into *γγεε-tetramethylheptan-δ-ol*, b. p. 210—212° (*phenylurethane*, m. p. 62—63°).

By repeated methylation of *iso*valerone in benzene solution and subsequent fractional distillation, the following products have been obtained: (i) *βγεζ-tetramethylheptan-δ-one*,

$$CHMe_2\cdot CHMe\cdot CO\cdot CHMe\cdot CHMe_2,$$

b. p. 76—78°/13 mm., which, when energetically treated, appears to yield small quantities of the corresponding *oxime*; (ii) *βγγεζ-pentamethylheptan-δ-one*, $CHMe_2\cdot CHMe\cdot CO\cdot CMe_2\cdot CHMe_2$, b. p. 88—89°/13 mm., which does not yield an oxime when heated with Crismer's reagent in alcoholic solution. *βγγεεζ-Hexamethylheptan-δ-one*,

$$CHMe_2\cdot CMe_2\cdot CO\cdot CMe_2\cdot CHMe_2,$$

b. p. 107—109°/14 mm., is prepared by the methylation of trimethyl*iso*valerone in toluene solution. When reduced with sodium and alcohol, it yields a small quantity of a *substance* which behaves like an unsaturated hydrocarbon, and *βγγεεζ-hexamethylheptan-δ-ol*,

$$CHMe_2\cdot CMe_2\cdot CH(OH)\cdot CMe_2\cdot CHMe_2,$$

b. p. 115—117°/13 mm. (*phenylurethane*, m. p. 91—92°).

H. W.

Optically Active Complex Glucinum Sugar Compounds. BENNO BLEYER and L. PACZUSKI (*Zeitsch. physikal. Chem.*, 1913, **84**, 1—14).—The authors have determined the influence of an alkaline solution of glucinum hydroxide on the rotatory power of mannitol. It is shown that when an alkaline solution of glucinum hydroxide is added to a solution of inactive mannitol, the solution becomes markedly lævorotatory. The influence of the alkaline glucinum solution is shown to depend on the presence of GlO_2'' ions in the solution, that is, it is due to sodium glucinate. The presence of glucinum hydroxide as a colloid could not produce so large a change in the rotation. A method is worked out, depending on the change of rotation, for determining the relative strength of the acid in amphoteric metal hydroxides. On adding solutions of sodium glucinate to mannitol, a condition is reached at which a constant rotation is reached; further additions cannot change this in either sense. This condition is reached when the concentration 13·84 grams mannitol, 72 grams sodium hydroxide, and 56·64 grams of glucinum sulphate per litre of solution is reached. A complex compound is formed by the action of sodium glucinate on mannitol, which is not hydrolysed at the concentrations examined, (1/640—10/640)*n*. This compound is similar to the complex glucinum hydroxydicarboxylic acid of Rosenheim and Itzig (A., 1899, i, 739).

J. F. S.

Unfermentable Residue in Hydrolytic Products of Starch. ARTHUR P. BRYANT and C. S. MINER (*Eighth Intern. Cong. App. Chem.*, 1912, **13**, 57—61).—Results are recorded which tend to show that some of the hydrolytic products of starch, such as "grape-sugar" and "liquid glucose," contain *iso*maltose. W. H. G.

Presence of Maltose in Acid Hydrolysed Starch Products. GEORGE DEFREN (*Eighth Intern. Cong. App. Chem.*, 1912, **13**, 111—112). —It has been found possible to isolate maltose from a crude glucose obtained by the hydrolysis of starch with acids. The dextrose present in the crude product was removed by fermentation, making use of *Saccharomyces apiculatus*, and the dextrin separated from the maltose subsequently by fractional precipitation with alcohol. W. H. G.

Hydrolysis of Starch by Acids with Some Additional Results on the Speed of Hydrolysis. GEORGE DEFREN (*Eighth Intern. Cong. App. Chem.*, 1912, **13**, 113—123).—An investigation on the hydrolysis of starch by acids. The relative speeds of hydrolysis using hydrochloric, sulphuric, oxalic, sulphurous and acetic acids are given, likewise results which show the effect of the concentration of the acid and the temperature on the rate of hydrolysis. The increase in the rate of hydrolysis with rise of temperature above 100° is very great, indicating that the starch molecule becomes very "labile" at these temperatures. W. H. G.

Osmotic Pressure of Colloids. V. Colloid Chemistry of the Dextrins. WILHELM BILTZ (and WILHELM TRUTHE) (*Zeitsch. physikal. Chem.*, 1913, **83**, 683—707. Compare A., 1910, ii, 22, 673; 1911, ii, 702; this vol., i, 593).—The molecular weight of a number of dextrins is determined by extrapolation to concentration zero from the calculated molecular weights obtained from the measurement of the osmotic pressure of dilute solutions. It is shown that even in dilute solutions the dextrins associate very markedly. The following values are found for the molecular weights: amylodextrin (*a*) 22200, amylodextrin (*b*) 20500, achroodextrin 10200, diastase dextrin (from grain) 11700, diastase dextrin (from beer) 8200, erythrodextrin 6800, erythrodextrin IIα 3000, acid dextrin 4000, achroodextrin I 1800, achroodextrin II 1200, dextrin β 950, sucrose 340, commercial dextrin (2 specimens) 5000, 6000, specially purified commercial dextrin 2800 and 2700, dextrin purified by dialysis 6200. The gold numbers of the various dextrins are determined, and it is shown that a relationship exists between the molecular weight and the gold number; generally a small gold number accompanies a large molecular weight. The authors have shown that in many cases the dextrins possess more than one gold number, and that there is an oscillating protecting action of the colloid between given concentrations. The viscosity of the dextrins in dilute solutions, that is, up to 5%, is determined, and it is shown that a parallelism exists between the viscosity and the molecular weight. It is also shown that the higher the molecular weight, the more the dextrins are adsorbed by ferric hydroxide gels. J. F. S.

Hydrolysis and Acetolysis of Cellulose. HERMANN OST (*Annalen*, 1913, **398**, 313—343. Compare this vol., i, 446).—The composition of the hydrocelluloses obtained as the initial product of the hydrolysis of cellulose by dilute mineral acids has long been a matter of dispute. The author finds that cellulose can be dried completely, without discoloration, by heating slowly to 100° and finally at 120—125°; the same is true of hydrocelluloses, some specimens of which, however, become discoloured at 125—150°. Since the ultimate analysis of completely dried cellulose and hydrocelluloses fails to disclose any differences in the percentages of carbon and of hydrogen, the author abandons his previous views that hydrocelluloses are hydrated celluloses, and inclines to Stern's opinion (T., 1904, **85**, 336) that there is no difference in the composition of celluloses and hydrocelluloses. The molecular magnitude of the latter is the smaller, as is indicated, not only by the smaller viscosity of their solutions, but also by their greater reducing action on copper salts, hydroxyl or aldehydo-groups being produced during the hydrolysis of the cellulose.

The acetolysis of cellulose is described in detail, the conditions under which cellobiose octa-acetate or dextrose α-penta-acetate (Ost, *loc. cit.*) are produced being definitely determined. The uncrystallisable syrup obtained in the acetolysis of cellulose resembles that obtained in the acetolysis of dextrose in acetic acid content, in rotatory power, and in yielding crystallised dextrose α-penta-acetate by further acetylation. Both syrups consist essentially of dextrose acetates mixed with acetates of *iso*maltose and dextrins and of other foreign substances.

Tho total yield of dextrose and cellobiose acetates obtained by the acetolysis of cellulose is 90% of that theoretically possible. Acetolysis, therefore, furnishes another proof that the cellulose molecule is composed only of dextrose residues. C. S.

Absorption Spectra of the Copper Derivatives of Primary Aliphatic Nitroamines. ANTOINE P. N. FRANCHIMONT and HILMAR J. BACKER (*Rec. trav. chim.*, 1913, **32**, 158—163. Compare T., 1912, **101**, 2256).—The authors have examined the absorption spectra of aqueous solutions of the copper salts of methylnitroamine, ethylnitroamine, ethylnitrosohydroxylamine, of copper nitrate and ammoniacal copper nitrate at equivalent concentrations. The copper salts of the nitroamines are much more strongly absorbent than a solution of copper nitrate with the same copper content, whilst the light which is not absorbed is less violet than in the case of the copper salt of ethylnitrosohydroxylamine. The spectra of the copper salts of methyl- and ethyl-nitroamines are practically identical, and do not show an absorption band.

The electrical conductivity of solutions of the copper salts of nitroamines is noticeably less than that of their sodium salts or of ordinary copper salts. The copper salt of ethylnitrosohydroxylamine conducts still more feebly.

Solutions of the copper salts of nitroamines give the ordinary reactions for copper, whilst that of ethylnitrosohydroxylamine, although yielding precipitates with sodium hydroxide and with

hydrogen sulphide, gives only a brown coloration with potassium ferrocyanide.

The authors are led to the conclusion that the copper derivative of ethylnitrosohydroxylamine is probably a complex internal salt, but in view of the differences existing between this substance and the copper salts of the nitroamines, hesitate to assign a similar structure to the latter substances, although their intense colour and feeble electrical conductivity point to a relationship between the metal and nitrogen.

H. W.

Oxalyl Derivatives of Amino-acids. D. J. MEYERINGH (*Rec. trav. chim.*, 1913, **32**, 140—157).—The author has prepared a series of oxalyl derivatives of amino-acids which contain the residues of two different amino-acids, by the action of ethyl chloroglyoxylate on the hydrochloride of the ester of an amino-acid, followed by treatment of the product so obtained with the potassium salt of a second amino-acid.

Ethyl chloroglyoxylate is best obtained by heating a mixture of equimolecular quantities of ethyl oxalate and phosphorus pentachloride until evolution of ethyl chloride ceases. It has b. p. 135°.

Methyl oxamidodiacetate, $C_2O_2(NH{\cdot}CH_2{\cdot}CO_2Me)_2$, has m. p. 158·5°, instead of 138—140° recorded by Kerp and Unger (A., 1897, i, 269).

Oxamidoacetic acid, $NH_2{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$, is obtained from oxamethane and potassium aminoacetate according to the method of Kerp and Unger (*loc. cit.*). The corresponding *methyl* ester, m. p. 157°, is obtained by treatment of the *silver* salt with an excess of methyl iodide and is converted by ammonia into the *amide*, needles, m. p. 251—252° (decomp.).

Ethyl ethoxalylaminoacetate, $CO_2Et{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et$, b. p. 188°/18 mm., m. p. 16°, is prepared in 84% yield by heating an equimolecular mixture of ethoxalyl chloride and ethyl aminoacetate hydrochloride in dry benzene until evolution of hydrogen chloride ceases. It is converted by ammonia into the corresponding di-amide.

Methyl ethoxalyl-α-aminopropionate, $CO_2Et{\cdot}CO{\cdot}NH{\cdot}CHMe{\cdot}CO_2Me$, b. p. 173·5°/19 mm., is similarly prepared from ethyl chloroglyoxylate and methyl α-aminopropionate hydrochloride. The *diamide*, prepared by means of liquid ammonia, forms slender needles, m. p. 216·5°. No evidence of the formation of an isomeric diamide could be obtained.

Methyl glycineoxalyl-α-aminopropionate,

$$CO_2H{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}CHMe{\cdot}CO_2Me,$$

m. p. 136—137°, is prepared by the addition of methyl ethoxalyl-α-aminopropionate to a solution of potassium aminoacetate, care being taken that the temperature does not exceed 5°. At higher temperatures, and in the presence of excess of alkali, the ester is readily saponified, the corresponding *acid* decomposing at 210° when rapidly heated.

When a solution of α-alanine in potassium hydroxide is added to ethyl ethoxalylglycine, *ethyl α-alanineoxalylglycine*,

$$CO_2H{\cdot}CHMe{\cdot}NH{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et,$$

m. p. 142·5°, is obtained if the temperature does not rise above 5°. At higher temperatures, and in the presence of more concentrated potassium hydroxide, alanine separates and the potassium salt of ethyl

oxalylaminoacetate is produced. In alcoholic solution, alanine always separates to some extent, and the *potassium* salt of *ethyl α-alanineoxalylglycine* is obtained.

Dimethyl α-alanineoxalylglycine,

$$CO_2Me\cdot CHMe\cdot NH\cdot CO\cdot CO\cdot NH\cdot CH_2\cdot CO_2Me,$$

m. p. 98·5°, is prepared by saturating a methyl alcoholic solution of methyl glycine oxalyl-α-aminopropionate with hydrogen chloride. *Methyl ethyl α-alanineoxalylglycine*,

$$CO_2Me\cdot CHMe\cdot NH\cdot CO\cdot CO\cdot NH\cdot CH_2\cdot CO_2Et,$$

m. p. 106°, is formed by similar treatment of a methyl alcoholic solution of ethyl α-alanineoxalylglycine or of an ethyl alcoholic solution of methyl glycineoxalyl-α-aminopropionate, whilst *diethyl α-alanineoxalylglycine*, $CO_2Et\cdot CHMe\cdot NH\cdot CO\cdot CO\cdot NH\cdot CH_2\cdot CO_2Et$, m. p. 120°, is similarly produced from ethyl α-alanineoxalylglycine or from the corresponding free acid.

α-Alanineoxalylglycinediamide,

$$NH_2\cdot CO\cdot CHMe\cdot NH\cdot CO\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH_2,$$

m. p. 272—274° (decomp.), is obtained by the action of liquid ammonia on dimethyl α-alanineoxalylglycine.

α-Amino*iso*butyric acid does not react with ethyl ethoxalylglycine in the presence of the calculated quantity of potassium hydroxide at 0°.

Methyl ethoxalyl-α-phenylaminoacetate, $CO_2Et\cdot CO\cdot NH\cdot CHPh\cdot CO_2Me$, m. p. 56°, is prepared by heating ethyl chloroglyoxylate and methyl α-phenylaminoacetate hydrochloride in benzene solution. The corresponding *diamide* has m. p. 229°. By the action of oxalyl chloride (1 mol.) on methyl α-phenylaminoacetate hydrochloride in dry benzene, two isomeric *forms* of dimethyl oxalyldi-(α-phenylaminoacetate), $C_2O_2(NH\cdot CHPh\cdot CO_2Me)_2$, are obtained which may be separated by taking advantage of their different solubilities in benzene. They have m. p. 169—170° and 195° respectively.

Unsuccessful attempts have been made to prepare acetyl and nitro-derivatives of several of the above substances.

The presence of the oxalyl group has been actually ascertained in each of the above derivatives. They have further been examined with regard to their ability to give the biuret reaction. It appears that only those substances show this reaction in which at least one of the amino-groups is intact. H. W.

Nitriles of Diaminodimethyl- and Diaminomethylethylsuccinic Acids and their Behaviour on Hydrolysis. OTTO DIELS and HAJIME OTSUKI (*Ber.*, 1913, **46**, 1877—1883).—The cyanohydrins of dimethyl diketone and methyl ethyl diketone react with ammonia, yielding the nitriles of diaminodimethyl- and diaminomethylethyl-succinic acids which, on hydrolysis with hydrochloric acid, are converted into compounds $C_6H_8N_3Cl$ and $C_7H_{10}N_3Cl$ respectively. The constitution of the latter compounds has not been definitely established, but from their pronounced basic properties and their behaviour toward nitrous acid, the conclusion is drawn that they contain only one amino-group. The halogen atom is very firmly attached, and cannot be removed by any of the usual reagents.

When treated with nitric acid, the compounds are completely decomposed, yielding a chloro-nitromethane. The formation of the latter compound indicates that the halogen is attached to one of the carbon atoms.

Methyl ethyl diketone cyanohydrin, OH·CMe(CN)·CEt(CN)·OH, is prepared by the action of hydrogen cyanide in ethereal solution on methyl ethyl diketone in the presence of potassium carbonate. It forms small, hygroscopic, crystalline plates, m. p. 76°, and when heated for five minutes with strong nitric acid is transformed into an *isomeride*, which sinters at 100°, m. p. 103°.

Diaminomethylethylsuccinonitrile, NH_2·CMe(CN)·CEt(CN)·NH_2, prepared by the action of concentrated aqueous ammonia on the preceding cyanohydrins at 0°, crystallises in hexagonal platelets or needles, m. p. 68°, and when maintained at 37° for two days with concentrated hydrochloric acid yields the *compound*, $C_7H_{10}N_3Cl$, which crystallises in lustrous, slender needles, m. p. 77·5°, forms a crystalline *hydrochloride* and *sulphate*, and on treatment with nitrous acid is converted into a *hydroxy*-compound, $C_7H_9ON_2Cl$, m. p. 147°.

s-*Diaminodimethylsuccinonitrile*, NH_2·CMe(CN)·CMe(CN)·NH_2, prepared from diacetylcyanohydrin (A., 1912, i, 942) and strong aqueous ammonia at 0°, crystallises in plates or leaflets, m. p. 166·5°. It is accompanied by a *substance*, $C_{12}H_{20}O_3N_6$, which forms small, tabular crystals, m. p. 234° (decomp.). On hydrolysis with concentrated hydrochloric acid at 37°, it yields the *compound*, $C_6H_8N_3Cl$. This forms long, lustrous needles, m. p. 140·5°, and is converted by the action of nitrous acid into a *hydroxy*-compound, $C_6H_7ON_2Cl$, which crystallises in lustrous needles, m. p. 227°, and when methylated by means of aqueous potassium hydroxide and methyl sulphate yields a *methyl ether*, $C_7H_9ON_2Cl$, crystallising in needles, m. p. 96°; if the methylation is carried out with diazomethane, an isomeric *methyl ether* of m. p. 54—55° is obtained. F. B.

The Origin of Optically Active Compounds in the Living Cell; the Artificial Preparation of Optically Active Compounds Without the Intervention of Asymmetrical Molecules or Asymmetrical Forces. EMIL ERLENMEYER (*Biochem. Zeitsch.*, 1913, **52**, 439—470).—In compounds of the type $C(R_1R_2R_3)—C(R_4R_5R_6)$ there are, according to van't Hoff, twelve isomerides possible, of which eight can be derived from the four others, simply by rotation about the C—C axis. Isomerides which can be derived from one another simply by a rotation of this description are designated by the author as "relative isomerides" in contradistinction to the isomerides ("bond-isomerides") which can only be derived from one another by changes in the bonds uniting the R groups. If the assumption is made that mirror images have the same solubilities as one another, they are not separable from one another by fractional crystallisation. If, however, a racemic mixture containing the two mirror images can be subjected to such treatment that the antipodes can be converted into their "relative isomerides," then it is possible that the two constituents can change at different rates, or that the rotation about the C—C axis can take place in opposite directions. If, therefore, it is possible, by any

method, to produce "relative isomerides" in a racemic mixture, then it is also conceivable that a mixture can be produced which contains isomerides which are no longer mirror images of one another, and which are postulated to be separable from one another by a process of fractional crystallisation. The author in conjunction with G. Hilgendorff has applied the above conceptions to the investigation of the asparagines. He confirms the observations of Piutti, that a mixture of the *d*- and *l*-substances can be separated by crystallisation from hot water. He shows, furthermore, that a mixture, in equimolar proportions, of these two isomerides has double the solubility of either constituent separately, and that by recrystallisation at 20° the two constituents are not separable from one another. If, however, the mixture is first heated with water for some hours, subsequent fractional crystallisation can yield crops of crystals, which rotate light in the opposite direction. It is assumed here that, in accordance with the theory given above, the isomerides which form mirror images are converted into "relative isomerides" by the action of heat which are no longer mirror images. Copper salts were also obtained by fractional crystallisation from the mixture of the heated acids, of which the various fractions differed markedly from one another both in colour and solubilities. An attempt to obtain optically active isomerides in a similar way from racemic acid failed. It is pointed out, however, that when the *d*- and *l*-tartaric acids are combined there is development of heat, and a product of higher melting point, and less soluble in water than either the *d*- or *l*-acids, is obtained; in the case of combination of the *d*- and *l*-asparagines no heat is developed, and the product is more soluble than the antipodes and has a lower m. p. Apparently a true racemic combination is not produced in this case. The action of heat on the sodium–ammonium salt of racemic acid led, however, to a very partial separation into optically active isomerides. It is claimed that the experiments described above afford the first examples of the production of optically active substances without intervention of asymmetrical substances and forces, and the biological significance of the results is discussed in some detail.

S. B. S.

Preparation of Carbonyl Cyanide. DANIEL BERTHELOT and HENRY GAUDECHON (*Compt. rend.*, 1913, **156**, 1990—1992. Compare this vol., i, 715).—It has already been shown that, in a manner analogous to the combination with chlorine, hydrogen and ammonia producing carbonyl chloride, formaldehyde and formamide respectively, carbon monoxide undergoes combination with cyanogen if a mixture is exposed to ultra-violet light, yielding carbonyl cyanide, CN·CO·CN.

Endeavours to prepare this substance by other methods reveal the fact that the silent electric discharge, which, although it frequently causes similar effects to ultra-violet light, exerts a quite distinct effect in other cases, also gives rise to a combination of the two gases. The mixture may contain varying proportions of the gases as long as neither becomes exhausted, but the action is most rapid when equal volumes are applied. With a tension of 6000 volts combination occurs much more rapidly than in ultra-violet light, and in one experiment

a mixture of 5 c.c. of carbon monoxide with an approximately equal volume of cyanogen gave a contraction of 3 c.c. in ten minutes. The yellow solid product is partly soluble in water and wholly soluble in alkalis. From the slow rate of its hydrolysis by dilute sulphuric acid, the substance evidently represents an even higher stage in the polymerisation of the simple molecule CN·CO·CN than the product of ultra-violet illumination.

Attempts were made to prepare the unpolymerised substance by chemical processes, such as the action of carbonyl chloride on cyanide of silver or mercury, or from carbon monoxide and cyanogen by mere heating, but the results were consistently negative.

D. F. T.

Some Complex Copper Alkali Ferrocyanides. KSHITIBHUSAN BHADURI and SARASHILAL SARKAR (*Zeitsch. anorg. Chem.*, 1913, **82**, 164—172).—Dextrose is added to a solution of potassium ferrocyanide, which is then mixed with Fehling's solution. A cream-coloured precipitate is obtained, which is crystalline if the solutions are dilute. It is washed with boiling water and dried in a vacuum over sulphuric acid. It becomes violet and blue with sulphuric acid, and yields a nitroprusside with nitric acid. The crystalline characters are described. The formula of the original salt is

$$K_2Cu_2Fe(CN)_6,2H_2O,$$

the blue salt being $K_2Cu_2Fe(CN)_6,K_2Cu_3[Fe(CN)_6]_2$, and the nitroprusside, $K_2Fe(CN)_5\cdot NO,2Cu_2Fe(CN)_5\cdot NO,13H_2O$. Alkali yields a compound $K_3CuFe(CN)_6,CuO,3\frac{1}{2}H_2O$. *Lithium copper ferrocyanide*, $Li_2Cu_2Fe(CN)_6,4H_2O$, is lemon-yellow, and the sodium compound has also been obtained. The *ammonium* salt is obtained by dissolving cupric oxide in ammonia, and adding dextrose and ammonium ferrocyanide, giving a red precipitate, $(NH_4)_2Cu_2Fe(CN)_6,3NH_3$, and, from the filtrate, pale blue crystals of $(NH_4)_3Cu_5[Fe(CN)_6]_2,8NH_3$. The compounds $2CuK_2Fe(CN)_6,8CuO,16H_2O$ and

$$(NH_4)_3Cu_4KFe_2(CN)_{12},5NH_3$$

have also been obtained. When copper sulphate is added to potassium ferricyanide and the precipitate is dissolved in ammonia, brown crystals of ammoniacal cupric ferrocyanide are obtained,

$$Cu_2Fe(CN)_6,3NH_3.$$

The nature of the reduction process is unknown. C. H. D.

The Action of Different Metals on Potassium Ferricyanide Solutions. GEORGE MCPHAIL SMITH [and RALPH ATKINSON LYNCH] (*Zeitsch. anorg. Chem.*, 1913, **82**, 63—70. Compare Beutel, A., 1912, i, 543).—Powdered iron prepared by reduction reduces potassium ferricyanide in an atmosphere of hydrogen:

$$4K_3Fe(CN)_6 + 2Fe = Fe_2Fe(CN)_6 + 3K_4Fe(CN)_6.$$

Nickel and zinc also reduce to ferrocyanide without passing into solution, and form precipitates. Silver reacts in the cold:

$$4K_3Fe(CN)_6 + 4Ag = Ag_4Fe(CN)_6 + 3K_4Fe(CN)_6,$$

but at 100° silver goes into solution as a complex salt. With mercury, metallic iron is first formed: $2K_3Fe(CN)_6 + 3Hg = 3K_2Hg(CN)_4 + 2Fe$. This iron then reacts as above, and, in presence of alkali hydroxide,

ferric hydroxide is ultimately formed. Gold dissolves slowly in ferricyanide solutions.

[With MICHELE CROCE.]—Silver ferrocyanide dissolves in potassium ferrocyanide solution, forming potassium silver cyanide, $KAg(CN)_2$.

C. H. D.

Univalent Nickel Compounds. II. ITALO BELLUCCI and R. CORELLI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 703—708. Compare this vol., ii, 604).—Continuing their work on the nature of the compound contained in the red liquid obtained by the reduction of potassium nickelocyanide, the authors criticise adversely the second also of the analytical methods employed by Moore (*loc. cit.*), so that they reject the formula Ni_3X_2 proposed by that author. By three analytical methods they obtain concordant results indicating that the red solution contains a cyano-salt in which nickel is univalent. The analytical methods employed were: (1) the measurement of the amount of hydrogen evolved by the solution in the warm; (2) titration with $N/10$-iodine solution; (3) titration with a standard hydrogen peroxide solution.

R. V. S.

New Compounds and Scissions of Azodicarboxylic Acid. OTTO DIELS and MAX PAQUIN (*Ber.*, 1913, **46**, 2000—2013).—The decomposition of derivatives of azodicarboxylic acid on dehydration, hydrolysis or heating is described. When azodicarboxylamide is heated with phosphoric oxide, nitrogen, water, cyanic acid and hydrogen cyanide are formed, according to the equation:

$$N_2(CONH_2)_2 = H_2O + N_2 + HCNO + HCN.$$

Substituted azoamides, such as azodicarboxyldiethylamide, yield *iso*-cyanates and *iso*nitriles: $N_2(CO\cdot NHEt)_2 = H_2O + N_2 + C_2H_5NCO + C_2H_5NC$. The same compound also readily forms a brick-red *silver* salt which decomposes at 144°, or when treated with iodine, into ethylcarbimide: $N_2(CO\cdot NAgEt)_2 = 2Ag + N_2 + 2CO{:}NEt$;

$$N_2(CO\cdot NAgEt)_2 + I_2 = 2AgI + N_2 + 2CO{:}NEt.$$

When azodicarboxylamide is heated with concentrated sulphuric acid, it decomposes into carbon dioxide, carbon monoxide, sulphur dioxide and nitrogen, but, in the cold, hydrazine sulphate and hydrazoic acid are formed. When boiled with dilute sulphuric acid, the compound gives a larger yield of hydrazoic acid, the other products including carbon monoxide, carbon dioxide, nitrogen and hydrazine and ammonium sulphates. Angeli (A., 1910, ii, 844) observed the production of hydrazoic acid under these conditions from azodicarboxylic acid itself, and explained it by assuming that di-imine, $NH{:}NH$, is first formed, and that it polymerises to the hypothetical tetrazen, which may decompose in two ways:

$$2NH{:}NH \longrightarrow NH_2\cdot N{:}N\cdot NH_2 \longrightarrow NH_3 + N_3H \text{ or } N_2 + N_2H_4.$$

The primary decomposition of azodicarboxylamide might also follow two courses:

$$N_2(CO\cdot NH_2)_2 + 2H_2O = 2CO_2 + 2NH_3 + NH{:}NH \text{ or}$$
$$N_2(CO\cdot NH_2)_2 = 2CO + NH_2\cdot N{:}N\cdot NH_2.$$

Methyl hydrazodicarboxylate, $N_2H_2(CO_2Me)_2$, was obtained in radiating bundles of broad needles by the action of methyl chloroformate on

hydrazine hydrate, and oxidised by concentrated nitric acid to *methyl azodicarboxylate*. The latter has b. p. 85°/7 mm., is hydrolysed by water to the hydrazo-ester, carbon dioxide and hydrazoic acid, and is oxidised by fuming nitric acid to oxalic acid.

Whereas primary amines convert the esters of azodicarboxylic acid into amides, secondary and tertiary amines usually form additive compounds which, on hydrolysis with dilute acids, yield the corresponding hydrazo-esters together with aldehydes and amines which contain one radicle less attached to the nitrogen atom than the original amine does. Thus the *compound* of ethyl azodicarboxylate with dimethylamine yields ethyl hydrazodicarboxylate, formaldehyde and methylamine, its constitution being therefore represented by the formula $CO_2Et{\cdot}N(CH_2{\cdot}NHMe){\cdot}NH{\cdot}CO_2Et$. The compound forms well-defined prisms or rhombic plates, m. p. 95°, decomposes, when the aqueous solution is boiled, into ethyl hydrazodicarboxylate, dimethylamine, nitrogen and carbon dioxide, and is oxidised by nitric acid to ethyl azodicarboxylate. When submitted to dry distillation, it decomposes vigorously, giving a good yield of hydrazomethane, together with ethyl hydrazodicarboxylate, ethylcarbimide and formaldehyde:

$$2CO_2Et{\cdot}N(CH_2{\cdot}NHMe){\cdot}NH{\cdot}CO_2Et = 2CH_2O + 2CO{:}NEt + N_2H_2(CO_2Et)_2 + N_2H_2Me_2.$$

When the decomposition and distillation are carried out under reduced pressure, however, the chief product is ethyl dimethylcarbamate:

$$2CO_2Et{\cdot}N(CH_2{\cdot}NHMe){\cdot}NH{\cdot}CO_2Et = N_2 + EtOH + CO + NMe{\cdot}CO_2Et.$$

The latter was characterised by conversion into methylnitroamine (Franchimont and Klobbie, A., 1889, 492).

The *compound*, $CO_2Et{\cdot}N(CHMe{\cdot}NHEt){\cdot}NH{\cdot}CO_2Et$, prepared by mixing ethyl azodicarboxylate with diethylamine, forms clusters of needles, m. p. 68°, is sparingly soluble in cold water or water at 80—90°, but is readily soluble at 50°, and yields acetaldehyde on hydrolysis. The *compound*, $CO_2Me{\cdot}N(CH_2{\cdot}NMePh){\cdot}NH{\cdot}CO_2Me$, obtained from methyl azodicarboxylate and dimethylaniline, crystallises from ether in prismatic columns and rhombic plates, m. p. 95—96°, and yields formaldehyde, methylaniline, and methyl hydrazodicarboxylate on hydrolysis. The *compound*,

$$NHEt{\cdot}CO{\cdot}N(CH_2{\cdot}NHMe){\cdot}NH{\cdot}CO{\cdot}NHEt,$$

prepared by mixing azodicarboxylethylamide with ether and dimethylamine in the cold in a sealed tube, forms rhombic plates, m. p. 109—111° (decomp.), and yields formaldehyde on hydrolysis.

J. C. W.

1 : 1-Dimethyl*cyclo*hexane. NICOLAI D. ZELINSKI and NICOLAI N. LEPESCHKIN (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 613—616).—β-Methyl-Δ^{β}-hepten-ζ-one was converted into the η-acetyl derivative, the latter transformed by the action of sulphuric acid into 6-acetyl-1 : 1-dimethyl*cyclo*hexan-5-one, and this hydrolysed to 1 : 1-dimethyl*cyclo*hexan-5-one, which, on reduction in ethereal solution by means of sodium and water, gave 1 : 1-*dimethyl*cyclo*hexan-5-ol*,

$$CH_2{<}{\begin{matrix}CH(OH){\cdot}CH_2\\CH_2\text{——}CH_2\end{matrix}}{>}CMe_2,$$

b. p. 185°/754 mm., D_4^{18} 0·9071, n_D^{18} 1·4558. Reduction of the

alcohol with hydriodic acid yields 1:1-dimethyl*cyclo*hexane, b. p. 119·2—119·7°, D_4^{16} 0·7843, D_4^{20} 0·7792, n_D^{16} 1·4320 (compare Crossley and Renouf, T., 1905, **87**, 1487). When treated with bromine in presence of aluminium bromide, this hydrocarbon is readily converted into tetrabromo-*p*-xylene, one of the methyl groups migrating to the para-position under the conditions of bromination (compare A., 1902, i, 143). T. H. P.

The Benzene Problem. KURT GEBHARD (*J. pr. Chem.*, 1913, [ii], **88**, 94—96).—A reply to Liebig (this vol., i, 607). F. B.

A New Method for the Introduction of Iodine into Aromatic Substances. KARL ELBS and A. JAROSLAVZEV (*J. pr. Chem.*, 1913, [ii], **88**, 92—94).—Iodo-derivatives of aromatic hydrocarbons may be readily prepared by boiling the latter with iodine and sodium persulphate in glacial acetic acid solution. Thus benzene yields iodo- and *p*-di-iodobenzene, whilst toluene gives rise to *o*- and *p*-iodotoluenes.

The following iodo-compounds have also been prepared by this method: 4-iodo-*m*-xylene, 4-iodo-*o*-xylene, 2-iodo-*p*-xylene, and iodo-*ψ*-cumene.

s-*Di*-p-*iododiphenylethane*, prepared from dibenzyl, has m. p. 152°; the position of the iodine atoms has been established by its oxidation to *p*-iodobenzoic acid by chromic acid in glacial acetic acid solution. F. B.

Some Aromatic Fluorine Compounds. FRÉDÉRIC SWARTS (*Bull. Acad. roy. Belg.*, 1913, 241—278).—The compounds described are mostly prepared by decomposing aromatic diazonium salts with hydrofluoric acid in vessels of silver or platinum. They were obtained for thermochemical investigations (compare A., 1907, ii, 9; 1908, ii, 354; 1909, ii, 297).

o-Fluoronitrobenzene could not be prepared: the para-isomeride forms colourless crystals, m. p. 27°, b. p. 205°/735 mm., and the *meta*-derivative has m. p. 3·6°, b. p. 200°/756 mm., D_{17} 1·3272, n_D 1·5207.

1-Fluoro-2:4-dinitrobenzene forms large, colourless, hard crystals m. p. 25·8°, b. p. 178°/25 mm.

m-*Fluoroacetanilide* crystallises in large, colourless prisms, m. p. 84·5°; the para-isomeride forms tiny needles, m. p. 152°. 4-*Fluoro*-3-*nitroacetanilide* separates in very pale yellow needles, m. p. 138·5°.

p-*Fluorophenol*, prepared by heating fluorophenetole with aluminium chloride, has b. p. 185·5°. It forms transparent, tabular crystals, m. p. 26·5—27°, but this modification changes on keeping into a stable form, m. p. 45°, consisting of acicular crystals resembling phenol.

m-*Fluorophenol*, prepared by decomposing *m*-fluorobenzenediazonium sulphate, forms large, prismatic crystals, m. p. 13·7°. o-*Fluorophenol*, b. p. 151—152°, m. p. 16·1°, has a penetrating odour.

ω-*Trifluoro*-m-*cresol*, $CF_3\cdot C_6H_4\cdot OH$, prepared by diazotising trifluorotoluidinesulphate and decomposing the diazonium compound with

dilute sulphuric acid, forms a viscid liquid, b. p. 178·3°, which yields crystals, m. p. –1·8°.

On diazotising *o*-phenetidine in hydrofluoric acid a mixture of *o*-fluorophenetole and ordinary phenetole is obtained. o-*Fluorophenetole* has b. p. 171·4°, m. p. –16·7°. m-*Fluorophenetole*, prepared in a similar manner, is a colourless liquid, b. p. 171·4°/755 mm., $D_{16\cdot4}$ 1·0716, n_D 1·4847.

p-*Fluorophenetole* cannot be separated from phenetole by distillation; after fractional crystallisation the pure product had m. p. –8·5°, b. p. 172·8°/766 mm., $D_{18\cdot2}$1·07148, n_D1·48257. The product described by Valentiner and Schwarz (*Zeitsch. angew. Chem.*, 1898, **11**, 441), b. p. 197°, as *p*-fluorophenetole is shown to be mainly *p*-chlorophenetole.

On nitration of *p*-fluorophenol, 4-*fluoro*-2-*nitrophenol* is obtained, crystallising in hexagonal prisms, m. p. 73·7°; the *sodium* and *potassium* salts form long, red needles which explode when heated.

The corresponding 4-*fluoro*-2-*nitrophenetole* yields colourless crystals, m. p. 33·7°. 4-*Fluoro*-2 : 6 *dinitrophenol* crystallises in very beautiful yellow prisms, m. p. 50·2°.

On nitration of *m*-fluorophenol, a *dinitro*-derivative is obtained in large, colourless, straw-like crystals becoming yellow on exposure to light, m. p. 72—74°; the constitution has not been established.

p-*Difluorobenzene* prepared from *p*-fluoroaniline is an oil, b. p. 88—89°, $D_{18\cdot5}$ 1·1725, n_D 1·4422, m. p. –23·7°.

On nitration 1 : 4-*difluoro*-2-*nitrobenzene* is obtained as a pale yellow oil, b. p. 103°/25 mm., m. p. –11·7°; it is very viscous at low temperatures. The oil has $D_{17\cdot2}$ 1·4671, n_D 1·5115. E. F. A.

Chloronitrotoluenes with Reactive Chlorine. WALTHER BORSCHE and ANNA FIEDLER (*Ber.*, 1913, **46**, 2117—2131. Compare A., i, 175).—In continuation of the earlier investigation which led to the isolation of pure 2-chloro-3 : 5-dinitrotoluene, the authors have turned their attention to the corresponding derivatives of *p*-and *m*-chlorotoluenes. Their results indicate, among other facts, that pure 4-chloro-3 : 5-dinitrotoluene has not been previously obtained (compare Hönig, A., 1887, 1034).

The further nitration of 4-chloro-3-nitrotoluene by gradual addition to a cooled mixture of equal volumes of sulphuric acid and nitric acid (D 1·52) gives an impure reaction product from which by repeated crystallisation from alcohol pure 4-chloro-3 : 5-dinitrotoluene, needles, m. p. 115—116°, can be separated. It reacts with ethyl sodiomalonate in warm ethereal solution, producing, after acidification, *ethyl* 2 : 6-*dinitro*-p-*tolylmalonate*, $C_6H_2Me(NO_2)_2\cdot CH(CO_2Et)_2$, colourless crystals, m. p. 90°, which on heating with a mixture of acetic acid and a little diluted sulphuric acid passes into 2 : 6-*dinitro*-p-*tolylacetic acid*,

$$C_6H_2Me(NO_2)_2\cdot CH_2\cdot CO_2H,$$

colourless needles, m. p. 241—242° (decomp.). 4-Chloro-3 : 5-dinitrotoluene also reacts with aniline, yielding 3 : 5-dinitro-4-anilinotoluene. The chlorodinitrotoluene can also be obtained in small quantity by the action of toluene-*p*-sulphonyl chloride on dinitro-*p*-cresol in the presence of diethylaniline. In preparing the compound by the first method a

substance, m. p. 108°, possibly 4-chloro-2 : 5-dinitrotoluene, which does not react with aniline, is simultaneously produced.

The main product in the nitration of *m*-chlorotoluene by Reverdin and Crepieux's method (A., 1900, i, 638) is 3-chloro-4 : 6-dinitro toluene, m. p. 91°. It reacts in warm ethereal solution with ethyl sodioacetoacetate, producing *ethyl* 4 : 6-*dinitro*-m-*tolylacetoacetate*,

$$C_6H_2Me(NO_2)_2\cdot CHAc\cdot CO_2Et,$$

yellow tablets, m. p. 98°, which on warming with sulphuric acid undergoes scission, yielding 4 : 6-*dinitro*-m-*tolylacetone*,

$$C_6H_2Me(NO_2)_2\cdot CH\cdot CO\cdot CH_3,$$

leaflets, m. p. 92°; also with ethyl sodiomalonate, it gives *ethyl* 4 : 6-*dinitro*-m-*tolylmalonate*, pale yellow crystals, m. p. 62°, which on heating with diluted sulphuric acid in acetic acid solution passes into 4 : 6-*dinitro*-m-*tolylacetic acid*, colourless needles, m. p. 176°; this substance when maintained at its m. p. loses carbon dioxide with production of 4 : 6-dinitro-1 : 3-xylene, m. p. 93—94°. *Ethyl* 4 : 6-*dinitro*-m-*tolylacetate*, colourless needles, m. p. 70°, is slowly converted by the action of sodium and more *m*-chlorodinitrotoluene in alcoholic solution at the ordinary temperature into *ethyl* 4 : 6 : 4′ : 6′-*tetranitro-di-m-tolylacetate*, $CO_2Et\cdot CH_2[C_6H_2Me(NO_2)_2]_2$, needles, m. p. 159—160°, and also condenses at 180° with salicylaldehyde in the presence of a little piperidine, producing 3-o′p-*dinitro*-m-*tolylcoumarin*, $\begin{matrix}C_6H_4\text{—}CH\\ |\qquad\quad\\ O\text{———}CO\end{matrix}\!\!>\!C\text{—}C_6H_2Me(NO_2)_2$, yellow needles, m. p. 240°, with a little 4 : 6-*dinitro-3-coumarino-2′-hydroxystilbene*,

$$\begin{matrix}C_6H_4\text{—}CH\\ |\qquad\quad\\ O\text{———}CO\end{matrix}\!\!>\!C\text{—}C_6H_2(NO_2)_2\cdot CH\!:\!CH\cdot C_6H_4\cdot OH.$$

4 : 6-Dinitro-*m*-toluidine is obtainable by heating the corresponding chlorodinitrotoluene with alcoholic ammonia at 100°, and if the ammonia be replaced by aniline, *phenyl*-4 : 6-*dinitro*-m-*tolylamine*,

$$C_6H_2Me(NO_2)_2\cdot NHPh,$$

orange-coloured leaflets, m. p. 145°, is obtained. The former of these products readily condenses at 180—190° with benzaldehyde in the presence of piperidine with formation of 4 : 6-*dinitro*-3-*anilinostilbene*, $NHPh\cdot C_6H_2(NO_2)_2\cdot CH\!:\!CHPh$, deep red leaflets, m. p. 182°. The chlorodinitrotoluene likewise condenses with piperidine when heated with the hydrochloride of the base and sodium acetate in alcoholic solution, giving 4 : 6-dinitro-3-piperidinotoluene, yellow rhombs, m. p. 116°; this can be further condensed with benzaldehyde, 4 : 6-*dinitro*-3-*piperidinostilbene*, yellowish-red crystals, m. p. 172°, being produced.

If the mother liquors from the crystallisation of 3-chloro-4 : 6-dinitrotoluene are treated with ethyl sodiomalonate or sodioacetoacetate, an unreactive isomeride, 3-*chloro*-2 : 4-*dinitrotoluene*, yellowish-white needles, m. p. 73°, remains unaffected; its structure is indicated by its conversion through the corresponding *dinitrotolylhydrazine* (*hydrochloride*, yellow needles) by the action of ammonium hydroxide into 4-*nitro*-5-*methyl*-1-*hydroxy*-1 : 2 : 3-*benzotriazole*,

$$C_6H_2Me(NO_2)\!<\!\begin{matrix}\text{——}N\\ N(OH)\end{matrix}\!\!>\!N,$$

decomp. at 176° (compare Borsche and Rantscheff, A., 1911, i, 329).]

2-Chloro-3 : 5-dinitrotoluene reacts with ethyl sodioacetoacetate in ethereal suspension with formation of *ethyl* α-4 : 6-*dinitro*-o-*tolylacetoacetate*, yellow needles, m. p. 79—80°, from which 4 : 6-*dinitro*-o-*tolylacetone*, pale yellow leaflets, m. p. 103—104°, can be obtained by hydrolysis with diluted sulphuric acid. In a similar manner, condensation with ethyl sodiomalonate yields *ethyl* 4 : 6-*dinitro*-o-*tolylmalonate*, yellow prisms, m. p. 87—88°, which on heating with diluted sulphuric acid in acetic acid solution is converted into 4 : 6-*dinitro*-o-*tolylacetic acid*, colourless needles, m. p. 202° (decomp.); this when heated readily loses a molecule of carbon dioxide with formation of 3 : 5-*dinitro*-1 : 2-*xylene*, m. p. 74—75°. D. F. T.

Solubilities of the Rare Earth Salts of Bromonitrobenzenesulphonic Acid. S. H. KATZ and CHARLES JAMES (*J. Amer. Chem. Soc.*, 1913, **35**, 872—874).—1 : 4 : 2-Bromonitrobenzenesulphonic acid, prepared by sulphonation of bromonitrobenzene, forms nicely crystalline salts with lanthanum ($8H_2O$), cerium ($8H_2O$), yttrium ($10H_2O$), praseodymium ($8H_2O$), neodymium ($8H_2O$), samarium ($10H_2O$), europium ($10H_2O$), gadolinium ($10H_2O$), erbium ($12H_2O$), thulium ($12H_2O$), and ytterbium ($12H_2O$). The solubility of each salt was determined at 25°, and it is interesting that on plotting the solubilities against the atomic weight, salts containing the same amount of water of crystallisation fall on distinct portions of the curve. D. F. T.

Nitration of Iodobenzene. ARNOLD F. HOLLEMAN (*Rec. Trav. chim.*, 1913, **32**, 134—139).—In a previous investigation of the nitration of iodobenzene (A., 1912, i, 87), the author has found that the quantity of ortho-isomeride formed is less than that obtained in the nitration of bromobenzene, whilst in the nitration of other aryl haloids, the quantity of this isomeride increases with the atomic weight of the halogen, and also that a greater amount of *o*-iodonitrobenzene is obtained at −30° than at 0°, although the amount of accessory product generally increases with increasing temperature of nitration.

[With A. F. H. LOBRY DE BRUYN and W. J. DE MOOY.]—The previous work has been repeated and a new source of error discovered due to the ready solubility of *o*-iodonitrobenzene in iodobenzene, in which *p*-iodonitrobenzene is practically insoluble. The iodobenzene is now added slowly to the nitric acid (D 1·482 for nitration at 0° and D 1·488 for nitration at −30°) with brisk stirring, smaller quantities of concentrated nitric acid being added from time to time if the mass becomes too viscous. Agitation is continued for two to three hours after completion of the addition of iodobenzene. The mass is then poured into water, filtered, dried, and distilled under diminished pressure. In this manner the determination of the point of solidification is greatly facilitated.

The authors are led to the conclusion that the iodobenzene does not differ from that of the other phenyl haloids. At −30°, 39·1% of the ortho- and 60·9% of the para-isomeride are obtained, whilst at 0° the figures are 41·1% ortho- and 58·7% para-isomeride. H. W.

Some Diphenylpentanes and the Corresponding *Dicyclo***hexylpentanes.** Paul Sabatier and Marcel Murat (*Compt. rend.*, 1913, **156**, 1951—1954. Compare this vol., i, 716; A., 1912, i, 617, 757).—The authors have already reduced various diphenylethanes, diphenylpropanes, and diphenylbutanes to the corresponding di*cyclo*hexyl derivatives, and in order to test the general character of the hydrogenation still further, have now submitted three of the eighteen theoretically possible diphenylpentanes to similar treatment.

By catalytic treatment of β-phenylpropionic acid with thoria or iron oxide, *$\alpha\epsilon$-diphenylpentan-γ-one*, $CH_2Ph{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CH_2Ph$, was first prepared, which, by contact with a not too active nickel at 180° in the presence of hydrogen, is converted smoothly into *$\alpha\epsilon$-diphenylpentane*, a fluorescent colourless liquid, b. p. 324° (corr.), D_0^0 0·9924, n_D^{19} 1·559. By hydrogenation under the influence of a very active nickel at 165°, this hydrocarbon is entirely reduced to *$\alpha\epsilon$-di*cyclo*hexylpentane*, $C_6H_{11}{\cdot}[CH_2]_5{\cdot}C_6H_{11}$, a colourless liquid, b. p. 311° (corr.), D_0^0 0·8832, n_D^{21} 1·479, which resists the action of a cold mixture of nitric and sulphuric acids.

Methyl *iso*valerate reacts with magnesium phenyl bromide, yielding *$\alpha\alpha$-diphenyl-γ-methylbutanol*, $CHMe_2{\cdot}CH_2{\cdot}CPh_2{\cdot}OH$, which undergoes dehydration when distilled under the ordinary pressure, with production of *$\alpha\alpha$-diphenyl-γ-methyl-Δ^{α}-butene*, $CHMe_2{\cdot}CH{:}CPh_2$, a pale yellow liquid, b. p. 298—299° (corr.), D_0^{21} 0·9792, n_D^{21} 1·581. When submitted to the action of hydrogen under the influence of a sluggish nickel catalyst at 180°, the last-named hydrocarbon undergoes reduction to *$\alpha\alpha$-diphenyl-γ-methylbutane*, $CHMe_2{\cdot}CH_2{\cdot}CHPh_2$, a colourless, slightly fluorescent liquid, b. p. 297° (corr.), D_0^0 0·9756, n_D^{21} 1·551, which is still further reduced under the catalytic influence of a very active specimen of nickel at 160—165°, giving *$\alpha\alpha$-di*cyclo*hexyl-γ-methylbutane*, $CHMe_2{\cdot}CH_2{\cdot}CH(C_6H_{11})_2$, a colourless liquid, b. p. 290—291° (corr.), D_0^0 0·9058, n_D^{21} 1·489.

Magnesium ethyl iodide reacts with *diphenylpropanone*,

$$CH_2Ph{\cdot}CO{\cdot}CH_2Ph,$$

which is obtainable by catalytic treatment of phenylacetic acid with iron oxide, producing *dibenzylethylcarbinol*, $CH_2Ph{\cdot}CEt(OH){\cdot}CH_2Ph$; this passes on mere distillation under ordinary pressure into *$\alpha\gamma$-diphenyl-β-ethyl-Δ^{α}-propylene*, $CHPh{:}CEt{\cdot}CH_2Ph$, b. p. 306—307°, D_0^{21} 1·0159, n_D^{21} 1·589. By means of a sluggish nickel catalyst at 230° this can be hydrogenated to *$\alpha\gamma$-diphenyl-β-ethylpropane*, $CH_2Ph{\cdot}CHEt{\cdot}CH_2Ph$, a colourless, fluorescent liquid, b. p. 304—305° (corr.), D_0^0 0·9855, n_D^{21} 1·553. When submitted to an active nickel catalyst below 180° it is reduced by hydrogen to *$\alpha\gamma$-di*cyclo*hexyl-β-ethylpropane*,

$$C_6H_{11}{\cdot}CH_2{\cdot}CHEt{\cdot}CH_2{\cdot}C_6H_{11},$$

a colourless liquid, b. p. 296° (corr.), D_0^0 0·8966, n_D^{21} 1·843, which is not attacked by a cold mixture of sulphuric and nitric acids.

A comparison of the m. p.'s and b. p.'s of the diphenyl derivatives in which the two phenyl groups are connected by a normal chain of carbon atoms reveals the fact that whilst the latter increases steadily with an increasing number of linking atoms, the m. p.'s exhibit an undulating increase similar to that observed with the dicarboxylic acids. It is also noteworthy that whilst all the diphenyl hydro-

carbons are fluorescent, this property is most marked in those having the two phenyl radicles coupled by a normal chain of methylene linkings; the di*cyclo*hexyl derivatives possess no fluorescence.

D. F. T.

The Constitution of Naphthalene. EUGEN BAMBERGER (*Ber.*, 1913, **46**, 1899—1903).—Since his earlier publications (a list of which is appended to the paper), the author's views on this subject have undergone modifications. Although he still regards the symmetry of naphthalene as highly probable, he realises that there has been no final proof. The formula suggested by Willstätter and Waser (A., 1912, i, 17) fails to express the reduction of naphthalene and its derivatives, which possess no true aromatic character, to aromatic compounds. This peculiar behaviour of naphthalene derivatives can be explained by other symmetrical formulæ in addition to the author's, provided that they do not include a true benzene ring, but the author repeats his earlier statement (*J. pr. Chem.*, 1890, **42**, [2], 205) that it is not possible to represent completely the various chemical phenomena presented by naphthalene derivatives in any one formula of the usual type.

D. F. T.

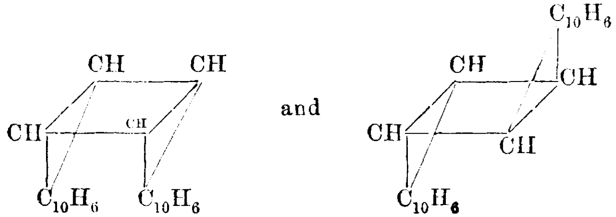
10-Bromophenanthrene-3- or -6-sulphonic Acid. HÅKAN SANDQVIST (*Annalen*, 1913, **398**, 125—137).—By heating with 96—97% sulphuric acid on the water-bath and finally at 150—155°, 10-bromophenanthrene is converted into an acid which is proved to be 10-bromophenanthrene-3- or -6-sulphonic acid, and is isolated as the potassium salt. The free acid, prepared from the chloride and water at 130—135°, is an almost colourless, crystalline powder. It contains $3H_2O$, and has m. p. 162—164·5° (anhydrous, 200—201·5°). A 10% aqueous solution of the acid, which is as clear and viscous as water, becomes syrupy by the addition of a little dilute hydrochloric, nitric, or sulphuric acid, and finally deposits crystals of the acid by further addition of the mineral acid. The following salts are described, the figures in brackets denoting the weight of anhydrous salt dissolved by 100 grams of water at 19 5°: *ammonium* salt containing H_2O (0·327), *sodium* salt containing $1\frac{1}{2}H_2O$ (0·142), *potassium* salt with H_2O (0·163), *calcium* salt with $4H_2O$, *barium* salt with $2\frac{1}{2}H_2O$, *cupric* salt with $4H_2O$; the last three salts are quantitatively insoluble. The *methyl* ester, m. p. 172·5—173°, *ethyl* ester, m. p. 173—173·3°, *chloride*, $C_{14}H_8O_2ClBrS$, m. p. 184·5—185°, *sulphonamide*, m. p. 280—281°, and dimorphous *anilide*, m. p. 185·5—186° or 193°, are described.

By oxidation with chromic acid in boiling glacial acetic acid, 10-bromophenanthrene-3-(or 6-)-sulphonyl chloride and methyl 10-bromophenanthrene-3-(or 6-)-sulphonate respectively yield substances, m. p. 230—238° and 230—233°, which are apparently phenanthraquinone-3-sulphonyl chloride, m. p. 232—234°, and methyl phenanthraquinone-3-sulphonate, m. p. 234°, respectively.

Potassium or methyl 10-bromophenanthrene-3-(or 6-)-sulphonate are not attacked by reducing agents in acid or neutral media; concentrated aqueous ammonia and zinc dust on the water-bath reduce the potassium salt, yielding phenanthrene-3-sulphonic acid.

C. S.

Photochemical Transformations of Acenaphthylene. II. KARL DZIEWOŃSKI and C. PASCHALSKI (*Ber.*, 1913, **46**, 1986—1992. Compare A., 1912, i, 844).—The two hydrocarbons, m. p. 306—307° and m. p. 232—234°, which are obtained by the action of sunlight on acenaphthylene are *cis-trans*-isomerides and may be represented by the formulæ :



The compounds are formed in different quantities according to the nature and concentration of the solution and to the intensity of the light. They both yield naphthalic anhydride on oxidation and are partly converted into the parent substance in the molten state, but they form entirely different picrates and bromo-compounds. Although it cannot be said which of the isomerides is the labile modification, it is proposed to call the higher and the lower melting forms *α*- and *β-heptacyclene* respectively.

The former is the chief product when a benzene solution of acenaphthylene is illuminated, but the *β*-form predominates when petroleum is used as the solvent. *β-Heptacyclene*, $C_{24}H_{16}$, forms large, monoclinic prisms or tablets, $a:b:c = 0.7223:1:0.9527$, $\beta = 119°8'$, and is readily soluble in benzene. Both substances yield new, complex hydrocarbons when kept in the molten state for some time, but, when the mass is quickly cooled, some acenaphthylene is obtained and this is probably the parent of the new compounds, for it is unstable above 110°.

α-Heptacyclene combines with two molecules of picric acid in ethylene dibromide solution, yielding the *picrate*,

$$C_{24}H_{16},2C_6H_2(NO_2)_3\cdot OH,$$

in orange needles, m. p. 225—227°, which are decomposed even by solvents, whereas *β*-heptacyclene forms a stable *picrate*,

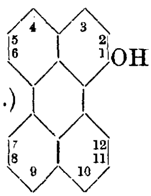
$$C_{24}H_{16},C_6H_2(NO_2)_3\cdot OH,$$

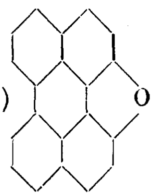
in carmine-red needles, m. p. 215—216°. The *α*-hydrocarbon reacts very sluggishly with bromine in the cold, but the *β*-form absorbs bromine at once. J. C. W.

Perylene and Its Derivatives. II. RICHARD WEITZENBÖCK and CHRISTIAN SEER [with A. VON BARTSCH] (*Ber.*, 1913, **46**, 1994—2000. Compare A., 1910, i, 616).—Attempts have been made to improve the yield of perylene or its derivatives. The best result was obtained by the condensation of 4 : 4′-dicyano-1 : 1′-dinaphthyl to 3 : 10-dicyanoperylene.

From bromonaphthalene and aluminium chloride, a 4% yield of perylene was obtained at 140°, but at 30—35° the product was 2 : 2′-dinaphthyl, which was probably formed by the rearrangement of 1 : 1′-dinaphthyl. *β*-Dinaphthylene oxide (Eckstein, A., 1905, i, 885)

was also heated with aluminium chloride, when alkali extracted from the product, 1-*hydroxyperylene* (I). This forms long, slender, yellow needles, m. p. 197°, which give yellow solutions with green fluorescence, and yield a *benzoate*, $C_{27}H_{16}O_2$, in slender, lemon-yellow needles, m. p. 170—170·5°, and a *methyl ether* in yellow nodules, m. p. 111°. The residue from the extraction with alkali contained 1 : 12-*furoperylene* (II), which forms a reddish-brown powder, and gives dark red solutions with yellowish-brown fluorescence.

(I.) 

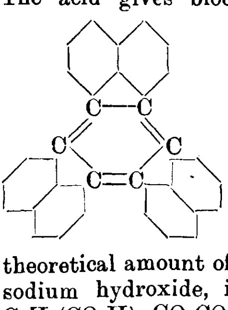
(II.) 

3 : 10-*Dicyanoperylene*, $C_{22}H_{10}N_2$, was obtained in good yield by the condensation of 4 : 4′-dicyano-1 : 1′-dinaphthyl (Seer and Scholl, this vol., i, 734) in brown, microscopic needles, m. p. 368—369°. It is sparingly soluble in acetic acid or xylene with intense green fluorescence, and yields 3 : 10-*perylenedicarboxylic acid*, $C_{22}H_{12}O_4$, when heated with alcoholic sodium hydroxide in a sealed tube. The acid forms reddish-brown, microscopic needles, and the solutions in alkalis are yellow with intense green fluorescence. The *ethyl* ester, $C_{26}H_{20}O_4$, forms brick-red leaflets, m. p. 247—248°.

4 : 4′-Di-iodo-1 : 1′-dinaphthyl (Willgerodt and Schlösser, A., 1900, i, 282) was prepared from naphthidine by treating the diazonium salt with potassium iodide. When heated with aluminium chloride, extensive decomposition took place. J. C. W.

Degradation of Decacyclene [Trinaphthylenebenzene]. KARL DZIEWOŃSKI [with J. PODGÓRSKA and A. MIKLASZEWSKI] (*Ber.*, 1913, **46**, 2156—2162).—When finely powdered decacyclene (A., 1903, i, 431) is heated for some hours with sodium dichromate and 30% sulphuric acid, it is broken down into *tribenzoylenebenzenetricarboxylic acid*, $C_6\left(<\overset{CO}{\underset{C_6H_3\cdot CO_2H}{|}}\right)_3$, which is formed in good quantity, as a brownish-red, voluminous, microcrystalline mass, m. p. above 360° The acid gives blood-red solutions in alkalis, and forms, by precipitation, a brown *silver* salt, $C_{30}H_9O_9Ag_3$, and a reddish-brown *barium* salt, $(C_{30}H_9O_9)_2Ba_3$. When the calcium salt is distilled with lime, a sublimate of large, orange-yellow needles of tribenzoylenebenzene (truxenequinone),

$$C_6\left(<\overset{CO}{\underset{C_6H_4}{|}}\right)_3$$



(Michael, A., 1906, i, 518) is formed. On heating the acid for three or four hours with the theoretical amount of potassium permanganate in a large excess of 2% sodium hydroxide, it is oxidised to dicarboxyphenylglyoxylic acid, $C_6H_3(CO_2H)_2\cdot CO\cdot CO_2H$ (Graebe and Bossel, A., 1896, i, 436), and an acidic by-product, but complete oxidation with an excess of permanganate results in the formation of hemimellitic acid (Graebe and Leonhardt, A., 1896, i, 437). The constitution of decacyclene is therefore represented by the annexed formula. J. C. W.

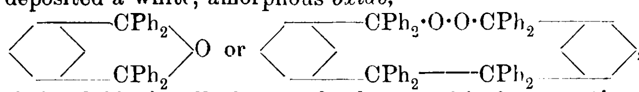
Strain Laws of Ring Systems. OSCAR HINSBERG (*J. pr. Chem.*, 1913, **88**, [ii], 58—60).—It has been shown previously (A., 1902, i, 238; 1904, i, 200) from a comparison of the stability of various azines and acridine derivatives, that the strain in tertiary ring systems, composed of 6-membered rings arranged in linear order, increases rapidly with the complexity of the molecule, so that a system containing five conjugated rings is either very unstable or incapable of existence.

The author refers to the unsuccessful attempts of W. A. and M. Mills (T., 1912, **101**, 2194) to prepare dinaphanthracene by the oxidation of its di- and tetra-hydro-derivatives in support of this view, and points out that their work renders it probable that the strain laws, developed by him for ring-systems containing carbon and nitrogen, are also applicable to systems composed wholly of carbon rings.

F. B.

Metaquinonoids. II. OTTO STARK and O. GARBEN (*Ber.*, 1913, **46**, 2252—2259).—The possibility that the yellow hydrocarbon, obtained previously (this vol., i, 362) by the removal of halogen from tetraphenyl-*m*-xylylene dichloride, is a triarylmethyl derivative and not a true metaquinonoid compound, is excluded on account of the comparatively great stability of the hydrocarbon towards air and oxygen, and its inability to form additive compounds with ether, ethyl acetate, benzene, alcohol, acetic acid, and acetic anhydride.

A benzene solution of the hydrocarbon, after being exposed to air for eight weeks, and occasionally treated with oxygen during this time, deposited a white, amorphous *oxide*,



which is insoluble in all the usual solvents with the exception of hot nitrobenzene, and when heated becomes discoloured and slowly decomposes at 200°, the decomposition being complete at 250°.

On treatment with hydrogen chloride in benzene, it yields an additive *compound* formed by the union of four molecules of the hydrocarbon with one of hydrogen chloride. This compound crystallises in white needles, m. p. 286—287° (decomp.), with previous darkening at 275°, and is considered to have the following constitution:

$$\begin{array}{l} CPh_2 \cdot C_6H_4 \cdot CPh_2 \cdot CPh_2 \cdot C_6H_4 \cdot CHPh_2 \\ \vdots \\ CPh_2 \cdot C_6H_4 \cdot CPh_2 \cdot CPh_2 \cdot C_6H_4 \cdot CPh_2Cl \end{array}.$$

It dissolves in boiling benzene, yielding deep yellow solutions, but the molecular weight in these solutions is only half that corresponding with the above formula. The authors interpret these results as indicating that the substance undergoes dissociation, at the position shown by the dotted line, into two triarylmethyl residues.

During the preparation of the hydrocarbon, an isomeride was obtained (*loc. cit.*) which had a higher m. p., and was supposed to be identical with Thiele's tetraphenyl-*p*-xylylene. The identity of the two compounds has now been fully established. The simultaneous

formation of the para-quinonoid hydrocarbon is due, however, not to a wandering of the groups in the meta-compound as was imagined previously, but to the original methyl *iso*phthalate, from which the hydrocarbon was prepared, being contaminated by considerable quantities of methyl terephthalate.

The *diethyl ether* of tetraphenyl-*m*-xylylene glycol, prepared by boiling the corresponding chloride with alcohol, has m. p. 116—117°; the *methyl ether*, m. p. 103—104°. The *diacetyl* derivative, prepared from the glycol and acetic anhydride, has m. p. 90—91·5°.

Tetraphenyl-*p*-xylylene glycol crystallises from glacial acetic acid in well developed prisms, m. p. 168—169°, containing the solvent (1 mol.), which is removed by heating the crystals under diminished pressure at 130—140°; the glycol then has m. p. 171—171·5°. The *diacetyl* derivative sinters at 198°, m. p. 203—204°.

Tetraphenyl-p-*xylylene dichloride*, prepared by passing hydrogen chloride into an acetic acid solution of the glycol, crystallises in slender, flat prisms, m. p. 239—240°, with previous sintering and darkening. F. B.

Nitro-derivatives of *p*-Phenetidine. FRÉDÉRIC REVERDIN and LUDWICK FÜRSTENBERG (*Arch. Sci. phys. nat.*, 1913, **35**, 594—605; *Bull. Soc. chim.*, 1913, [iv], **13**, 671—681).—The present work has been undertaken in continuation of the experiments of Reverdin and de Luc (A., 1909, i, 377, 913) on the nitration of *p*-anisidine. The initial materials in the various experiments are aceto-*p*-phenetidide, toluenesulpho-*p*-phenetidide, o-*nitrotoluenesulpho*-p-*phenetidide*,

$$OEt\cdot C_6H_4\cdot NH\cdot SO_2\cdot C_6H_3Me\cdot NO_2,$$

needles, m. p. 128°, and m-*nitrophenylsulpho*-p-*phenetidide*,

$$OEt\cdot C_6H_4\cdot NH\cdot SO_2\cdot C_6H_4\cdot NO_2,$$

prismatic needles, m. p. 129—130°, the two latter substances being obtained by the action of the corresponding chlorides on an alcoholic solution of *p*-phenetidine in the presence of sodium acetate.

2 : 3-Dinitro-*p*-phenetidine (compare Wender, A., 1890, 751) is formed by the action of concentrated sulphuric acid on 2 : 3-*dinitro*-p-*toluenesulphophenetidide*, white needles, m. p. 163°, obtained by the addition of nitric acid (D 1·52) to a solution of toluenesulpho-*p*-phenetidide in glacial acetic acid.

3 : 5-*Dinitro*-o-*nitrotoluenesulpho*-p-*phenetidide*,

$$OEt\cdot C_6H_2(NO_2)_2\cdot NH\cdot SO_2\cdot C_6H_3Me\cdot NO_2,$$

slender needles, m. p. 163°, is prepared by the action of nitric acid (D 1·4) on a solution of *o*-nitrotoluenesulpho-*p*-phenetidide in glacial acetic acid. Energetic treatment with concentrated sulphuric acid converts it into 3 : 5-dinitro-*p*-aminophenol, m. p. 230°, from which the position of the nitro-groups is ascertained, whilst a milder treatment leads to the formation of 3 : 5-*dinitro*-p-*phenetidine*, red leaflets, m. p. 138—139°. The same base can be obtained by the saponification of the product formed when 3-nitrotoluenesulpho-*p*-phenetidide is nitrated in acetic acid solution.

When phenacetine is nitrated in sulphuric acid solution under definite conditions, 2 : 6-dinitro-*p*-phenacetine, $OEt\cdot C_6H_2(NO_2)_2\cdot NHAc$, white needles, m. p. 148°, is formed, which, when hydrolysed by dilute

sulphuric acid, is converted into 2 : 6-*dinitro*-p-*phenetidine*, yellow leaflets, m. p. 172°. The constitution of the base follows from the identity with the product obtained by the ethylation of *iso*picramic acid.

Unsuccessful attempts have been made to prepare 2 : 5-dinitro-*p*-phenetidine by the nitration of phenacetine or of *m*-nitrobenzenesulpho-*p*-phenetidide. In the latter case, the main product of the change was a 2 : 3-dinitro-derivative, m. p. 178°, which, on hydrolysis, yielded 2 : 3-dinitro-*p*-phenetidine, smaller quantities of a 3 : 5-dinitro-derivative being also formed

2 : 3 : 5-*Trinitrotoluenesulpho*-p-*phenetidide*, white needles, m. p. 217°, is prepared by nitrating 2 : 3-dinitrotoluenesulpho-*p*-phenetidide, and, when acted on by sulphuric acid, yields 2 : 3 : 5-*trinitro*-p-*phenetidine*, fine red needles with green reflex, m. p. 126—127°. The constitution of this substance is deduced from its analogy with the trinitro-*p*-anisidine obtained by Reverdin (A., 1910, i, 470) in which the nitro-groups are in the 2 : 3 : 5-positions, that in position 2 being mobile (compare Meldola and Kuntzen, T., 1910, **97**, 444). This is established by converting it into dinitroguaiacol, dinitrocatechol, and dinitroveratrole of known constitution.

2 : 3 : 5-*Trinitroaceto*-p-*phenetidide*, $OEt{\cdot}C_6H(NO_2)_3{\cdot}NHAc$, white needles, m. p. about 245°, is obtained by the action of acetic anhydride and a trace of concentrated sulphuric acid on the free amine.

The following derivatives have been prepared by the replacement of the mobile nitro-group of 2 : 3 : 5-trinitro-*p*-phenetidine ; 3 : 5-*dinitro*-2-*anilino*-p-*phenetidine*, $OEt{\cdot}C_6H(NO_2)_2(NH_2){\cdot}NHPh$, brown leaflets, m. p. 151—152° ; 3 : 5-*dinitro-2-methylamino*-p-*phenetidine*,

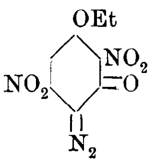
$$OEt{\cdot}C_6H(NO_2)_2(NH_2){\cdot}NHMe,$$

red needles, m.·p. 166—167° ; 3 : 5-*dinitro*-2-*dimethylamino*-p-*henetidine*, $OEt{\cdot}C_6H(NO_2)_2(NH_2){\cdot}NMe_2$, m. p. 119—120° ; 3 : 5-*dinitro*-2 *phenoxy*-p-*phenetidine*, $OEt{\cdot}C_6H(OPh)(NO_2)_2{\cdot}NH_2$, red needles, m. p. 185—186° ; 3 : 5-*dinitro-2-amino*-p-*phenetidine*, $OEt{\cdot}C_6H(NO_2)_2(NH_2)_2$, m. p. 250° ; 3 : 5-*dinitro*-2-*piperidino*-p-*phenetidine*,

$$OEt{\cdot}C_6H(NO_2)_2(NH_2){\cdot}C_5NH_{10},$$

red leaflets, m. p. 143—144°.

2 : 5-*Dinitro*-1-*ethoxy*-3 : 4-*quinonediazide* (annexed formula : compare Meldola and Reverdin, T., 1910, **97**, 1204) is formed by the addition of sodium nitrite to a solution of 2 : 3 : 5-dinitro-*p*-phenetidine in sulphuric acid. It separates from acetic acid in orange prisms, m. p. 186°.



3 : 5-*Dinitro*-2-*hydroxy*-p-*phenetidine*, brown needles or blackish crystals with green metallic reflex, m. p. 166—167°, is prepared by boiling a solution of 2 : 3 : 5-trinitro-*p*-phenetidine in acetone with an alcoholic solution of sodium acetate. When the amino-group is removed in the usual manner, 3 : 5-*dinitro*-2-*hydroxyphenetole*, yellow leaflets, m. p. 155°, is obtained, the *barium* and *silver* salts of which were also examined. The latter, when treated with an alcoholic solution of ethyl iodide, yields slightly impure 3 : 5-dinitro-1 : 2-diethoxybenzene, m. p. 90—91°, probably identical with the product described by Blanksma (A., 1905, i, 431) to which the m. p. 94—95° is now assigned. H. W

The Molecular Rearrangement of Triphenylmethylhydroxylamine. JULIUS STIEGLITZ and PAUL N. LEECH (*Ber.*, 1913, **46**, 2147—2151).—In accordance with Stieglitz's views as to the molecular rearrangement of bromoamides, hydroxamic acids, etc. (A., 1897, i, 43), which regard the Beckmann rearrangement with an oxime to occur by the steps

$$CR_2{:}N{\cdot}OH \xrightarrow{HCl} CR_2Cl{\cdot}NH{\cdot}OH \xrightarrow{H_2O} CR_2Cl{\cdot}N{:} \longrightarrow CRCl{:}NR,$$

it is found that triphenylmethylhydroxylamine, $CPh_3{\cdot}NH{\cdot}OH$, which in constitution closely resembles the first class of product in the above series of changes, when treated in ethereal solution with phosphorus pentachloride is converted into benzophenoneanil, $CPh_2{:}NPh$, m. p. 111—112°. The above course of the rearrangement is thus confirmed.

D. F. T.

The Molecular Rearrangement of Triphenylmethylbromoamine. JULIUS STIEGLITZ and ISABELLE VOSBURGH (*Ber.*, 1913, **46**, 2151—2156).—In an endeavour to decide which of the tautomeric forms $R{\cdot}CO{\cdot}NMX$ and $R{\cdot}C(OM){:}NX$ (M = metal, X = halogen) of the metallic salts of the halogenamides is to be regarded as the intermediate stage in the production of amines from halogen-amides by Hofmann's rearrangement, the authors have prepared and examined triphenylmethylbromoamine, $CPh_3{\cdot}NHBr$, with which the possibility of tautomerism is excluded. By the action of alkali, the elements of hydrogen bromide are eliminated from this substance with formation of benzophenoneanil. The series of changes must therefore be $CPh_3{\cdot}NHBr \longrightarrow CPh_3{\cdot}NMBr \longrightarrow CPh_3{\cdot}N{:} \longrightarrow CPh_2{:}NPh$. The former of the alternative structures thus receives support without excluding the possibility of the second formula being the correct one for the structure involved.

Triphenylmethylbromoamine, colourless crystals, m. p. 63°, was obtained by the action of bromine on triphenylmethylamine in chloroform solution in the presence of sodium hydroxide solution. By heating with soda-lime at 100—120°, or with a hot methyl alcoholic solution of sodium methoxide, it is converted into benzophenoneanil, m. p. 111—112°.

When heated to its m. p., triphenylmethyldichloroamine rapidly loses chlorine with the formation of benzophenoneanil with a little chlorobenzophenoneanil.

D. F. T.

Oxidation of Organic Developers with Silver Salts. *p*-Aminophenol and Metol. FRITZ KROPF (*J. pr. Chem.*, 1913, [ii], **88**, 73—77).—On the addition of silver nitrate to an aqueous solution of *p*-aminophenol or *p*-methylaminophenol, the liquid acquires a bluish-violet colour and benzoquinone is produced.

In ammoniacal solution a blue coloration is produced, but no definite compound could be isolated from the reaction product.

When dissolved in aqueous sodium hydroxide and treated with silver bromide, *p*-aminophenol yields a *substance* which crystallises in brown leaflets having a metallic glance, m. p. 194° (not sharp), and gives a dark blue coloration on treatment with phenol and ammonia.

The addition of silver bromide to a solution of *p*-aminophenol in aqueous sodium hydroxide and in the presence of potassium metabisulphite results in the formation of a small amount of a white substance, which is probably a sulphonic acid; under similar conditions metol yields a strongly green fluorescent solution, but no definite compound could be isolated.

The amount of silver reduced in the above reactions, and also the amount of sulphite which disappears, depends on the conditions under which the reduction is carried out. F. B.

Nitration of Anisole to Trinitroanisole. ALFRED L. BROADBENT and FIN SPARRE (*Eighth Inter. Cong. App. Chem.*, 1912, **4**, 15—17).—No experimental details of the preparation of 2 : 4 : 6-trinitroanisole from anisole appear to have been published; the literature contains merely statements that the nitration is possible.

After considerable difficulties, the authors have evolved the following details which permit a yield of 85% of that theoretically expected from the anisole taken.

A mixture of 130 grams of nitric acid (D 1·52) with 220 grams of sulphuric acid (D 1·84), which is mechanically agitated by a stirrer, is cooled to $-5°$ by immersion in a freezing mixture of ice and salt whilst 30 grams of anisole are added in small drops. The addition should occupy two to three hours, and the temperature of the mixture should never reach 0°. After all the anisole has been introduced, the temperature is raised to 65—70° for twenty minutes with continued stirring, and the mixture is then poured into water. After washing with warm water and dilute sodium carbonate solution successively, with subsequent drying, the product has m. p. 64—65°, D^{20} 1·408, and is slowly hydrolysed by water to methyl alcohol and picric acid.

D. F. T.

Hydrolysis of Trinitroanisole by Alkalis and Water. WALTER E. MASLAND and FIN SPARRE (*Eighth Inter. Cong. App. Chem.*, 1912, **4**, 77).—Pure trinitroanisole is hydrolysed fairly rapidly by hot solutions of the alkali carbonates and slowly by hot water; the action of each of these in the cold is much more feeble. Picric acid is produced in each case. D. F. T.

Action of Nitric Acid on Halogen Derivatives of *o*-Alkylphenols. II. Nitric Acid Derivatives of 3 : 4 : 5- and 3 : 5 : 6-Tribromo-*o*-cresols. THEODOR ZINCKE and NELSON W. JANNEY (*Annalen*, 1913, **398**, 343—353).—3 : 4 : 5- and 3 : 5 : 6-Tribromo-*o*-cresols react with nitric acid in the sense of the equation: $C_7H_5OBr_3 + 2HNO_3 = C_7H_5O_6N_2Br_3 + H_2O$, but the two products exhibit quite different behaviour. 3 : 4 : 5-Tribromo-*o*-cresol and nitric acid, D 1·48, yield by keeping 3 : 4 : 5-*tribromo-*o*-cresol nitroquinitrol*,

$$NO_2\cdot O\cdot C(OH)<\begin{matrix}CMe{=\!=\!=}CH\\CBr(NO_2)\cdot CBr\end{matrix}>CBr,$$

m. p. 126° (decomp.), colourless needles, which is not reconverted into the tribromo-*o*-cresol by reduction, yields tribromo-*p*-toluquinone by warming with concentrated sulphuric acid, and by boiling with

toluene, glacial acetic acid, or tetrachloroethane is converted by loss of nitrosyl bromide into 4 : 5-*dibromo-o-toluquinone 2-nitrate*,

$$NO_2\cdot O\cdot C(OH){<}{}^{CMe:CH}_{CO-CBr}{>}CBr,$$

m. p. 173° (decomp.), pale yellow prisms. The latter is stable, dissolves in alkalis, and is reduced by stannous chloride, hydrochloric acid, and a little alcohol, to 4 : 5-*dibromo*-2 : 3-*dihydroxytoluene*, m. p. 104°, colourless needles, which forms a *diacetyl* derivative, m. p. 137—138°, and is oxidised by nitric acid, D 1·15, to 4 : 5-*dibromo-o-toluquinone*, $C_7H_4O_2Br_2$, m. p. 96—98°, dark red, crystalline powder.

3 : 5 : 6-Tribromo-*o*-cresol and nitric acid, D 1·48, at 0° yield 3 : 5 : 6-*tribromo-o-cresolnitroquinitrol*, $NO_2\cdot O\cdot C(OH){<}{}^{CBr=\!=\!=CH}_{CMe(NO_2)\cdot CBr}{>}CBr$, m. p. 96° (decomp.), faintly yellow leaflets or needles, which regenerates the tribromo-*o*-cresol by reduction with stannous chloride solution after being initially heated with glacial acetic acid for a short time. C. S.

Bromo-derivatives of *o*-Cresol. NELSON W. JANNEY (*Annalen*, 1913, **398**, 354—372).—The author describes the preparation of some of the unknown brominated *o*-cresols; usually the constitutions are determined by converting the substance ultimately into a quinone of the ortho- or of the para series.

4-*Bromo-o-cresol*, m. p. 80°, broad needles, prepared from diazotised 4-bromo-*o*-toluidine in the usual manner, forms a *benzoate*, m. p. 41°, and is converted by nitric acid, D 1·4, in glacial acetic acid into a *nitro*- and a *dinitro*-derivative, the latter, m. p. 169°, crystallising in yellow prisms.

3 : 4-*Dibromo-o-cresol*, m. p. 94—95°, colourless needles, is obtained by brominating 4-bromo-*o*-cresol in chloroform in the presence of a little iron. It forms an *acetate*, m. p. 49°, is converted by nitric acid, D 1·52, in glacial acetic acid into the preceding bromo-dinitro-*o*-cresol, and yields 3 : 4-dibromo-5-nitro-*o*-cresol (see below) by treating its solution in glacial acetic acid with powdered sodium nitrite. 3 : 6-*Dibromo-o-cresol*, m. p. 38° (*benzoate*, m. p. 104°, white needles), is prepared in a similar manner from 6-bromo-*o*-cresol. Its constitution follows from the fact that it yields only oily products by treatment with sodium nitrite and acetic acid; were it 5 : 6-dibromo-*o*-cresol, it must have yielded 5 : 6-dibromo-3-nitro-*o*-cresol identical with that obtained from 3 : 5 : 6-tribromo-*o*-cresol (see below).

3 : 5-Dibromo-*o*-cresol is already known. By treatment with sodium nitrite and acetic acid at 12—15°, it is converted into 5-bromo-3-nitro-*o*-cresol, by the reduction of which 5-bromo-3-amino-*o*-cresol (*diacetyl* derivative, m. p. 203°) is obtained. The hydrochloride of the last substance, dissolved in glacial acetic and concentrated hydrochloric acids, is converted by moist chlorine into the *diketo-chloride*, $CClBr{<}{}^{CCl:CMe}_{CCl_2-CO}{>}CO$, m. p. 80°, stout, yellow prisms, by the reduction of which by stannous chloride 4 : 6-*dichloro-5-bromo-2 : 3-dihydroxytoluene*, m. p. 186°, colourless needles (*diacetate*, m. p. 176—177°), is obtained. By oxidation with nitric acid, D 1·4, the last compound is

converted into 4 : 6-*dichloro*-5-*bromo*-o-*toluquinone*, m. p. 121—122°, red, crystalline powder.

By treatment with nitric acid, D 1·4, and glacial acetic acid, 3 : 5-dibromo-*o*-cresol yields Auwers' 3-bromo-5-nitro-*o*-cresol, and finally 3 : 5-dinitro-*o*-cresol. By reduction with alcohol and stannous chloride, the former is converted into 3-*bromo*-5-*amino*-o-*cresol*, m. p. 146°, stout prisms (*acetyl* derivative, m. p. 152°; *diacetyl* derivative, m. p. 167°), from the *hydrochloride* of which 3-bromo-*p*-toluquinone is obtained by oxidation with potassium dichromate and dilute sulphuric acid.

3 : 4 : 5-Tribromo-*o*-cresol, m. p. 89° (not 79°, as stated in the literature), which is only occasionally obtained pure by the bromination of *o*-cresol, is prepared in 90—95% yield by the action of bromine and iron on 4-bromo-*o*-cresol in cold chloroform. It is most conveniently obtained by treating a solution of 3 : 5-dibromo-*o*-cresol in glacial acetic acid with 10% calcium hypobromite, and warming the resulting *keto-bromide*, $C_7H_5OBr_3$, m. p. 110° (decomp.), yellow prisms, with concentrated sulphuric acid. The action of sodium nitrite and glacial acetic acid on 3 : 4 : 5-tribromo-*o*-cresol yields Zincke and Hedenström's 3 : 4-dibromo-5-nitro-*o*-cresol, which by successive reduction, conversion into the diketo-chloride, and reduction is converted into 3 : 6-*dichloro*-4-*bromo*-p-*toluquinol*,

$$OH\cdot C{<}{\begin{matrix}CMe{:}CCl\\CCl\cdot CBr\end{matrix}}{>}C\cdot OH,$$

m. p. 200—201°, white prisms or needles (*diacetate*, m. p. 226—227°). By oxidation with nitric acid, the quinol is converted into 3 : 6-*dichloro*-4-*bromo*-p-*toluquinone*, m. p. 233°, yellow, hexagonal leaflets. The production of a para-quinone proves the constitution of 3 : 4 : 5-tribromo-*o*-cresol and also of 3 : 4-dibromo-*o*-cresol.

3 : 5 : 6-*Tribromo*-o-*cresol*, m. p. 91°, prismatic needles (*acetate*, m. p. 76—77°), is prepared from 6-bromo-*o*-cresol in a similar manner as 3 : 4 - 5-tribromo-*o*-cresol from 4-bromo-*o*-cresol. By treatment with sodium nitrite and glacial acetic acid at 12—15°, it yields 5 : 6-*dibromo*-3-*nitro*-o-*cresol*, m. p. 100°, pale yellow needles (*acetate*, m. p. 74°), from which 4 : 6-dichloro-5-bromo-2 : 3-dihydroxytoluene and 4 : 6-dichloro-5-bromo-*o*-toluquinone, identical with the corresponding substances obtained from 3 : 5-dibromo-*o*-cresol, are obtained by reduction and treatment of the keto-chloride in the usual manner. C. S.

[1-Methyl*cyclo*pentane-1-carboxylic Acid.] I. PETROV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 644).—For this acid the author finds the constants, b. p. 216—217°, D_0^0 1·0386 (compare Tschitschibabin, this vol., i, 467). T. H. P.

Four Different Anhydrides of Dibenzylacetic Acid. The Catalytic Action of Metaphosphoric Acid on Acid Chlorides. HERMANN LEUCHS, JOHANNES WUTKE, and ERICH GIESELER (*Ber.*, 1913, **46**, 2200—2215).—According to Staudinger and Ott (A., 1908, i, 602) the action of thionyl chloride on malonic acids results primarily in the formation of the semi-chlorides which may subsequently part with carbon dioxide to give the acetyl chlorides, or lose hydrogen chloride

to form malonic anhydrides and finally ketens, as in the following case:

$$CHMe_2{\cdot}COCl \longleftarrow CMe_2{<}\begin{matrix}COCl\\CO_2H\end{matrix} \longrightarrow CMe_2{<}\begin{matrix}CO\\CO\end{matrix}{>}O \longrightarrow CMe_2C{:}CO.$$

In the case of dibenzylmalonic acid, the chief product is dibenzylacetyl chloride, but a by-product is also formed which is a simple polymeride of dibenzylketen and is shown to be tetrabenzyl*cyclo*butan-1 : 3-dione, $C(CH_2Ph)_2{<}\begin{matrix}CO\\CO\end{matrix}{>}C(CH_2Ph)_2$. That its formation is due to the intervention of dibenzylketen is assumed from the fact that the substance could not be obtained from dibenzylacetic acid or dibenzylacetyl chloride.

In order to moderate the action of thionyl chloride, with the hope of obtaining the semi-chloride of dibenzylmalonic acid, the reagent was diluted with ether, but it was found that the action was too moderate, the product being the ordinary anhydride of dibenzylacetic acid, $[CH(CH_2Ph)_2{\cdot}CO]_2O$.

Attempts were made to prepare the *cyclo*butane derivative from dibenzylacetyl chloride. When this substance was heated at 250°, it gradually parted with hydrogen chloride, but the product was a third anhydride, m. p. 145°. In some experiments on the preparation of the chloride, it was found that, unless an excess of phosphorus pentachloride was employed, the metaphosphoric acid, or some similar product from the phosphoryl chloride, exerted a catalytic influence on the elimination of hydrogen chloride, so that, on distillation in a vacuum, very little acid chloride was obtained, the chief product being a fourth, oily anhydride. This recalls the formation of bis-α-hydrindone-(2 : 2)-spiran by the action of phosphorus pentachloride on dibenzylmalonic acid (A., 1912, i, 179), in which case it is now found that the yield can be improved by the above process. Since the oil forms a hydrazone and is similar in deportment to methyl-, ethyl- and phenyl-α-hydrindones, it is 2-benzyl-1-hydrindone,

$$C_6H_4{<}\begin{matrix}CH_2\\CO\end{matrix}{>}CH{\cdot}CH_2Ph.$$

The solid anhydride, m. p. 145°, is bimolecular, does not yield a hydrazone, forms dibenzylacetic acid and 2-benzylhydrindone on hydrolysis with alcoholic potassium hydroxide, and dibenzylacetyl chloride and 2-chloro-2-benzyl-1-hydrindone under the influence of phosphorus pentachloride. It is therefore the *O*-dibenzylacetyl derivative of 1-hydroxy-2-benzylindene, the enolic form of 2-benzylhydrindone,

$$C_6H_4{<}\begin{matrix}CH_2{\cdot}C{\cdot}CH_2Ph\\ \quad\;\, \| \\ \text{———}C{\cdot}O{\cdot}CO{\cdot}CH(CH_2Ph)_2\end{matrix}.$$

Dibenzylmalonic acid was boiled with thionyl chloride, and, after distilling off the dibenzylacetyl chloride at 203—204°/15 mm., the residue was extracted with light petroleum, leaving a 10% yield of *tetrabenzyl*cyclo*butan*-1 : 3-*dione*, $C_{32}H_{28}O_2$, which crystallised from benzene in colourless, light needles, m. p. 249—251°, and sublimed at 220—230°/18 mm. When hydrolysed by alcoholic sodium hydroxide, it gave s-*tetrabenzylacetone*, $CO[CH(CH_2Ph)_2]_2$, in the form of well-defined prisms, m. p. 124·5—125·5° (compare tetraphenylacetone,

Staudinger, A., 1911, i, 306). The ordinary *dibenzylacetic anhydride*, $C_{32}H_{30}O_3$, crystallised from alcohol in prisms, m. p. 75—76°, and formed dibenzylacetamide and ammonium dibenzylacetate when treated with ammonia in ether.

Dibenzylacetyl chloride, $C_{16}H_{15}OCl$, was prepared by the action of thionyl chloride on dibenzylacetic acid. The residue after distillation contained a little of the true anhydride, m. p. 75—76°, but no *cyclo*butane derivative. The chloride is a viscous, almost colourless oil, b. p. 150°/0·25 mm., and the pale yellow, crystalline mass described by Schneidewind (A., 1888, 704), was probably not dibenzylacetyl chloride. After heating the oil for an hour at 245—255° in a low vacuum, and subsequently distilling off the unchanged chloride in a high vacuum, the residue was extracted with chloroform, precipitated by petroleum, and the 1-*dibenzylacetoxy*-2-*benzylindene*, $C_{32}H_{28}O_2$, was recrystallised from benzene in the form of shining, four or six-sided leaflets, m. p. 144—145°. On oxidation it yielded benzoic and phthalic acids and benzaldehyde, and on treatment with phosphorus pentachloride in chloroform suspension, it gave dibenzylacetyl chloride and 2-*chloro*-2-*benzylhydrindone*, $C_6H_4{<}\begin{matrix}CH_2\cdot CCl\cdot CH_2Ph \\ \text{——}CO\end{matrix}$. The latter is insoluble in cold petroleum, forms long, colourless, glistening leaflets, m. p. 74—75°, and may be prepared by passing chlorine into a chloroform solution of 2-benzylhydrindone.

When dibenzylacetic acid is treated with a slight excess of phosphorus pentachloride, the chief product is the acid chloride, but when an insufficient amount of the reagent is employed and the product is evacuated at 200—250°, hydrogen chloride is eliminated and 2-*benzylhydrindone* distils over, mixed with a little unchanged acid. The distillate is added to an ethereal solution of ammonia, filtered, and re-distilled, giving a yellow, viscous, almost odourless oil, b. p. 223·5—224·5° (corr.)/20 mm. Phosphorus pentachloride converts it into 1-*chloro*-2-*benzylindene*, $C_6H_4{<}\begin{matrix}CH_2 \\ CCl\end{matrix}{\geqslant}C\cdot CH_2Ph$, which crystallises in massive prisms, m. p. 64—65°, b. p. 206°(corr.)/13 mm., and yields benzaldehyde and benzoic and phthalic acids on oxidation. Its *dibromide*, $C_{16}H_{13}ClBr_2$, forms massive, sparkling, six-sided plates, m. p. 97—98°, which are hydrolysed in aqueous alcohol to 2-*bromo*-2-*benzylhydrindone*, $C_{16}H_{13}OBr$. The latter is best obtained by the action of bromine on β-benzylhydrindone, and forms colourless, sparkling, six-sided leaflets or prisms, m. p. 80—81°.

The *phenylhydrazone* of 2-benzylhydrindone, $C_{22}H_{20}N_2$, crystallises in light yellow, four-sided tablets, and, like the hydrazone of hydrindone itself (Kipping, T., 1894, **65**, 493), it has not a constant m. p. When the ketone is heated to 130° with an excess of phenylhydrazine, however, a *product*, $C_{28}H_{25}N_3$, is obtained in short, colourless prisms or tablets, m. p. 190—192°. J. C. W.

[Polymerisation.] Carl Liebermann (*Ber.*, 1913, **46**, 2084—2086).—Polemical. A reply to Kronstein (this vol., i, 725).

D. F. T.

Some Derivatives of Diphenyleneacetic [Fluorene-9-carboxylic] Acid and Bisdiphenylenesuccinic [9 : 9′-Difluoryl-9 : 9′-dicarboxylic] Acid. ROBERT STOLLÉ and F. WOLF (*Ber.*, 1913, **46**, 2248—2252).—The action of thionyl chloride on fluorene-9-carboxylic acid leads to the formation of fluorene-9-carboxyl chloride, 9-chlorofluorene-9-carboxyl chloride, and 9 : 9′-difluoryl-9 : 9′-dicarboxyl chloride, according to the condition under which the action is carried out.

When heated for one to two hours with thionyl chloride in carbon tetrachloride solution, fluorene-9-carboxylic acid yields the corresponding chloride, which has m. p. 77° and reacts with ammonia and aniline yielding the amide, m. p. 251°, and anilide (compare Vorländer and Pritzsche, this vol., i, 724, and Staudinger, A., 1906, i, 861).

9 : 9′-*Difluoryl*-9 : 9′-*dicarboxyl chloride*,

$$C_{12}H_8{:}C(COCl)\cdot C(COCl){:}C_{12}H_8,$$

obtained together with fluorene-9-carboxyl chloride by heating fluorene-9-carboxylic acid for several hours with thionyl chloride, forms colourless crystals, m. p. 213° (decomp.), and decomposes into bisdiphenylene-ethane (9 : 9′-difluoryl; Graebe and Mantz, A., 1896, i, 442) when heated with concentrated hydrochloric acid. It is also produced by passing chlorine into a boiling solution of fluorene-9-carboxyl chloride in carbon tetrachloride. It reacts with sodium methoxide and sodium ethoxide, yielding the methyl ester, m. p. 237° (Kolvenbach, *Diss.*, Königsberg, 1897), and ethyl ester respectively (compare Staudinger, A., 1906, i, 825); the *anilide* forms a colourless powder, m. p. 250°.

If the action of thionyl chloride on fluorene-9-carboxylic acid or its chloride is continued for 200 hours, 9-chlorofluorene-9-carboxyl chloride (Klinger, A., 1912, i, 558) is produced.

Prolonged heating leads to the decomposition of thionyl chloride into chlorine and sulphur monochloride: $4SOCl_2 = 2SO_2 + 3Cl_2 + S_2Cl_2$. It is possible that the chlorinating action of thionyl chloride mentioned above is to be referred to this decomposition, but whether the formation of 9 : 9′-difluoryl-9 : 9′-dicarboxyl chloride is due to the direct oxidation of fluorene-9-carboxyl chloride, or to the interaction of the latter compound with 9-chlorofluorene-9-carboxyl chloride, has not yet been determined. F. B.

New Method for the Ketonic Decomposition of β-Ketonic Esters. HANS MEERWEIN (*Annalen*, 1913, **398**, 242—250).—When heated at 200° with 0·5—1 volume of water, esters of β-ketonic acids undergo the ketonic decomposition quantitatively or nearly so. That the change is not due to an ordinary hydrolysis of the ester and subsequent elimination of carbon dioxide is proved by the fact that only those β-ketonic esters which are capable of enolising undergo the change. It is very probable that the enolic modification is the form which is concerned in the decomposition, since the facility with which the ketone is produced runs pari passu with the tendency of the β-ketonic ester to enolise; thus, strongly acidic, cyclic β-ketonic esters such as ethyl succinosuccinate are decomposed most readily, then follow acyclic, non-alkylated esters such as ethyl acetoacetate and benzoyl-

acetate, and finally alkylated esters such as ethyl benzyl-, methyl-, or ethyl-acetoacetate, in the last case a temperature of 250° being requisite.

The author is of opinion that the course of the decomposition is represented by the scheme

$$R{\cdot}CO{\cdot}CH_2{\cdot}CO_2R' \rightarrow R{\cdot}CO{\cdot}CH{:}C(OH){\cdot}OR' \xrightarrow{H_2O} R{\cdot}CO{\cdot}CH_3 + CO_2 + R'{\cdot}OH.$$

In support of this opinion are the facts that ethyl benzylmalonate is converted into ethyl β-phenylpropionate, and ethyl $\alpha\gamma$-dicarbethoxyglutaconate into ethyl glutaconate, by water at 250° and 200° respectively.

The following changes are described: methyl 1-phenyl*cyclo*hexan-3-one-4-carboxylateacetate into methyl 1-phenyl*cyclo*hexan-3-one-5-acetate (A., 1908, i, 545), methyl *cyclo*pentanone-2-carboxylate into *cyclo*pentanone, ethyl succinosuccinate into *cyclo*hexan-1 : 4-dione, methyl benzoylacetate into acetophenone, ethyl acetoacetate into acetone, ethyl benzylacetoacetate into methyl β-phenylethyl ketone, ethyl methylacetoacetate into methyl ethyl ketone, and ethyl ethylacetoacetate into methyl propyl ketone. C. S.

Action of Hydroxylamine on Ketones of the Type R·CH:CH·CH:CH·CO·R. V. RICCARDO CIUSA and G. B. BERNARDIS (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 708—711. Compare A., 1910, i, 684).—The substance $C_{26}H_{34}O_9N_4$, m. p. 213°, mentioned in the paper cited, contains one molecule of alcohol of crystallisation; it does not react with bromine or with benzaldehyde, and it dissolves in alkalis. It is therefore composed of two molecules of the hydroxylamineoxime of cinnamylidenepyruvic acid united so as to saturate reciprocally their double linkings. The substance gives an insoluble, green copper salt, and a cherry-red coloration with iron salts; in other respects it does not behave like an hydroxamic acid, and is to be regarded as an α-oximino-acid. The compound immediately yields a *sodium* salt, $C_{24}H_{26}O_8N_4Na_2$, when treated with sodium carbonate, and this salt yields with acids a *substance*, $C_{24}H_{28}O_8N_4$, m. p. 205°; this compound has similar properties to the original one, but does not unite with alcohol. When the substance $C_{24}H_{28}O_8N_4$,EtOH, is boiled with dilute sulphuric acid, the *ethyl* ester, m. p. 207°, is obtained in small quantity.

When the action between hydroxylamine hydrochloride and ethyl cinnamylidenepyruvate is effected in the presence of sodium acetate, there is produced, in addition to the substance $C_{24}H_{28}O_8N_4$,EtOH, a sparingly soluble *sodium* salt, $C_{26}H_{31}O_8N_4Na$, which, on treatment with dilute sulphuric acid, furnishes an *isomeride* of the above-mentioned ethyl ester, m. p. 207°. This isomeride has m. p. 198°, and its properties resemble those of the compound of m. p. 207°.

From the mother liquors of the above reaction, the *oxime* of ethyl cinnamylidenepyruvate, $C_{14}H_{16}O_3N$, m. p. 181°, can be obtained. This substance is the sole product of the reaction when no sodium acetate is added.

When the sodium salt of the oxime of cinnamylidenepyruvic acid

(*loc. cit.*) is treated with dilute sulphuric acid, the corresponding *cinnamylidene-a-oximinopropionic acid* is produced; it crystallises with $\frac{1}{2}H_2O$, gives a green copper salt, and a cherry-red coloration with ferric salts. The above-mentioned sodium salt also yields the ethyl ester, m. p. 181°, already described. R. V. S.

o-**Thiolcinnamic Acid.** CH. CHMELEWSKI and PAUL FRIEDLÄNDER (*Ber.*, 1913, **46**, 1903—1908).—The above substance was prepared in order to examine its tendency to the formation of an anhydride analogous to coumarin; earlier experimental results appear to indicate that unsaturated ring systems of five carbon atoms and one sulphur atom are less easily produced, and are less stable than those corresponding with thiophen, but thiolcinnamic acid closely resembles coumaric acid in its behaviour towards dehydration.

o-*Thiolcinnamic acid*, $SH\cdot C_6H_4\cdot CH{:}CH\cdot CO_2H$, was obtained from *o*-aminocinnamic acid by converting it into the corresponding *thiocyano*-compound, $CNS\cdot C_6H_4\cdot CH{:}CH\cdot CO_2H$, needles, m. p. 175°, and then evaporating to dryness its solution in sodium hydroxide, together with sodium sulphide solution. The substance can be obtained more conveniently by introducing the solution of the diazocinnamic acid into a warm concentrated solution of sodium disulphide, and reducing the resultant *dithiocinnamic acid*, $(CO_2H\cdot CH{:}CH\cdot C_6H_4)_2S_2$, yellow needles, m. p. 221°, to the thiol acid by the action of zinc dust and sodium hydroxide solution. It was also prepared, through the diazo-compound, from the *xanthate*, $CO_2H\cdot CH{:}CH\cdot C_6H_4\cdot S\cdot CS\cdot OEt$. *o*-Thiolcinnamic acid, colourless needles, undergoes partial dehydration and oxidation on heating, consequently its m. p., 165°, is not sharp; its *methyl* ester forms tablets, m. p. 114°. o-*Methylthiolcinnamic acid*, $SMe\cdot C_6H_4\cdot CH{:}CH\cdot CO_2H$, leaflets, m. p. 176°, obtained by the action of methyl sulphate on an alkaline solution, is more stable than the thiol acid. When heated above its m. p., or, much better, by boiling with acetic anhydride and subsequently distilling in a vacuum, *o*-thiolcinnamic acid is dehydrated to *thiocoumarin* [1:2-*benzthiopyrone*],

$$C_6H_4<\begin{matrix}CH{:}CH\\ S\!=\!=\!CO\end{matrix},$$

colourless needles, m. p. 80—80·5°, which is volatile with steam, and has an odour surprisingly like that of coumarin itself. It is insoluble in cold solutions of alkali, but dissolves in warm sodium hydroxide, and can be precipitated unaltered by mineral acids. As the acid undergoes isomeric change more readily than the corresponding coumaric acid, the warming with alkali must not be prolonged, otherwise *thiocoumarinic acid* is produced, of which the derived *methylthiolcoumarinic acid* has m. p. about 136°.

In behaviour towards oxidation, *o*-thiolcinnamic acid differs markedly from *o*-coumaric acid. Although frequently oxidation yields the corresponding dithio-acid, oxidation by ferric salts in neutral solution or, better, by potassium ferricyanide in alkaline solution causes elimination of hydrogen and of carbon dioxide with separation of thionaphthen, $C_6H_4<\begin{matrix}CH\\ S\end{matrix}>CH$.

Reduction of *o*-thiolcinnamic acid in alkaline solution by sodium amalgam produces *o-thiolphenylpropionic acid*,

$$SH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot CO_2H,$$

colourless needles, m. p. 118°, which above their m. p., or when heated with diluted sulphuric acid, undergo dehydration to *thiohydrocoumarin* [*dihydro*-1 : 2-*benzthiopyrone*], $C_6H_4<\begin{matrix}CH_2\cdot CH_2\\ S\text{——}CO\end{matrix}$, an oil of pleasant odour. D. F. T.

Preparation of Tyrosine. ELI K. MARSHALL, jun. (*J. Biol. Chem.*, 1913, **15**, 85—86).—The usual method of preparing tyrosine from silk is laborious and expensive. The method recommended is to obtain it from a pancreatic digest of caseinogen. The fluid on cooling deposits an abundant crystalline yield of tyrosine. W. D. H.

Action of Nitric Acid on Heptachloro-*o*-quinocatechol Hemiether. C. LORING JACKSON and GEORGE L. KELLEY (*Amer. Chem. J.*, 1913, **49**, 435—473).—When heptachloro-*o*-quinocatechol hemiether, $OH\cdot C_6Cl_4\cdot O\cdot C_6Cl_3O_2$ (Jackson and Carleton, A., 1908, i, 428), is warmed with glacial acetic acid and a little fuming nitric acid, the product sometimes yields a compound, m. p. 159—165° (decomp.), and sometimes a compound, m. p. 176—198° (decomp.); in each case the m. p. depends on the rate of heating.

The former compound, m. p. 159—165°, is probably the *tetrachlorocatechol hemiether* of *dichloronitrohydroxy*cyclo*pentadienecarboxylic acid*, $OH\cdot C_6Cl_4\cdot O\cdot C_5Cl_2(OH)(NO_2)\cdot CO_2H$; it forms white or cream-coloured crystals.

The compound, m. p. 176—198°, is regarded as the *tetrachlorocatechol hemiether* of 2 : 4 : 5-*trichloro*-2-*nitro*-1 : 3-*dihydroxy*cyclo*pentene*-1-*carboxylic acid*, $OH\cdot C_6Cl_4\cdot O\cdot C(OH)<\begin{matrix}CCl(NO_2)\cdot C(OH)\cdot CO_2H\\ CCl\text{=====}CCl\end{matrix}$; it crystallises in nearly white needles, and is decomposed by boiling water with formation of tetrachlorocatechol, carbon dioxide, an oxide of nitrogen, and a tarry residue. The *methyl* ester, m. p. 221° (decomp.), forms clusters of creamy-white needles. On treating the compound (m. p. 176—198°) with methyl alcohol and sulphuric acid, it is converted into the *tetrachlorocatechol hemiether* of *methyl* 2 : 4 : 5-*trichloro*-2-*nitro*cyclo*pentene*-1 : 3-*oxide*-1-*carboxylate*,

$$OH\cdot C_6Cl_4\cdot O\cdot C\begin{matrix}\diagup CCl(NO_2)\diagdown\\ \text{——}O\text{——}\\ \diagdown CCl\text{=}CCl\diagup\end{matrix}C\cdot CO_2Me,$$

m. p. 221—228° (decomp.), which crystallises in rhombic plates or needles; its *acetyl* derivative, m. p. 189° (decomp.), forms white, rhombic prisms.

When the compound (m. p. 176—198°) is heated with acetic anhydride or acetyl chloride, it yields the *acetyl* derivative of the *tetrachlorocatechol hemiether* of 2 : 4 : 5-*trichloro*cyclo*pentadien*-1-*one*,

$$OAc\cdot C_6Cl_4O\cdot C<\begin{matrix}CCl\cdot CO\\ CCl:CCl\end{matrix},$$

m. p. 165—168°, which crystallises in white, lustrous, rhombic plates;

on evaporating the mother liquor from this reaction, a viscous residue is obtained which when dissolved in benzene and treated with pyridine furnishes the *tetrachlorocatechol ether* of 2 : 5-*dichloro*-1 : 1-*diacetoxy*cyclo*pentadiene*, $C_6Cl_4O_2 \cdot C_5Cl_2(OAc)_2$, m. p. 188°, which forms white prisms or needles. The *tetrachlorocatechol hemiether* of 2 : 4 : 5-*tri-chlorocyclopentadien-1-one*, $OH \cdot C_6Cl_4O \cdot C{<}\begin{matrix} CCl \cdot CO \\ CCl{:}CCl \end{matrix}$, m. p. 182—188° (decomp.), obtained by hydrolysing the acetyl derivative, crystallises in clusters of white needles. When a benzene solution of this compound or its acetyl derivative is treated with pyridine, the *tetrachlorocatechol ether* of *dichlorocyclopentadienone*,

$$C_6Cl_4{<}\begin{matrix} O \cdot C{:}CCl \\ O \cdot C{:}CCl \end{matrix}{>}CO,$$

m. p. 264—272° (decomp.), is obtained, which forms thin, bright red, hexagonal plates and is converted by sodium methoxide into the *tetrachlorocatechol hemiether* of *dichloro*-1-*hydroxy*-1 : 4-*dimethoxy*cyclo-*pentadiene*, $OH \cdot C_6Cl_4 \cdot O \cdot C_5Cl_2(OMe)_2 \cdot OH$, m. p. 175—180° (decomp.), which crystallises in white cubes ; the corresponding *diethoxy*-compound has m. p. 93°.

By the action of benzoyl chloride on the compound, melting at 176—198°, the *benzoyl* derivative of the tetrachlorocatechol hemi-ether of 2 : 4 : 5-trichloro*cyclo*pentadien-1-one,

$$OBz \cdot C_6Cl_4O \cdot C{<}\begin{matrix} CCl \cdot CO \\ CCl{:}CCl \end{matrix},$$

m. p. 172°, is obtained, which forms white, lustrous scales.

When a solution of hexachloromethoxy-*o*-quinocatechol hemiether, $OH \cdot C_6Cl_4 \cdot O \cdot C_6Cl_2O_2 \cdot OMe$ (Jackson and Kelley, A., 1912, i, 275), in glacial acetic acid is warmed with fuming nitric acid, it is converted into a substance, m. p. 202—208° (decomp.), which is probably the *tetrachlorocatechol hemiether* of *dichloronitrodihydroxymethoxy*cyclo-*pentenecarboxylic acid*, $OH \cdot C_6Cl_4 \cdot O \cdot C_5Cl_2(NO_2)(OH)_2(OMe) \cdot CO_2H$; it forms white crystals, and yields an *acetyl* derivative, m. p. 146° (decomp.).

By the action of glacial acetic acid and fuming nitric acid on hexachloroethoxy-*o*-quinocatechol hemiether (Jackson and Kelley, *loc. cit.*), a compound, m. p. 210—215° (decomp.), is produced, which crystallises in rhombic plates or prisms, and is provisionally regarded as the *nitric acid* compound of the *tetrochlorocatechol hemiether* of *dichloro-ethoxy*-o-*quinone*, $OH \cdot C_6Cl_4 \cdot O \cdot C_6Cl_2O_2 \cdot OEt,HNO_3$. Another substance, m. p. 130—158° (decomp.), was also obtained in this reaction, which seems to be the corresponding compound containing $2HNO_3$.

E. G.

Quinonecarboxylic Esters. KARL BRUNNER (*Monatsh.*, 1913, **34**, 913—930).—Although esters of substituted *p*-benzoquinone-carboxylic acids are known, previous attempts (von Rakowski and Leppert, A., 1875, 1197 ; Brunner, *Monatsh.*, 1881, **2**, 464 ; Nef, A., 1887, 255 ; Juch, A., 1905, i, 701) to prepare *p*-benzoquinone-carboxylic acid have been unsuccessful. Since this failure was possibly attributable to the employment of aqueous solutions, the

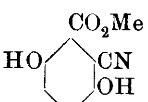
author has been led to study the oxidation of methyl gentisate in the absence of water and has thus prepared *methyl* p-*benzoquinonecarboxylate* and a number of its derivatives.

When a solution of methyl gentisate in benzene is shaken with a mixture of silver oxide and potassium carbonate for five minutes at 40—50°, methyl *p*-benzoquinonecarboxylate, yellowish-red crystals, m. p. 53·5—54°, is obtained. The dry substance may be preserved unchanged for months in the dark. It is rapidly decomposed when warmed with water. When mixed in warm ethereal solution with an equimolecular quantity of methyl gentisate, it is converted into *methyl quinhydronecarboxylate*, dark red crystals with metallic glance, m. p. 85—86° which, when warmed with sulphurous acid and water, is transformed into methyl gentisate, m. p. 87°. When mixed with aniline in ethereal solution, methyl *p*-benzoquinonecarboxylate yields *methyl dianilino*-p-*benzoquinonecarboxylate*, $C_8H_4O_4(NHPh)_2$, deep red, silky needles, m. p. 202—203°.

Methyl cyanoquinolcarboxylate, $C_9H_7O_4N$, is formed when an aqueous solution of sodium cyanide is added to a cold acidified alcoholic solution of methyl *p*-benzoquinonecarboxylate. It has m. p. 225—226°, and dissolves sparingly in ether and benzene to yield solutions which have an intense blue fluorescence. Small quantities of a substance, m. p. above 220°, are obtained as a by-product. When treated with potassium hydroxide and acetic anhydride, methyl cyanoquinolcarboxylate yields a *diacetyl* derivative, colourless crystals, m. p. 107·5—108°.

Methyl cyanoquinolcarboxylate is converted by concentrated sulphuric acid at 100° into *p*-dihydroxyphthalimide, sulphur-yellow needles, m. p. 273—274°. This substance appears to be in all respects identical with that prepared by Thiele and Meisenheimer (A., 1900, i, 299), from dicyanoquinol, except that it gives up its water of crystallisation with greater readiness. This phenomenon apparently depends to some extent, however, on the size of the crystals. The *lead* salt, $C_8H_3O_4NPb,H_2O$, carmine needles, is also described.

When methyl cyanoquinolcarboxylate is successively treated with concentrated aqueous potassium hydroxide and sulphuric acid, *p*-dihydroxyphthalic acid is obtained in practically white crystals, m. p. 219—220° (decomp.). The air-dried acid appears to be anhydrous. According to Thiele and Günther (A., 1906, i, 744) it has m. p. 213° and contains $\frac{1}{2}H_2O$. The *lead* salt, $C_8H_4O_6Pb,\frac{1}{2}H_2O$, crystallises in leaflets. When sublimed in a vacuum at 230—240°, the acid is converted into *p*-dihydroxyphthalic anhydride, yellow, hygroscopic needles, m. p. 232—233° (compare Thiele and Günther, *loc. cit.*), which yields the corresponding diacetyl derivative, m. p. 156—156·5°. The identity of these products obtained from methyl cyanoquinolcarboxylate with those obtained from dicyanoquinol by Thiele and Günther, leads the author to propose the annexed formula for the product examined by him.



Ethyl p-*benzoquinonecarboxylate* is prepared by a method similar to that adopted for the methyl ester. Its isolation is more difficult, however, since it melts slightly above the ordinary

temperature and readily decomposes when in the liquid state. It forms yellowish-red leaflets, m. p. 22°, which decompose when preserved even at a low temperature. With aniline in ethereal solution, it yields *ethyl dianilino*-p-*benzoquinonecarboxylate*, dark red, almost black needles, m. p. 178—179°. H. W.

Action of Bromine on Aliphatic-Aromatic Compounds. HUGO BAUER and GUSTAV ENDRES (*J. pr. Chem.*, 1913, [ii], **87**, 545—552).—An account of the action of bromine on *o*- and *p*-benzylbenzoic acids, phenylphthalide, homophthalic acid, phthalidecarboxylic acid and di-*p*-nitrodiphenylmethane.

p-Benzylbenzoic acid reacts with bromine in the cold yielding a *tribromo*-derivative, which crystallises in slender scales, m. p. 218—220°. When heated with bromine for three or four hours in a sealed tube at 110—120°, it gives rise to *dibromotetraphenylethylenedi*-p-*carboxylic acid*, $CO_2H\cdot C_6H_3Br\cdot CPh{:}CPh\cdot C_6H_3Br\cdot CO_2H$, m. p. 260—262°.

α-Phenylphthalide and bromine at 120° yields the dilactone of dihydroxytetraphenylethanecarboxylic acid (Ullmann, A., 1896, i, 563), which is also obtained from *o*-benzylbenzoic acid at 110—120°. If the action of bromine on *o*-benzylbenzoic acid is carried out at the ordinary temperature, the lactone is accompanied by a *bromo*-o-*benzylbenzoic acid*, m. p. 137°.

Phthalidecarboxylic acid, $CO{<}{C_6H_4 \atop O}{>}CH\cdot CO_2H$, and bromine at 120° yield hydrogen bromide, carbon dioxide, and phthalic anhydride; the same products are also obtained from homophthalic acid, $CO_2H\cdot C_6H_4\cdot CH_2\cdot CO_2H$.

From the product of the action of bromine on di-*p*-nitrodiphenylmethane, only di-*p*-nitrobenzophenone could be isolated. F. B.

Hydrogenation of Santonic Acid. A Dihydrosantonin. II. GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 711—714. Compare this vol., i, 730).—The author discusses the question of the constitution of santonin in the light of the results obtained by himself and other recent workers, and points out that the production of a dihydrosantonin cannot be reconciled with the views of Wienhaus and von Oettingen (this vol., i, 474).

Dihydrosantonin, $C_{15}H_{20}O_3$, crystallises in long prisms, m. p. 99° (*loc. cit.*), and has $[\alpha]_D^{18}$ +75·19° in 1·463% alcoholic solution. Its oxime, $C_{15}H_{21}O_3N$, forms tufts of colourless prisms, m. p. about 235°. The semicarbazone crystallises in colourless prisms, m. p. 243°. R. V. S.

Constitution of Santonin. ANGELO ANGELI (*Ber.*, 1913, **46**, 2233—2235).—The author points out that Asahina (this vol., i, 731), has overlooked the work of Angeli and Marino (A., 1907, i, 321) on the oxidation of santonin to heptanetetracarboxylic acid, the formation of which led them to the conclusion that santonin contains a bridged ring. F. B.

The Ethers and Esters of Fluorescein. HANS VON LIEBIG (*J. pr. Chem.*, 1913, [ii], **88**, 26—48).—In previous papers (A., 1912, i, 376; this vol., i, 79) the author has described four monomethyl ethers and esters of fluorescein, a strongly yellow form of m. p. 266°, two pale yellow ethers of m. p. 265° (corresponding with Fischer and Hepp's [A., 1895, i, 291] ether of m. p. 262°) and 272°, and also a colourless ether of m. p. 256—257°, obtained by hydrolysing the dimethyl ether of m. p. 208° with ethyl alcoholic potassium hydroxide. It is now found that, during the hydrolysis, part of the methyl is replaced by ethyl, so that the colourless ether of m. p. 256—257° really consists of the lactone form of the monoethyl ether,

$$O<\begin{matrix}C_6H_3(OEt)\\C_6H_3(OH)\end{matrix}>C<\begin{matrix}-O-\\C_6H_4\end{matrix}>CO,$$

which, in a pure condition, crystallises in white prisms, m. p. 253—254°.

If the hydrolysis is carried out with methyl alcoholic potassium hydroxide, the colourless monomethyl ether of m. p. 272° is obtained. This ether represents the lactone form of the monomethyl ether, whilst the yellow ether of m. p. 266° has the quinonoid constitution

$$O<\begin{matrix}C_6H_3(OMe)\\ \text{——}C_6H_3O\end{matrix}>C{\cdot}C_6H_4{\cdot}CO_2H;$$

the ether of m. p. 265° (or 262°) is either a mixture or, more probably, a polymeric form similar to the quadrimolecular monomethyl ether described previously.

The monomethyl ester, obtained by warming fluorescein with methyl alcohol and sulphuric acid, has m. p. 282—283°, and not 252° as given by Feuerstein and Wallach (A., 1901, i, 723); the corresponding monoethyl ester has m. p. 251—252°, and not 242°.

By methylating the monomethyl ester of fluorescein with methyl sulphate, Kehrmann and Dengler (A., 1909, i, 249) obtained a red compound of m. p. 176—177°, which they considered to be the methyl ester of the monomethyl ether of fluorescein. The author finds, however, that the product of the action consists of a mixture of the dimethyl ether of m. p. 198° (Kehrmann's 3 : 6-dimethoxyfluorane) and Fischer and Hepp's (*loc. cit.*) coloured dimethyl ether of m. p. 208°.

When the dimethyl ether of m. p. 198° is heated with methyl alcohol and concentrated hydrochloric acid, and the resulting solution diluted with water and saturated with sodium chloride, a *hydrochloride* of the trimethyl ether of fluorescein is obtained, which, after precipitation from alcoholic solution by means of ether, has the composition $4C_{23}H_{20}O_6,5HCl,10H_2O$ (compare Kehrmann and Scheunert, A., 1912, i, 1034); the addition of concentrated hydrochloric acid to a warm aqueous solution of this chloride causes the precipitation of a *chloride* of the composition $2C_{23}H_{18}O_5,3HCl,8H_2O$, crystallising in stout, orange prisms having a bluish glance. The *sulphate* of the trimethyl ether of fluorescein is prepared by heating the dimethyl ether of m. p. 198° with methyl alcohol and sulphuric acid; it has m. p. 226°.

That the above salts are derivatives of the trimethyl ether to fluorescein has been established by reducing the sulphate with zinc dust and glacial acetic acid, when the trimethyl ether of fluorescin

was obtained, identical with that previously prepared by the direct methylation of fluorescein with methyl sulphate.

Oxidation of the trimethyl ether of fluorescin by means of lead dioxide in hot glacial acetic acid solution gives rise to the dimethyl ether of fluorescein, having m. p. 198°, and the above-mentioned trimethyl ether of fluorescein, which was isolated in the form of its *nitrate*, $C_{23}H_{18}O_5,HNO_3$, crystallising in light yellow leaflets.

Hydrolysis of the trimethyl ether of fluorescin with alcoholic potassium hydroxide leads to the formation of the *dimethyl ether* of fluorescin, $C_{22}H_{18}O_5$, which crystallises from alcohol in white needles, m. p. 204—205°, and is also obtained, together with the trimethyl ether, by methylating fluorescin with aqueous potassium hydroxide and methyl sulphate.

When oxidised by means of lead dioxide in hot glacial acetic acid solution the dimethyl ether of fluorescin yields the dimethyl ether of fluorescein of m. p. 198°.

The monomethyl ether of fluorescein of m. p. 265° forms a potassium salt, $C_{21}H_{13}O_5K,C_{21}H_{12}O_5K_2,4H_2O$.

When heated with ethyl iodide and alcoholic potassium hydroxide, fluorescein yields a quadrimolecular *monoethyl ether* of the composition $3C_{20}H_{12}O_5,C_{22}H_{16}O_5,H_2O$, m. p. 330—331°, in addition to the diethyl ethers of m. p. 159° and 181°.

When esterified with methyl alcohol and sulphuric acid the monomethyl ethers of fluorescein of m. p. 265°, 266°, and 272° are converted into the dimethyl ether-ester of m. p. 208°, $OMe{\cdot}C_{19}H_{10}O_2{\cdot}CO_2Me$, which crystallises in orange-yellow needles or dark red prisms, and is precipitated in the form of its *sulphate*, $2C_{22}H_{16}O_5,H_2SO_4,H_2O$, dark red, prismatic crystals (decomp. 140°) by the addition of water to the product of the esterification.

If, after esterification, the mixture is treated with aqueous sodium hydroxide and the precipitated ester purified by conversion into the *hydrochloride*, $C_{22}H_{16}O_5,HCl,2H_2O$, a second modification of the dimethyl ether-ester is obtained; this crystallises in yellowish-red prisms, m. p. 198°, and on repeated crystallisation from ethyl acetate is transformed into the dimethyl ether of m. p. 208°.

The *ethyl* ester of the monomethyl ether of fluorescein,

$$OMe{\cdot}C_{19}H_{10}O_2{\cdot}CO_2Et,$$

prepared by esterifying the monomethyl ether with ethyl alcohol and sulphuric acid, has m. p. 194—195°, and yields a *hydrochloride*,

$$C_{23}H_{18}O_5,HCl,$$

crystallising in yellowish-red needles; the *methyl* ester of the monoethyl ether of fluorescein, $OEt{\cdot}C_{19}H_{10}O_2{\cdot}CO_2Me$, obtained in a similar manner, crystallises in yellowish-red prisms or needles, m. p. 216°; the *ethyl* ester of the monoethyl ether forms a *hydrochloride*,

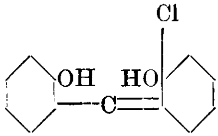
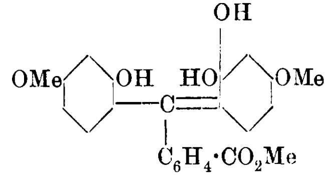
$$OEt{\cdot}C_{19}H_{10}O_2{\cdot}CO_2Et,HCl,$$

crystallising in yellowish-red needles.

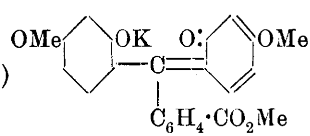
A solution of the sulphate of the monomethyl ester of fluorescein (m. p. 282—283°) in sodium hydrogen carbonate deposits a *sodium* salt of the composition $C_{21}H_{14}O_5,NaHSO_4$ as a fine red powder.

According to the author (A., 1912, i, 381), the salts of fluorescein and its ethers with acids owe their solubility in water to the rupture

of the oxygen bridge of the pyrone ring and formation of compounds having the structure represented in (I).

(I.)  (II.) 

If this view is correct the salts of the trimethyl ether of fluorescein should give rise on hydrolysis to the compound (II), which with potassium hydroxide would form a quinonoid having the annexed formula (III), and, from analogy with the quinonoid salts of quinolphthalein and 4:5-dinitrofluorescein (this vol., i, 80; compare also Baeyer, A., 1910, i, 249), this salt should have a blue colour.

(III.) 

Such an *o*-quinonoid *potassium* salt has been prepared by triturating the trimethyl ether of fluorescein with 33% aqueous potassium hydroxide. It has the composition $C_{23}H_{19}O_6K,H_2O$, and rapidly decomposes when kept, yielding a brown *substance*, which has m. p. about 120°, with previous sintering, and dissolves in methyl and ethyl alcohols, yielding solutions coloured respectively pure green and brownish olive-geeen; from these solutions the addition of alkalis causes the separation of the dimethyl ether of fluorescein.

When freshly prepared and treated with water, the blue potassium salt partly dissolves with the formation of a deep blue solution, from which acetic acid precipitates a *hydrate* of the trimethyl ether-ester of fluorescein, $C_{23}H_{20}O_6,H_2O$, in yellow flocks. This melts and loses water at 173°. It dissolves in alkali hydroxides with a blue colour, and is, therefore, considered to be the parent substance of the blue potassium salt. On treatment with water, the greater part of the blue potassium salt is converted into an insoluble brown *substance*, which crystallises in needles, is insoluble in alkalis, and probably represents the trimethyl ether-ester of fluorescein of the following constitution: $O<\substack{C_6H_3(OMe) \\ C_6H_3(OMe)}>C(OH)\cdot C_6H_4\cdot CO_2Me$. F. B.

[Fluorescein.] Hans von Liebig (*J. pr. Chem.*, 1913, [ii], **88**, 96).—A correction. Owing to an error in the thermometer the m. p.'s of a number of ethers and esters of fluorescein recorded in previous papers (A., 1912, i, 376; this vol., i, 79) are too high.

The lactone form of the monomethyl ether has m. p. 266° (not 272°), the quinonoid form 259° (not 266°), and the monomethyl ester m. p. 274—275° (not 282°). The lactone form of the monomethyl ether, previously described as melting at 253—254°, has m. p. 247—248°. The monoethyl ester has m. p. 247°. F. B.

Fluorescein Methyl Ethers. Otto Fischer and Eduard Hepp (*Ber.*, 1913, **46**, 1951—1959. Compare A., 1895, i, 291).—A reply to

von Liebig (this vol., i, 79) and to Kehrmann and Dengler (A., 1909, i, 249). The divergence of the results of these workers from those previously obtained by the authors is probably to be attributed to impure fluorescein. The fluorescein used by the authors was always previously purified through the diacetyl derivative.

Methylation of purified fluorescein by methyl iodide and alcoholic potassium hydroxide gives as main product the orange-red dimethyl ether, m. p. 208°, together with a little of the colourless lactonic dimethyl derivative, m. p. 197—198°, which previously escaped detection. A similar result is obtained by the application of diazomethane in nitrobenzene solution. Fluorescein monomethyl ester, m. p. 282°, obtained by the interaction of fluorescein and methyl alcohol in the presence of sulphuric acid or hydrogen chloride, also gives a similar product to the above whether further methylated in methyl alcohol by methyl iodide and potassium hydroxide or in nitrobenzene solution by methyl sulphate. In the latter case no indication whatever of a substance, m. p. 176—177° (Kehrmann and Dengler, *loc. cit.*), was observed.

By hydrolysis of fluorescein dimethyl ether, m. p. 208°, with methyl-alcoholic potassium hydroxide, the colourless lactonic fluorescein monomethyl ether, m. p. 265—266°, can be obtained; on methylation of this by methyl sulphate in nitrobenzene solution the chief product is the dimethyl ether, m. p. 197—198°. D. F. T.

Substituted Crotonolactoneacetic [αγ-Monolactones of γ-Hydroxydihydromuconic] Acids. ERICH BESCHKE [with GEORG KÖHRES and F. MARSCHALL] (*Annalen*, 1913, **398**, 265—298).—The interaction of phenanthraquinone, ethyl bromoacetate, and zinc in boiling benzene leads to the formation of *γ-hydroxy-βγ-diphenylene-Δ^α-dihydromuconic acid αγ-lactone*, $\begin{array}{l}C_6H_4\cdot C(CH_2\cdot CO_2H)\cdot O\\ |\qquad\quad |\\ C_6H_4\cdot C{=\!=\!=\!=\!=\!=}CH\end{array}\!\!>CO$, m. p. 216°, colourless crystals, which exhibits considerable stability towards dilute alkaline potassium permanganate, zinc dust and acetic acid, and bromine. Its *sodium* salt, $C_{18}H_{11}O_4Na$, reacts with aqueous bromine to form, after acidification, *α-bromo-γ-hydroxy-βγ-diphenylene-Δ^α-dihydromuconic acid αγ-lactone*, $C_{18}H_{11}O_4Br$, m. p. 198°, by the reduction of which by zinc dust and alcohol the original acid is regenerated.

The addition of saturated aqueous sodium hydroxide to a boiling alcohol solution of γ-hydroxy-βγ-diphenylene-Δ^α-dihydromuconic acid γ-lactone yields *sodium γ-hydroxy-βγ-diphenylene-Δ^α-dihydromuconate*, $\begin{array}{l}C_6H_4\cdot C(OH)\cdot CH_2\cdot CO_2Na\\ |\qquad\quad |\\ C_6H_4\cdot C{:}CH\cdot CO_2Na\end{array}$, an aqueous solution of which is reduced by 3% sodium amalgam to *phenanthrene*-9 : 10-*diacetic acid*,

$$\begin{array}{l}C_6H_4\cdot C\cdot CH_2\cdot CO_2H\\ |\qquad\quad ||\\ C_6H_4\cdot C\cdot CH_2\cdot CO_2H\end{array},$$

m. p. 305°, colourless crystals. This acid forms an *ethyl* ester, $C_{22}H_{22}O_4$, m. p. 94°, and is converted by heating into 2-*ketophenanthhydrindene*, $\begin{array}{l}C_6H_4\cdot C\cdot CH_2\\ |\qquad\quad ||\\ C_6H_4\cdot C\cdot CH_2\end{array}\!\!>CO$, m. p. 219°, colourless leaflets (*oxime*, m.p. 258° [decomp.])

γ-Hydroxy-$\beta\gamma$-diphenylene-Δ^{α}-dihydromuconic acid $\alpha\gamma$-lactone forms an *ethyl* ester, $C_{20}H_{16}O_4$, m. p. 104°, from which the acid is regenerated by hydrolysis with acids. However, when a cold alcoholic suspension of the ester is treated with sodium ethoxide and the resulting yellow solution is acidified, *ethyl hydrogen $\beta\gamma$-diphenylenemuconate*, $\begin{array}{l}C_6H_4{\cdot}C{:}CH{\cdot}CO_2Et\\ C_6H_4{\cdot}C{:}CH{\cdot}CO_2H\end{array}$, is obtained as a viscous, yellow mass which by keeping or warming changes to the *ethyl* ester, m. p. 234°, colourless crystals, of the *$\alpha\delta$-lactone* of δ-hydroxy-$\beta\gamma$-diphenylene-Δ^{α}-dihydromuconic acid, $\begin{array}{l}C_6H_4{\cdot}CH{\cdot}CH(CO_2Et)\\ C_6H_4{\cdot}C{:}CH\text{———}CO\end{array}\!\!>\!O$, m. p. 280° (decomp.), colourless crystals. By treating a boiling alcoholic solution of ethyl γ-hydroxy-$\beta\gamma$-diphenylene-Δ^{α}-dihydromuconic acid $\alpha\gamma$-lactone with concentrated aqueous sodium hydroxide, *sodium-$\beta\gamma$-diphenylenemuconate*,

$$\begin{array}{l}C_6H_4{\cdot}C{:}CH{\cdot}CO_2Na\\ C_6H_4{\cdot}C{:}CH{\cdot}CO_2Na\end{array},$$

is obtained, from which a yellow acid is obtained by acidification; by recrystallisation the yellow acid, *$\beta\gamma$-diphenylenemuconic acid*, is changed into the lactone, m. p. 280° (decomp.), of δ-hydroxy-$\beta\gamma$-diphenylene-Δ^{α}-dihydromuconic acid. An aqueous alkaline solution of $\beta\gamma$-diphenylenemuconic acid is reduced by sodium amalgam to phenanthrene-9 : 10-diacetic acid, from which phenanthraquinone is obtained by oxidation with chromic and acetic acids.

By oxidation with chromic and acetic acids at 75° and finally at 90°, the lactone of δ-hydroxy-$\beta\gamma$-diphenylene-Δ^{α}-dihydromuconic acid is converted into the *lactone*, $\begin{array}{l}C_6H_4{\cdot}CH{\cdot}CH_2{\cdot}O\\ C_6H_4{\cdot}CH{\cdot}CO{-}CO\end{array}$, m. p. 211°, colourless crystals, which forms a *phenylhydrazone*, $C_{23}H_{18}O_2N_2$, m. p. 234°, faintly yellow leaflets, and *o-aminoanilino*-derivative, $C_{23}H_{18}O_2N_2$, m. p. 236°, with *o*-phenylenediamine, and is oxidised by chromic acid in boiling glacial acetic acid to the *lactone*, $\begin{array}{l}C_6H_4{\cdot}C{\cdot}CH_2{\cdot}O\\ C_6H_4{\cdot}C{\cdot}CO{-}CO\end{array}$, m. p. 302°, yellow crystals. The latter lactone, which is more conveniently obtained directly by the oxidation of the lactone of δ-hydroxy-$\beta\gamma$-diphenylene-Δ^{α}-dihydromuconic acid, forms a *phenylhydrazone*, m. p. 292°, yellow needles, *anilino*-derivative, $C_{23}H_{15}O_2N$, m. p. 263°, yellow needles, *o-aminoanilino*-derivative, m. p. 269° (decomp.), and *phenazine*, $C_{23}H_{14}ON_2$, m. p. 271°, yellowish-red needles. C. S.

Synthesis of Derivatives of *dicyclo*-[1,3,3]-Nonane. I. HANS MEERWEIN and WILHELM SCHÜRMANN (*Annalen*, 1913, **398**, 196—242).—Derivatives of *dicyclo*-[1 : 3 : 3]-nonane (annexed formula) have been prepared from formaldehyde and ethyl malonate by a very simple and smooth reaction.

$$\begin{array}{lll}CH_2{\cdot} & CH{-} & CH_2\\ CH_2 & CH_2 & CH_2\\ CH_2{\cdot} & CH{-} & CH_2\end{array}$$

Perkin, in conjunction with Haworth (T., 1898, **73**, 330) and Bottomley (T., 1900, **74**, 294), has shown that formaldehyde and malonic esters condense to form, under different conditions, methylenemalonic esters, methylenebismalonic esters, or pentane-$\alpha\alpha\gamma\gamma\epsilon\epsilon$-hexacarboxylic esters. By this

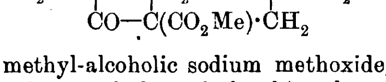
method the authors have prepared *methyl methylenemalonate*,

$$CH_2:C(CO_2Me)_2,$$

as a mixture, b. p. 150—180°/15 mm, of the uni- and bi-molecular forms (the latter is an amorphous, white powder which is depolymerised by distillation at 200—203°), and also *methyl pentane-ααγγεε-hexacarboxylate*, $CH(CO_2Me)_2\cdot CH_2\cdot C(CO_2Me)_2\cdot CH_2\cdot CH(CO_2Me)_2$, m. p. 62—63°, hard, colourless prisms. The latter, which can also be obtained by the interaction of methyl methylenebismalonate and methyl methylenemalonate in alcoholic sodium methoxide at the ordinary temperature, is converted by boiling methyl alcoholic sodium methoxide into methyl carbonate and *methyl* cyclo*hexan*-1-*one*-2 : 4 : 4 : 6-*tetracarboxylate*, $CO<\begin{matrix}CH(CO_2Me)\cdot CH_2\\CH(CO_2Me)\cdot CH_2\end{matrix}>C(CO_2Me)_2$, m. p. 121—122°, colourless, rhombic prisms, methyl *bicyclo*-[1,3,3]-nonane-2 : 6-dione-1 : 3 : 5 : 7-tetracarboxylate (see below) being also formed. Methyl *cyclo*hexan-1-one-2 : 4 : 4 : 6-tetracarboxylate exists as the ketonic modification in the solid state, but is rapidly enolised by alcohol, the solution in this solvent producing a reddish-violet coloration with ferric chloride. By acidifying a solution of the ester in alcoholic sodium methoxide, the enol is precipitated as a viscous oil, the ethereal solution of which deposits almost quantitatively the ketonic modification after a short time. This property of rapidly ketonising is utilised to separate the ester from the accompanying *dicyclo*nonanedionetetracarboxylate.

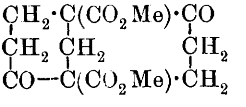
By heating with half volume of water at 200° for thirty minutes (compare following extract), methyl *cyclo*hexan-1-one-2 : 4 : 4 : 6-tetracarboxylate undergoes the ketonic decomposition and yields *methyl* cyclo*hexan*-1-*one*-4 : 4-*dicarboxylate*, b. p. 160—161°/14 mm, which has no acid properties, does not give a coloration with ferric chloride, forms a *semicarbazone*, m. p. 190° (decomp.), and *dicinnamylidene* derivative, $C_{28}H_{26}O_5$, m. p. 186°, yellow needles dissolving to a blue solution in concentrated sulphuric acid, and yields Perkin's *cyclo*hexan-1-one-4-carboxylic acid (T., 1904, **85**, 424; 1906, **89**, 1648) by hydrolysis.

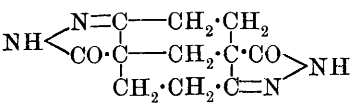
All the substances, namely, methyl methylenemalonate and methyl methylenebismalonate, and methyl pentane-ααγγεε-hexacarboxylate, produced by the interaction of formaldehyde and methyl malonate, yield more or less *methyl* bicyclo-[1,3,3]-*nonan*-2:6-*dione*-1 : 3 : 5 : 7-*tetracarboxylate* (annexed formula), m. p. 163—164°, colourless prisms, by boiling with concentrated methyl-alcoholic sodium methoxide, the best yield being obtained by using methyl methylenebismalonate (1 mol.) and methyl methylenemalonate (2 mols.).



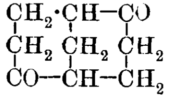
The constitution of the *dicyclo*nonane derivative, which can also be prepared by heating methyl malonate (4 mols.) and methylene iodide (3 mols.), or methyl *cyclo*hexan-1-one-2 : 4 : 4 : 6-tetracarboxylate and methyl methylenemalonate, with methyl alcoholic sodium methoxide, is proved, not only by the preceding method of preparation, but also by the following reactions.

Methyl *dicyclo*-[1,3,3]-nonan-2 : 6-dione-1 : 3 : 5 : 7-tetracarboxylate develops a reddish-violet coloration with alcoholic ferric chloride, forms a pale green *copper* derivative and a crystalline *disodium* derivative, $C_{17}H_{18}O_{10}Na_2$, and possesses pronounced acid properties, indicating that the substance is a cyclic β-ketonic ester. By heating with water at 170—180°, it is converted quantitatively into *methyl* dicyclo-[1,3,3]-*nonan*-2 : 6-*dione*-1 : 5-*dicarboxylate* (annexed formula), m. p. 187—188°, colourless prisms or quadratic plates. This ester is insoluble in alkalis and does not develop a coloration with ferric chloride. However, it still contains two β-ketonic groups because it reacts with hydrazine hydrate and with phenylhydrazine in glacial acetic acid to form respectively the *dipyrazolone* (annexed formula), m. p. 300° (decomp.), colourless prisms, and corresponding *diphenyldipyrazolone*, m. p. 270°, pale yellow leaflets.





The decomposition of methyl *dicyclo*-[1,3,3]-nonan-2 : 6-dione-1 : 3 : 5 : 7-tetracarboxylate by dilute alkali hydroxide is too profound to be of any service, but by hydrolysis by aqueous barium hydroxide at 105° and acidification of the resulting barium salt, the ester yields 3 : 7-*dimethyl* 1 : 5-*dihydrogen* dicyclo-[1,3,3]-*nonan*-2 : 6-*dione*-1 : 3 : 5 : 7-*tetracarboxylate*, m. p. 205—207° (decomp.), small prisms or needles, which gives a violet coloration with ferric chloride, regenerates the original ester, m. p. 163—164°, by treatment of its silver salt with methyl iodide, and is converted by heating into *methyl* dicyclo-[1,3,3]-*nonan*-2 : 6-*dione*-3 : 7-*dicarboxylate*, $C_{13}H_{16}O_6$, m. p. 136—137°, colourless prisms. The latter is soluble in alkalis, develops a reddish-violet coloration with ferric chloride, and forms a *dipyrazolone*, $C_{11}H_{12}O_2N_4$, decomp. above 300°, and *diphenyldipyrazolone*, $C_{23}H_{20}O_2N_4$, decomp. above 300°, thus indicating that the original *dicyclo*nonane derivative, methyl *dicyclo*-[1,3,3]-nonan-2 : 6-dione-1 : 3 : 5 : 7-tetracarboxylate, must contain four β-keto-groups.



dicyclo-[1,3,3]-*Nonan*-2 : 6-*dione* (annexed formula), m. p. 141°, b. p. 180°/20 mm., rhombic prisms, is obtained in about 34% yield by boiling methyl *dicyclo*nonanedionetetracarboxylate or methyl *dicyclo*nonanedione-1 : 5-dicarboxylate with dilute hydrochloric acid, or quantitatively by heating 3 : 7-dimethyl 1 : 5-dihydrogen *dicyclo*nonanedionetetracarboxylate, or methyl *dicyclo*nonanedione-3 : 7-dicarboxylate with water at 200°. *dicyclo*Nonanedione is volatile with steam, forms a *diphenylhydrazone*, $C_{21}H_{24}N_4$, and a *di-oxime*, $C_9H_{14}O_2N_2$, m. p. 205—206° (decomp.), regular octahedra, and is stable to potassium permanganate, these reactions indicating that the substance is a dicyclic diketone. It condenses very readily with alcoholic benzaldehyde, or cinnamaldehyde in the presence of a little concentrated sodium hydroxide, yielding 3 : 7-*dibenzylidene*dicyclo-[1,3,3]-*nonan*-2 : 6-*dione*, $C_{23}H_{20}O_2$, m. p. 201°, faintly yellow needles, and the *dicinnamylidene* derivative, $C_{27}H_{24}O_2$, m. p. 246°, pale yellow powder, which dissolve in concentrated

sulphuric acid with a pale yellow and orange-red colour respectively. The significance of these slight colorations is important, because Wallach, Stobbe, and others have shown that the dibenzylidene and dicinnamylidene derivatives of cyclic ketones of the type

$$[CH_2]_x<\begin{matrix}C(:CHAr)\\C(:CHAr)\end{matrix}>CO$$

develop intensely yellow and violet colorations respectively with concentrated sulphuric acid. Hence the inference is drawn that only one methylene group is attached directly to a carboxyl group in the *dicyclo*-nonanedione.

The oxidation of *dicyclo*nonanedione by warm nitric acid, D 1·2, yields Guthzeit and Engelmann's pentane-$\alpha\beta\delta\epsilon$-tetracarboxylic acid (*anhydride*, $C_9H_8O_6$, m. p. 161°; *methyl* ester, $C_{13}H_{20}O_8$, m. p. 60°, b. p. 210°/20 mm.). The formation of this acid proves that the diketone must have either the formula assigned to it by the authors (which is proved by the formation of methyl *dicyclo*nonanedionetetracarboxylate, and therefore indirectly of the diketone, from a substance already containing a *cyclo*hexane ring [see above]) or the formula $CH_2<\begin{matrix}CO-\\CH_2\end{matrix}>CH\cdot CH_2\cdot CH<\begin{matrix}CO-\\CH_2\end{matrix}>CH_2$; against the latter tells the fact that the formation of a *cyclo*butane derivative has never been observed when there is a possibility for the reaction to produce a *cyclo*hexane derivative. C. S.

Quantitative Investigation of the Photochemical Transformation of *o*-Nitrobenzaldehyde into *o*-Nitrosobenzoic Acid. FRITZ WEIGERT and LUDWIG KUMMERER (*Ber.*, 1913, **46**, 1884—1885. Compare this vol., ii, 370; Kailan, *ibid.*, i, 51, 733).—A further criticism of Kailan's work on this subject. F. B.

Quantitative Investigation of the Photochemical Transformation of *o*-Nitrobenzaldehyde into *o*-Nitrosobenzoic Acid. II. ANTON KAILAN (*Ber.*, 1913, **46**, 2175—2179. Compare this vol., i, 51). —In reply to Weigert and Kummerer's criticism (this vol., ii., 370) that the titration of *o*-nitrosobenzoic acid using phenolphthalein is not trustworthy in presence of much *o*-nitrobenzaldehyde, the author shows that the method gives satisfactory results. J. C. W.

Bromination of Certain Ketones and of Some Secondary Hydroaromatic Alcohols. FERNAND BODROUX and FELIX TABOURY (*Compt. rend.*, 1913, **156**, 1840—1841. Compare A., 1912, i, 567).—Bromination was effected by the addition of a solution of the ketone or alcohol in carbon tetrachloride to an excess of bromine dissolved in the same solvent. After six hours, excess of bromine and carbon tetrachloride were removed by means of a current of air.

1-Methyl-2-*cyclo*hexanone yielded *tetrabromomethyl*cyclo*hexanone*, small, white needles, m. p. 105—107°, together with a small quantity of a mixture of tribromomethyl*cyclo*hexanones which could not be separated from one another. 1-Methyl-2-*cyclo*hexanol gave a poor yield of a mixture of tribromomethyl*cyclo*hexanones.

1-Methyl-3-*cyclo*hexanone was practically quantitatively converted

into a tribromomethyl*cyclo*hexanone. The latter was very difficult to purify, but had m. p. 55—58°.

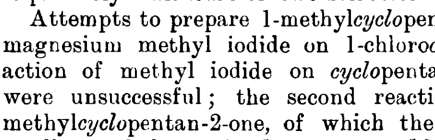
1-Methyl-4-*cyclo*hexanone yielded a *tetrabromo*-derivative, white needles, m. p. 79°. The same substance was obtained from 1-methyl-4-*cyclo*hexanol.

1 : 3-Dimethyl-4-*cyclo*hexanone gave a *tetrabromo*-derivative, white prisms, m. p. 62—63°.

The bromo-derivatives of the homologues of *cyclo*hexanone are somewhat unstable. At temperatures slightly above their m. p.'s, they are decomposed into bromine, hydrogen bromide, and bromo-phenols. The same transformation occurs slowly at the ordinary temperature under the influence of light. H. W.

Catalytic Hydrogenation of the Two Methyl*cyclo*pentanones. MARCEL GODCHOT and FELIX TABOURY (*Bull. Soc. chim.*, 1913, [iv], **13**, 591—599).—It is shown that the reduction of the methyl*cyclo*pentanones by Sabatier and Senderens' method is quite analogous to that of *cyclo*pentanone (A., 1911, i, 385; 1912, i, 34), the products being the corresponding methyl*cyclo*pentanols and dimethyl*cyclo*pentyl*cyclo*pentanones, the latter predominating (compare Zelinsky, A., 1911, i, 988).

1-Methyl*cyclo*pentan-3-one yields 1-methyl*cyclo*pentan-3-ol (*phenylurethane*, m. p. 82°, colourless needles from alcohol) and 3-*methyl*cyclo*pentyl*-2′(or 3′)-*methyl*cyclo*pentan*-5′-*one* (annexed formulæ), D_{16}^{16} 0·9365, n_D^{16} 1·4700, b. p. 245°, a colourless liquid having an odour of menthol; it yields a *semicarbazone*, m. p. 137°, crystallising in needles, and with hydroxylamine a *product*, m. p. 75—100°, which is probably a mixture of two stereoisomeric oximes.



Attempts to prepare 1-methyl*cyclo*pentan-2-one by (1) the action of magnesium methyl iodide on 1-chloro*cyclo*pentan-2-one and (2) the action of methyl iodide on *cyclo*pentanone in presence of sodamide were unsuccessful; the second reaction yielded *cyclo*pentylidene-3-methyl*cyclo*pentan-2-one, of which the *oxime*, m. p. 85°, colourless needles, and the *semicarbazone*, m. p. 193°, were prepared.

The 1-methyl*cyclo*pentan-2-one required was prepared by Bouveault's method (A., 1900, i, 171). On reduction by nickel at 150°, 1-methyl*cyclo*pentan-2-ol, D_{16}^{16} 0·9238, n_D 1·4466, b. p. 146—147° (*phenylurethane*, m. p. 84°), was obtained with 2-*methyl*cyclo*pentyl*-3′-*methyl*cyclo*pentan*-2′-*one* as a principal product. The latter has D_{16}^{16} 0·9238, n_D 1·4724, b. p. 239—241°, and is a colourless liquid with an odour of menthol; it yields a *semicarbazone*, m. p. 202—203°, crystallising from alcohol in needles. Looft (A., 1894, i, 405) has already prepared a methyl*cyclo*pentanol, which may be identical with that described above. T. A. H.

Ketimines. CHARLES MOUREU and GEORGES MIGNONAC (*Compt. rend.*, 1913, **156**, 1801—1806).—The authors have succeeded in

isolating a series of ketimines of the general formula $CR_2:NH$, the bromomagnesium derivatives of which are formed as intermediate products in the preparation of ketones by the action of Grignard's reagents on nitriles.

For the preparation of purely aromatic ketimines, the solid product of the action of the aryl-nitrile on the magnesium aryl haloid is brought, little by little, into a mixture of crushed ice and ammonium chloride, the mixture extracted with ether, the ethereal solution dried and saturated with dry hydrogen chloride. The precipitated imine-hydrochloride is filtered, suspended in ether, and decomposed by dry ammonia gas. After removal of ammonium chloride, the imine is obtained by evaporating the ethereal solution. Mixed fatty-aromatic ketimines are generally more readily decomposed by water, and their isolation is preferably effected by passing dry hydrogen chloride directly into the ethereal suspension of the magnesium derivative. The free imine is isolated from the hydrochloride so formed in the same manner as that adopted for aromatic ketimines.

Ketimines are generally oils or solids of low m. p. which yield crystalline salts. The hydrochlorides dissolve readily in chloroform, and are decomposed by water into the corresponding ketone and ammonium chloride. The free bases are much less sensitive to the action of water than the salts. Ketimines readily combine with bromine. They yield acyl derivatives which are decomposed by cold dilute hydrochloric acid with the formation of ketones. The constants of the following ketimines are given: *Phenyl ethyl ketimine*,

$$CEtPh:NH,$$

has b. p. 101·5—102·5°/13·5 mm., D_4^{22} 0·9902, n_D^{22} 1·5476. Its *hydrochloride* and *acetyl* derivative have m. p. 145° and 126° respectively. *Phenyl propyl ketimine*, has b. p. 99°/8 mm., D_4^{18} 0·9751, n_D^{18} 1·5353. *Phenyl* iso*butyl ketimine*, b. p. 113—114°/12·5 mm., D_4^{20} 0·9489, n_4^{2} 1·5270. *Phenyl* cyclo*hexyl ketimine*, b. p. 135—138°/5 mm. *Diphenyl ketimine*, b. p. 127°/3·5 mm., D_4^{19} 1·0847, n_D^{19} 1·6191. *Phenyl* o-*tolyl ketimine*, b. p. 136—137°/4 mm., $D_4^{18\cdot5}$ 1·0614, $n_D^{18\cdot5}$ 1·6065. *Phenyl* p-*tolyl ketimine*, m. p. 37°, b. p. 147°/5 mm., D_4^{20} 1·0617, n_D^{20} 1·6097. *Phenyl* a-*naphthyl ketimine*, m. p. 68—69°, b. p. 181·5°/4·5 mm.. H. W.

Catalytic Formation of Benzophenone by Calcium Carbonate. PAUL SABATIER (*Anal. Fis. Quim.*, 1913, **11**, 274—275).—When the vapour of benzoic anhydride is passed over calcium carbonate at about 500°, benzene, benzophenone, and traces of anthraquinone are formed. G. D. L.

Transformation of 2 : 6-, 2 : 4′- and 2 : 4-Dibromobenzophenones into Bromofluorenones. PIETER J. MONTAGNE and JACOB MOLL VAN CHARANTE (*Rec. trav. chim.*, 1913, **32**, 164—173. Compare A., 1910, i, 42).—When 2 : 6-, 2 : 4′-, or 2 : 4-dibromobenzophenone is heated, hydrogen bromide is evolved, and a bromofluorenone formed. Concurrently a certain amount of bromination occurs, due apparently to the hydrogen bromide evolved, and, since different by-products are obtained from 2 : 4′- and 2 : 4-dibromobenzophenone, it appears that it is the unchanged original substance which is thus affected.

8-*Bromofluorenone*, $C_6H_3Br\overset{CO}{\langle\!\text{————}\!\rangle}C_6H_4$, m. p. 135°, b. p. ca. 395° (decomp.), is obtained when 2 : 6-dibromobenzophenone is heated at its b. p. during two to three days. On reduction by means of sodium amalgam in boiling alcoholic solution, it is converted into fluorenyl alcohol, m. p. 153°, whilst oxidation by concentrated sulphuric acid and mercuric sulphate transforms it into phthalic anhydride.

When 2 : 4′-dibromobenzophenone is heated, it yields a mixture of unchanged material and two substances which can be separated by sublimation under reduced pressure. At about 170—180°, 6-*bromofluorenone* is obtained. After recrystallisation from benzene, it forms needles and plates, m. p. 165·5°, or compact crystals, m. p. 162·5°. After re-solidification the latter melt at 165·5°. Reduction with sodium amalgam in boiling alcoholic solution transforms it into fluorenone, m. p. 82°, whilst, when oxidised with concentrated sulphuric acid and mercuric sulphate, it yields phthalic anhydride. The residue obtained from the sublimation of 6-bromofluorenone, when sublimed at about 225°, gives a dibromofluorenone, $C_{13}H_6OBr_2$, yellow crystals, m. p. 215·5—216°.

When 2 : 4-dibromobenzophenone is treated in the same manner as the 2 : 4′-isomeride, it yields 6-bromofluorenone. The residue left in the sublimation apparatus, after repeated crystallisations from benzene and alcohol, gives 6 : 8-dibromofluorenone, m. p. 225°. H. W.

αβ-Unsaturated Diketones. OTTO DIELS and PETER SHARKOFF (*Ber.*, 1913, **46**, 1862—1870. Compare A., 1911, i, 464).—Under the influence of 33% aqueous potassium hydroxide, dimethyl diketone monoxime readily condenses with benzaldehyde, cinnamaldehyde and furfuraldehyde, yielding oximes of αβ-unsaturated ketones of the formula $CHR\colon CH\cdot C(NOH)\cdot COMe$, from which the corresponding ketones cannot be obtained by any of the usual methods. The removal of the oximino-group may, however, be effected by distilling a mixture of the oxime with phthalic anhydride or succinic anhydride in superheated steam, but the yield of unsaturated diketone thus obtained is very small.

Styryl methyl diketone monoxime, $CHPh\colon CH\cdot C(N\cdot OH)\cdot COMe$, prepared from benzaldehyde and dimethyl diketone monoxime, crystallises from alcohol in long, colourless needles, m. p. 147° (corr.), and dissolves in aqueous alkali hydroxides, yielding yellow solutions; with 33% potassium hydroxide it forms a *potassium* salt. It is accompanied by an orange-yellow *substance*, probably

$$CHPh[CH_2\cdot CO\cdot C(N\cdot OH)\cdot CH\colon CHPh]_2,$$

m. p. 216—220° (decomp.).

That the condensation of the aldehyde takes place at the methyl group adjacent to the oximino-group has been established by the conversion of the styryl methyl diketone monoxime by boiling with strong hydrochloric acid into 3-*acetyl*-5-*phenyl*-4 : 5-*dihydro*iso*oxazole*, $\begin{array}{l}CHPh\cdot CH_2\\ |\\ O\text{————}N\end{array}\!\!\!>\!C\cdot COMe$, which crystallises in stout prisms, m. p. 97—98°, and when warmed with aqueous potassium hydroxide is transformed into a *substance*, m. p. about 254° (decomp.).

On treatment with oxalyl chloride in ethereal solution the oxime yields a *compound*, CHPh:CH·C(COMe):N·O·COCl, which crystallises in colourless needles, m. p. 59°, and is decomposed by water with the formation of cinnamic acid. The *dibromide* of styryl methyl diketone forms yellow crystals, m. p. 86°, and slowly decomposes when kept.

Cinnamylidenediacetyl monoxime (*β-styrylvinyl methyl diketone monoxime*), CHPh:CH·CH:CH·C(N·OH)·COMe, crystallises in slender, yellow needles, m. p. 148°, which become strongly electric when rubbed, give an intense purple-red coloration with sulphuric acid, and on distillation with phthalic anhydride in superheated steam yield *cinnamylidinediacetyl*, brownish-yellow needles, m. p. 49°.

Furfurylidenediacetyl monoxime (*β-furylvinyl methyl diketone monoxime*), C_4H_3O·CH:CH·C(N·OH)·COMe, has m. p. 132°, and with strong aqueous potassium hydroxide yields a *potassium* salt. F. B.

Curcumin. Victor Lampe and J. Miłobędzka (*Ber.*, 1913, **46**, 2235—2240).—The authors are endeavouring to confirm, by direct synthesis, the formula, $CH_2[CO·CH:CH·C_6H_3(OMe)·OH]_2$, proposed for curcumin by Miłobędzka, Kostanecki, and Lampe (A., 1910, i, 628), and with this object in view have first of all turned their attention to the preparation of the parent substance, dicinnamoylmethane (IV), the synthesis of which was finally accomplished from ethyl cinnamoylacetoacetate by the method indicated in the following scheme :

(I) CHPh:CH·CO·CH(COMe)·CO_2Et $\longrightarrow$
(II) CHPh:CH·CO·CH_2·COMe + CHPh:CH·COCl $\longrightarrow$
(III) COMe·CH(CO·CH:CHPh)$_2$ $\longrightarrow$
(IV) CH_2(CO·CH:CHPh)$_2$ + $CH_3·CO_2H$.

Cinnamoylacetone (II), prepared by hydrolysis and simultaneous elimination of carbon dioxide from ethyl cinnamoylacetoacetate (I), crystallises in yellow prisms, m. p. 86—88°, and develops a yellowish-green coloration with sulphuric acid. Its alcoholic solution gives with copper acetate a green precipitate, and with ferric chloride a deep red coloration. When boiled with hydroxylamine hydrochloride in alcoholic solution, it is converted into 3(or 5)-*styryl*-5(or 3)-*methyl*-*isooxazole*, $\begin{matrix}\text{CMe:CH}\\ \text{O——N}\end{matrix}\!\!>\!\text{C·CH:CHPh}$ or $\begin{matrix}\text{CMe·CH}\\ \text{N——O}\end{matrix}\!\!>\!\text{C·CH:CHPh}$, which crystallises in white leaflets, m. p. 92—94°. On successive treatment with sodamide and cinnamoyl chloride in ethereal solution, it yields *dicinnamoylacetone* (III). This has m. p. 112—114°, gives the same reactions as cinnamoylacetone with cupric acetate and ferric chloride, and yields strongly yellow, fluorescent solutions with sulphuric acid.

Dicinnamoylmethane (IV), prepared by boiling dicinnamoylacetone with 50% acetic acid, crystallises in bronze-yellow, prismatic needles, m. p. 144°. In its chemical properties it strongly resembles curcumin. Thus, it dyes cotton a pale yellow without a mordant, dissolves in sulphuric acid, yielding an orange-red solution having a yellow fluor-

escence, and gives with copper acetate and ferric chloride in alcoholic solution a green precipitate and a deep red coloration respectively. When boiled with alcoholic hydroxylamine hydrochloride it is converted into 3 : 5-*distyrylisooxazole*, $\begin{array}{l}\mathrm{CHPh{:}CH{\cdot}C{\cdot}CH} \\ \quad\quad\quad\quad\;\; \| \\ \quad\quad\quad\quad\;\mathrm{N{-}O}\end{array}\!\!>\mathrm{C{\cdot}CH{:}CHPh}$, crystallising in almost colourless, prismatic needles, m. p. 170—172°.

Attempts to prepare ethyl dicinnamoylmalonate by the successive action of sodium and cinnamoyl chloride on ethyl malonate in ethereal solution led to the formation of *ethyl* 4-*cinnamoyl*-1-*phenyl*-Δ^1-cyclo*penten*-3 : 5-*dione*-4-*carboxylate*, $\begin{array}{l}\mathrm{CPh{\cdot}CO} \\ \| \\ \mathrm{CH{-}CO}\end{array}\!\!>\mathrm{C}<\!\!\begin{array}{l}\mathrm{CO{\cdot}CH{:}CHPh} \\ \mathrm{CO_2Et}\end{array}$, which forms prismatic needles, m. p. 188—189°, and is accompanied by *ethyl* 1-*phenyl*-Δ^1-cyclo*penten*-3 : 5-*dione*-4-*carboxylate*,

$$\begin{array}{l}\mathrm{CPh{\cdot}CO} \\ \| \\ \mathrm{CH{-}CO}\end{array}\!\!>\mathrm{CH{\cdot}CO_2Et},$$

This crystallises in prismatic needles, m. p. 107—109°, and yields deep red alcoholic solutions. F. B.

Diketones Obtained by the Action of Xylylene Dibromides on the Sodium Derivative of Phenyl *iso*Propyl Ketone, and their Decomposition by Sodamide. PH. DUMESNIL (*Compt. rend.*, 1913, **157**, 53—55. Compare A., 1911, i, 719, and Haller and Bauer, A., 1911, i, 726).—*o*-, *m*-, and *p*-Xylylene dibromides react with the sodium derivative of phenyl *iso*propyl ketone in benzene solution to give the corresponding *bis*-(*β*-*benzoyl*-*β*-*methylpropyl*)*benzenes*,

$$\mathrm{C_6H_4(CH_2{\cdot}CMe_2{\cdot}COPh)_2}.$$

The *ortho*-derivative is obtained as small, colourless crystals, m. p. 68°, giving a *dioxime*, m. p. 240°; the *meta* in large, colourless crystals, m. p. 44°, giving a *dioxime*, m. p. 210°, and the *para* in colourless needles, m. p. 113°, yielding a *dioxime*, m. p. 278°. All three of these diketones are decomposed, by warming them with sodamide in xylene solution, into the corresponding bis-dimethylacetamides. o-*Xylylene-bisdimethylacetamide*,

$$\mathrm{C_6H_4(CH_2{\cdot}CMe_2{\cdot}CO{\cdot}NH_2)_2},$$

is a colourless, crystalline solid, m. p. 130°; the *meta*-isomeride, colourless needles, m. p. 162°; and the *para*-isomeride, m. p. 238°. They are all hydrolysed by heating with 50% sulphuric acid in sealed tubes for six hours at 150° to the corresponding *acids* having respectively m. p.'s 135°, 155°, and 217°. W. G.

Di-iminonaphthol Hydrochlorides. III. OSWALD MILLER (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 580—608. Compare A., 1911, i, 308, 465).—When crystallised from water and from alcohol, di-iminonaphthol hydrochloride shows different solubilities in 50% aqueous alcohol. Further, whilst hydration in neutral aqueous solution of the salt obtained from water gives yields of amino-*α*-naphthaquinone varying regularly with the temperature, the hydrochloride separated from alcohol always yields smaller and inconstant proportions of the quinone owing to the simultaneous formation of a third amino naphthaquinone or *β*-oximinonaphthol.

From these isomeric di-iminonaphthol hydrochlorides ammonia separates identical bases, but dissociation into base and hydrogen chloride is peculiar to the normal or α-salt; the β'-salt, which does not dissociate, decomposes immediately into β-oximinonaphthol and ammonia.

The decomposition of the hydrochlorides in aqueous solution proceeds normally at temperatures up to about 60°, beyond which the primary products of the reaction yield two secondary products: (1) a dark blue colouring matter, which results from the condensation of α-oximinonaphthol and dissolves in alcohol, giving a blue solution with an intense brick-red fluorescence; it dissolves in varying degree in the products of the reaction, and of the product obtained at 94° it forms about 0·5%. (2) 2-Hydroxy-α-naphthaquinone, which is formed by hydration of the amino-group of aminoquinone, $\cdot NH_2 + H_2O = \cdot ONH_4$. The velocity of this hydration differs for these three quinones, being almost negligible for amino-α-naphthaquinone, only slightly greater for β-oximinonaphthol, and more or less considerable for α-oximinonaphthol. Hence, when the hydration is continued for only ten hours, it may be assumed that the 2-hydroxy-α-naphthaquinone formed is derived entirely from α-oximinonaphthol.

The actual amounts of the three primary products of the reaction are calculated from the equations: (I) amino-α-naphthaquinone $= \alpha + 0{\cdot}046\alpha + 0{\cdot}84$; (II) α-oximinonaphthol $= \beta - 0{\cdot}046\alpha - 4{\cdot}20 + 0{\cdot}247$, and (III) β-oximinonaphthol $= \beta' - 0{\cdot}47\beta'/100 + 4{\cdot}20$, where α, β, and β' are the experimental quantities of the three products per 100 grams of the hydrochloride.

When crystallised from dilute hydrochloric acid, all the different modifications of the hydrochloride are converted into one and the same form, identical in its decomposition products with that obtained by repeated crystallisation of the crude salt from water. This salt, termed the *A*-salt, is the one mostly employed in the present investigation.

In the decomposition of the hydrochloride (*A*-salt) by acid, the yields of amino-α-naphthaquinone and of α-oximinonaphthol obtained are diminished by repeated crystallisation from either water or acid, and the same is the case with the amount of α-oximinonaphthol converted into hydroxynaphthaquinone and colouring matter; on the other hand, the proportions of β-oximinonaphthol formed gradually increase. By two or three crystallisations from 95% alcohol, the *A*-salt is transformed into another, which has constant properties and is termed the *B*-salt. If the conversion of the *B*-salt into the *A*-salt by crystallisation from *N*/10-hydrochloric acid is determined by absorption of the acid by the salt, the inverse change consists in the gradual removal of the acid from the salt under the influence of the solvent. The *A*-salt mnst hence contain, not only chemically combined, non-esterifiable acid, but also a certain amount of acid in another form of combination, and capable of esterification by the action of alcohol.

The change produced in the *A*-salt by crystallisation is also effected by prolonged heating or by remaining over sodium hydroxide.

From these results it appears highly probable that the principal

part in the transformations of di-iminonaphthol hydrochlorides is played by traces of free hydrochloric acid fixed by the crystals on their formation in an acid solution, the maximum and minimum (zero) of such fixation being represented by the *A*- and *B*-salts respectively.

The composition of the *B*-salt having been found to vary with the acidity of the surrounding medium, a *C*-salt, the acidity of which remains constant, was prepared by suitable heating and crystallisation. When this salt is heated with dilute hydrochloric acid solutions of different concentrations, it is found that the transformation of the *B*-salt reaches its limiting value with 0·018 mol. of hydrochloric acid per mol. of *C*-salt, further addition of acid producing no extra increase in the yield of amino-α-naphthaquinone. The amounts of (1) amino-α-naphthaquinone, (2) α-oximinonaphthol, (3) β-oximinonaphthol, and (4) 2-hydroxy-α-naphthaquinone obtained with different concentrations of hydrochloric acid are shown in the form of curves. The second and third curves are approximately straight lines and are therefore in good agreement with the law of mass action. Curve (1), however, rises at first rapidly and then gradually to a limit, its course being closely similar to that of an adsorption curve. It seems, therefore, that when di-iminonaphthol is crystallised from water containing free hydrochloric acid, the latter is adsorbed to some extent on the faces of the crystals. Thus, adsorption in a heterogeneous system is not limited to substances in a colloidal state, but takes place also with crystalloids.

Further experiments show that in a 1% solution of the *B*-salt maintained at 94·5°, two processes occur simultaneously: (1) decomposition of the normal *A*-salt in 0·66% solution, with formation of α- and β-aminonaphthaquinones, and (2) decomposition of the β′-salt, not yet isolated, in 0·33% solution, with formation of β-oximinonaphthol.

β-Oximinonaphthol crystallises in shining, flat, reddish-brown needles having the same composition as the α-compound,

$$C_{10}H_7O_2N,\tfrac{1}{2}H_2O.$$

The two isomeric di-iminonaphthol hydrochlor[i]des are regarded as having the structures:

$$(\alpha)\ C_6H_4<\begin{matrix}CO\cdot C(NH_2)\\ C(:NH_2Cl)-\end{matrix}>CH \quad \text{and} \quad (\beta)\ C_6H_4<\begin{matrix}C\!-\!\!-\!\!-\!\!-\!\!-C:NH_2Cl\\ C(NH_2):CH\end{matrix}.$$

The following salts of di-iminonaphthol have been prepared and analysed: the normal *sulphate*, $(C_{10}H_8ON_2)_2,H_2SO_4,4H_2O$; the *acid acetate*, $C_{10}H_8ON_2,2C_2H_4O_2$, and the normal *acetate*, $C_{10}H_8ON_2,C_2H_4O_2,xH_2O$. T. H. P.

Lakes. II. PAUL PFEIFFER [and PH. FISCHER, J. KUNTNER, P. MONTI, and Z. PROS] (*Annalen*, 1913, **398**, 137—196. Compare A., 1911, i, 899).—The main object of the paper is to show that in hydroxyketones and hydroxyquinones, particularly of the anthraquinone series, the formation of normal salts occurs quite differently from that of internally complex salts.

The author has already shown in connexion with his theory of

halochromy (A., 1911, i, 788) that carbonyl compounds and stannic chloride form additive compounds of the type $Cl_4Sn\langle{}^{O:CRR'}_{O:CRR'}$. When the ketone or quinone contains a hydroxyl group in the ortho-position to the carbonyl group, a substituted compound is formed which is represented by the formula $\begin{matrix} RC{=}O \\ | \\ Ar{-}O \end{matrix}\!\!>SnCl_3$, and is closely related to the tin lakes (*loc. cit.*). The correctness of this view is supported by the following new facts. Acetophenone, benzophenone, xanthone, and *p*-methoxychalkone form with stannic chloride additive compounds of the first type, whilst their *o*-hydroxy-derivatives yield substituted, internally complex salts of the second type. The formation of the substituted compound is preceded by that of the additive compound because in the cases of *o*-hydroxyacetophenone, resacetophenone, and benzylidenepaeonol, the additive compound,

$$Cl_4Sn\langle{}^{O:CRAr}_{O:CRAr'}$$

can be isolated; by loss of hydrogen chloride, it changes to the internally complex salt, $\begin{matrix} RC{:}O \\ | \\ Ar{\cdot}O \end{matrix}\!\!>SnCl_3$. So also, alizarin dimethyl ether and stannic chloride in dry benzene at the ordinary temperature yield $Cl_4Sn\ldots OC\langle{}^{C_6H_4}_{C_6H_2(OMe)_2}\rangle CO$, which is converted by warming into $Cl_3Sn\langle{}^{O:C\text{———}C_6H_4}_{O\cdot C_6H_2(OMe)}\rangle CO$, methyl chloride being evolved.

The theory that the $SnCl_3$ compounds are internally complex salts containing Sn...O is supported by the fact that the colours of these substances are in harmony with the generalisations made with respect to the colours of $SnCl_4$ additive compounds (*loc. cit.*); for example, in the case of resacetophenone derivatives, $OMe{\cdot}C_6H_3\langle{}^{O\text{—}SnCl_3}_{CMe:O}$ is colourless, $CHPh{:}CH{\cdot}C\langle{}^{C_6H_3(OMe){\cdot}O}_{O\cdots\cdots SnCl_3}$ is orange-yellow, and

$$OMe{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}C\langle{}^{C_6H_3(OMe){\cdot}O}_{O\cdots\cdots SnCl_3}$$

is orange-red. The violet-black colour of the $SnCl_3$ compound of alizarin (and also of alizarin β-methyl ether), in comparison with the red colour of the $SnCl_3$ compound of 1-hydroxyanthraquinone, is in agreement with the rule that in halochromatic substances the presence of a hydroxyl or methoxyl group in the meta-position to the carbonyl group causes a deepening of the colour (*loc. cit.*).

Only *o*-hydroxyketones and *o*-hydroxyquinones yield $SnCl_3$ substituted compounds; the *m*- and *p*-hydroxy-isomerides form $SnCl_4$ additive compounds of the normal type. *o*-, *m*-, and *p*-Hydroxyacetophenones, benzylidenepaeonol (2-hydroxy-4-methoxyphenyl styryl ketone), phenyl *o*-hydroxystyryl ketone, 1-, 2- and 4-hydroxyxanthones, and 1- and 2-hydroxyanthraquinones have been examined; of these,

o-hydroxyacetophenone, benzylidenepaeonol, 1-hydroxyxanthone, and 1-hydroxyanthraquinone alone yield $SnCl_3$ substituted compounds. The fact that resacetophenone, resobenzophenone, 2:4′-dihydroxybenzophenone, euxanthone, and alizarin form mono-substituted $SnCl_3$ compounds, not disubstituted $SnCl_2$ compounds, also proves that only the hydroxyl group in the ortho-position to the carbonyl group is concerned in the formation of the internally complex $SnCl_3$ salt.

The $SnCl_3$ derivatives of o-hydroxyketones and of o-hydroxyquinones, being internally complex salts, must be closely related to the tin lakes of these substances, which are typical representatives of internally complex salts (Tschugaeff, A., 1907, i, 17, 392, 830; Werner, A., 1908, i, 441). On the fibre these lakes do not contain chlorine, and therefore must be derived from the author's compounds simply by replacement of chlorine by oxygen or a hydroxyl group: $C_6H_4<\begin{matrix}O—SnCl_3\\ \vdots \\ CR:O\end{matrix}$ $\longrightarrow C_6H_4<\begin{matrix}O—SnO(OH)\\ \vdots \\ CR:O\end{matrix}$. The author shows that the $SnCl_3$ compounds are converted into tin lakes by hydrolysis. The careful addition of water to the orange solution of the $SnCl_3$ compound of alizarin in pyridine precipitates an orange-red *substance*,

$$(HO)OSn<\begin{matrix}O:C——C_6H_4\\ \vert \\ O\cdot C_6H_2(OH)\end{matrix}>CO,\tfrac{1}{2}C_5NH_5,$$

which is unstable to acids, stable to aqueous ammonia on the water-bath, and dyes silk and wool, but not cotton, orange-red.

The close relationship between the tin lakes and the author's $SnCl_3$ compounds is also made evident by the following analogy—only hydroxyketones and -quinones containing a hydroxyl group in the ortho-position to the carbonyl group form $SnCl_3$ compounds—only dyes containing a hydroxyl group in the ortho- or peri-position to the chromophoric group are mordant dyes according to Möhlau and Steimming (*Zeitsch. Farb. Text-chem.*, 1904, **3**, 358).

According to the preceding, internally complex $SnCl_3$ salts of hydroxyanthraquinones are obtained by substitution at the ortho-hydroxyl group. Hence it might be anticipated that this hydroxyl group is also concerned in the formation of the normal salts. Experiment shows that this is not so; 1-hydroxyanthraquinone and quinizarin do not form pyridine salts in hot pyridine, whilst 2-hydroxyanthraquinone, 2:6-dihydroxyanthraquinone, alizarin, 1:7-dihydroxyanthraquinone, and purpurin form pyridine salts, the number of pyridine molecules added being equal to the number of hydroxyl groups in the meta-position to a carbonyl group.

Hence in the formation of normal salts with weak bases just those hydroxyl groups are concerned which do not exhibit any tendency to complex salt formation with tin tetrachloride. Strong bases, such as the hydroxides of the alkali and the alkaline earth metals, react with both m- and o-hydroxyl groups, but preferably with the former; 2-hydroxyanthraquinone dissolves easily in 1% aqueous sodium carbonate, whilst 1-hydroxyanthraquinone does not.

It follows from the preceding that hydroxyl groups in the ortho-

position to the carbonyl group are concerned in complex salt formation, whilst the production of normal salts is due primarily to hydroxyl groups in the meta-position, normal salt formation at an *o*-hydroxyl group being a secondary effect. This is readily explicable. The hydrogen atom of the *o*-hydroxyl group is attached co-ordinatively to the oxygen atom of the carbonyl group, and therefore its acidic function is weaker than that of the hydrogen atom of the hydroxyl group in the meta-position. Normal salt formation, therefore, occurs firstly at the *m*-hydroxyl group by the addition, in accordance with the modern view of the phenomenon of neutralisation, of the hydroxide, with the formation of an aquo-salt which then loses water.

The compounds obtained by the action of stannic chloride on hydroxyacetophenones, hydroxychalkones, hydroxybenzophenones, and hydroxyxanthones are described. The production of a $SnCl_4$ additive compound or of an $SnCl_3$ substituted compound, and also the colours of the products, are quite in accordance with the rules previously stated except in the cases of quinizarin and purpurin which yield the compounds $C_6H_4{<}{}^{CO}_{CO}{>}C_6H_2{<}{}^{O}_{O}{>}SnCl_2$ and

$$C_6H_4{<}{}^{CO}_{CO}{>}C_6H(OH){<}{}^{O}_{O}{>}SnCl_2$$

respectively.

The following *substances* have been prepared by warming the carbonyl compound with stannic chloride, alone or in the presence of dry benzene: $OMe\cdot C_6H_3(OSnCl_3)\cdot COMe$, m. p. about 235°, almost colourless leaflets containing $\frac{1}{2}C_6H_6$, from paeonol;

$$CO_2Me\cdot C_6H_4\cdot OSnCl_3,$$

m. p. 230°, colourless leaflets, from methyl salicylate;

$$CO_2Et\cdot C_6H_4\cdot OSnCl_3,$$

m. p. about 220°, colourless leaflets, from ethyl salicylate;

$$NH_2\cdot CO\cdot C_6H_4\cdot OSnCl_3,$$

m. p. about 260°, white crystals containing $\frac{1}{2}C_6H_6$, from salicylamide; $OH\cdot C_6H_3(OSnCl_3)\cdot COPh$, m. p. 295—297°, yellow crystals containing $\frac{1}{4}C_6H_6$, from resobenzophenone; $OMe\cdot C_6H_3(OSnCl_3)\cdot COPh$, m. p. about 262°, yellow crystals, from resobenzophenone methyl ether; $OH\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot OSnCl_3$, m. p. 294—296°, yellow leaflets, from 2 : 4′-dihydroxybenzophenone; $C_6H_4{<}{}^{-O-}_{CO}{>}C_6H_3\cdot OSnCl_3$, m. p. 282—284°, yellow crystals containing $\frac{1}{2}C_6H_6$, from 1-hydroxyxanthone; $SnCl_4,2C_6H_4{<}{}^{-O-}_{CO}{>}C_6H_3\cdot OH$, m. p. 239°, yellowish-brown powder, from 2-hydroxyxanthone; $SnCl_4,C_6H_4{<}{}^{-O-}_{CO}{>}C_6H_3\cdot OH$, m. p. about 230°, yellow crystals, from 4-hydroxyxanthone (m. p. 242°, not 224° as stated in the literature);

$$OMe\cdot C_6H_3(OSnCl_3)\cdot CO\cdot CH{:}CHPh,$$

m. p. about 278°, orange-yellow, crystalline powder, from benzylidenepaeonol; $OMe\cdot C_6H_3(OSnCl_3)\cdot CO\cdot CH{:}CH\cdot C_6H_4\cdot OMe$, m. p. indefinite at about 250°, orange-red crystals containing $\frac{1}{4}C_6H_6$, from *p*-anisylidenepaeonol; $OMe\cdot C_6H_3(OSnCl_3)\cdot CO\cdot CH{:}CH\cdot C_6H_3{:}O_2{:}CH_2$, decomp. above

200°, orange-red crystals containing $\frac{1}{2}C_6H_6$, from piperonylidenepaeonol; $C_6H_4{<}\substack{CO\\CO}{>}C_6H_3{\cdot}OSnCl_3$, brownish-red powder containing $\frac{1}{2}C_6H_6$, from 1-hydroxyanthraquinone; $C_6H_4{<}\substack{CO\\CO}{>}C_6H_2(OH){\cdot}OSnCl_3$, violet-black, crystalline powder containing $\frac{1}{4}C_6H_6$, from alizarin;

$$C_6H_4{<}\substack{CO\\CO}{>}C_6H_2(OMe){\cdot}OSnCl_3,$$

violet-black powder containing $\frac{1}{2}C_6H_6$, from alizarin β-methyl ether; $C_6H_4{<}\substack{CO\\CO}{>}C_6H_2{<}\substack{O\\O}{>}SnCl_2$, red, crystalline powder, from quinizarin; $C_6H_4{<}\substack{CO\\CO}{>}C_6H(OH){<}\substack{O\\O}{>}SnCl_2$, almost black, crystalline powder containing C_6H_6, from purpurin; $SnCl_4,C_6H_4{<}\substack{CO\\CO}{>}C_6H_2(OMe)_2$, brownish, or golden-yellow leaflets, from alizarin dimethyl ether; $SnCl_4,2C_6H_4{<}\substack{CO\\CO}{>}C_6H_2(OMe)_2$, m. p. 242°, brownish-orange leaflets, from hystazarin dimethyl ether.

In addition to the normal pyridine salts of the hydroxyanthraquinones previously mentioned, the following have been prepared:

$$CH_3{\cdot}CO{\cdot}C_6H_3(OH)_2,C_5NH_5,$$

colourless crystals, from resacetophenone;

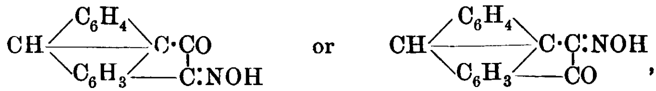
$$C_6H_5{\cdot}CO{\cdot}C_6H_3(OH)_2,C_5NH_5,$$

m. p. 58°, colourless plates, from resobenzophenone;

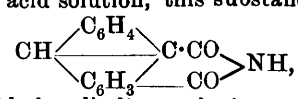
$$OH{\cdot}C_6H_3{<}\substack{O\\CO}{>}C_6H_3{\cdot}OH,C_5NH_5,$$

yellow needles, from euxanthone. C. S.

Some Derivatives of Aceanthrenequinone and 1 : 9-Anthracene. M. KARDOS (*Ber.*, 1913, **46**, 2086—2091).—The action of aceanthrenequinone with an equimolecular proportion of hydroxylamine hydrochloride and a half-molecular proportion of sodium carbonate in the presence of alcohol at water-bath temperature, yields *aceanthrenequinoneoxime*,



yellow prisms, m. p. 251° (decomp.), which dissolves in sulphuric acid to a brown colour changing to red on warming. When caused to undergo the Beckmann rearrangement, by heating for several hours with hydrogen chloride in acetic acid solution, this substance forms *anthracene-1 : 9-dicarboxylimide*,



needles, m. p. 293—294°, which is reducible by alkaline reducing agents to a yellow solution, and dissolves in sulphuric acid to a beautiful red solution which fluoresces slightly; there are obtained simultaneously *anthracene-1 : 9-dicarboxylic acid*, which readily passes into its *anhydride*, m. p. 289—290° (*methyl* ester, m. p. 149°), and also *anthracene-1 : 9-dicar-*

boxylamic acid, which in the free state rapidly passes into the imide; its solutions in alkali exhibit a beautiful sky-blue fluorescence; the *sodium* and *silver* salts were analysed. Endeavours to methylate the remaining carboxylic group of the acid amide by means of methyl sulphate yielded the *anhydride* of *methyl anthracene*-1 : 9-*carboxylamate,* $CH\begin{matrix}\diagup C_6H_4 \diagdown C\cdot C(OMe) \\ \diagdown C_6H_3 \diagup CO \end{matrix}\!\!>N$ or $CH\begin{matrix}\diagup C_6H_4 \diagdown C\cdot CO \\ \diagdown C_6H_3 \diagup C(OMe) \end{matrix}\!\!>N$, m. p. 170—171°.

Anthracene-1 : 9-dicarboxylimide is obtainable in theoretical yield by warming aceanthrenequinoneoxime with sulphuric acid for about a half-hour; heating with potassium hydroxide and a little water at 200—230° converts the imide into a green *dye,* $C_{32}H_{12}O_4N_2$; this on reduction by hyposulphite yields a red vat which colours cotton reddish-violet, passing on exposure to the air to a beautiful green. Similar dyes can be produced from halogen-substituted aceanthrenequinones.

In an examination of the action of malonyl chloride on anthracene (compare Freund and Fleischer, A., 1910, i, 490; Liebermann and Zsuffa, A., 1911, i, 202) it is found that the condensation product is *anthracene*-1 : 9-*indandione,* $CH\begin{matrix}\diagup C_6H_4 \diagdown C-CO \\ \diagdown C_6H_3 \diagup\!\!-\!\!-CO \end{matrix}\!\!>CH_2$, a red powder, m. p. 280° (decomp.) with previous blackening, which in sulphuric acid gives a carmine-red solution with a strong fluorescence; *sodium* salt, red leaflets. On oxidation with alkaline potassium permanganate solution, it produces anthraquinone-1-carboxylic acid. When heated with benzaldehyde at 130°, condensation occurs with formation of the *benzylidene* derivative, $CH\begin{matrix}\diagup C_6H_4 \diagdown C-CO \\ \diagdown C_6H_3 \diagup\!\!-\!\!-CO \end{matrix}\!\!>C{:}CHPh$, a brownish-red powder, decomp. at 290°, which gives a reddish-violet solution in sulphuric acid. D. F. T.

Influence of Constitution on the Rotatory Power of Optically Active Substances. V. Keto-enolic Transformations of Derivatives of Menthyl Acetoacetates. HANS RUPE and EDUARD LENZINGER (*Annalen,* 1913, **398**, 372—378).—*l*-Menthyl *d*-phenylacetoacetate exists in the solid state as the ketonic modification. In benzene it is initially dextrorotatory, but in course of time becomes lævorotatory as the change to the enolic modification proceeds and the *l*-menthyl group becomes the only source of optical activity. It has previously been shown that the rate of transformation is very variable, and been suggested that this variation is caused by the presence of catalysts such as the alkali in the glass vessel. This hypothesis has now been proved. A 9·958% solution, D_4^{20} 0·8891, of *l*-menthyl *d*-phenylacetoacetate in benzene containing a trace of piperidine had $[\alpha]_D^{20}$ + 26·09° initially and a final constant value, $[\alpha]_D^{20}$ − 67·20° after ten hours. A similar solution (c = 10·02, D = 0·8895) containing a drop of piperidine

had initially $[\alpha]_D^{20}$ $+26\cdot23°$, and a final constant value, $-67\cdot09°$, after eight minutes. Within certain limits, the velocity of the keto-enolic change is a function of the concentration of the catalyst.

l-Menthyl *d*-benzoylphenylacetate exhibits a constant rotation in benzene; also, its alcoholic solution does not develop a coloration with ferric chloride. Hence the stability of the ketonic modification is greatly increased when the methyl group in menthyl phenylacetoacetate is replaced by a phenyl group. However, again the presence of a trace of piperidine increases the velocity of the change from the ketonic to the enolic modification because a solution ($c=9\cdot98$, D_4^{20} 0·8924) of *l*-menthyl *d*-benzoylphenylacetate in benzene containing a trace of piperidine has $[\alpha]_D^{20}$ $+20\cdot76°$ initially and $-62\cdot83°$ after eighteen hours. C. S.

Cardol. LEOPOLD SPIEGEL and M. CORELL (*Ber. Deut. pharm. Ges.*, 1913, **23**, 356—378. Compare Spiegel and Dobrin, A., 1896, i, 653). —Cardol can be distilled in superheated steam or under reduced pressure. In the latter case the principal fraction has b. p. 190°/3 mm., but is of variable composition, as shown by the analysis of two specimens. It is named apo*cardol*, and its reactions with bromine, ozone, permanganate, nitric acid, and on distillation with zinc dust are described. In most cases these do not lead to well-defined products, but the zinc dust distillation yielded ethylene, propylene, 1 : 3-butadiene, and a *substance*, $C_{12}H_{12}O$, m. p. 10°, b. p. 98—100°/14 mm.

In addition to *apo*cardol a fraction, b. p. 200—220°/2—5 mm., is obtained. T. A. H.

Constituents of Ethereal Oils. Eudesmol and its Derivatives. Globulol. FRIEDRICH W. SEMMLER and ERNST TOBIAS (*Ber.*, 1913, **46**, 2026—2032).—The authors have carried out a series of experiments on the sesquiterpene alcohols, eudesmol, which is widely distributed in eucalyptus oils, and globulol, which occurs in the ethereal oil from *Eucalyptus Globulus*. The former has been investigated by Baker and Smith, who consider it to be an oxide having the formula $C_{10}H_{16}O$, and describe a dinitro-derivative, $C_{10}H_{14}(NO_2)_2O$, and a dibromide, $C_{10}H_{16}OBr_2$. The authors, however, are led to the conclusion that it is a bicyclic sesquiterpene alcohol, $C_{15}H_{26}O$, containing one double bond.

Eudesmol has b. p. 156°/10 mm., D^{20} 0·9884, n_D^{20} 1·516, m. p. 78° (Baker and Smith give m. p. 79—80°), $[\alpha]_D^{20}$ $+31°21'$ in chloroform solution. When boiled with acetic anhydride and sodium acetate, it yields *eudesmol acetate*, $CH_3\cdot CO_2\cdot C_{15}H_{25}$, b. p. 165—170°/11 mm., D^{20} 0·9933, n_D^{20} 1·49204, $[\alpha]_D^{20}+31°$.

Dihydroeudesmol, $C_{15}H_{28}O$, b. p. 155—160°/12·5 mm., m. p. 82°, is obtained when an ethereal solution of eudesmol is reduced by hydrogen in the presence of platinum. When treated with sodium acetate and acetic anhydride, it yields the corresponding *acetate*, b. p. 158—164°/10 mm., D^{20} 0·9776, n_D^{20} 1·4788, $[\alpha]_D^{20}+13°$, from which dihydroeudesmol is recovered unchanged after saponification with

alcoholic potassium hydroxide. When boiled with absolute formic acid, dihydroeudesmol yields *dihydroeudesmene*, $C_{15}H_{26}$, b. p. 126—130°/10 mm., D^{20} 0·9067, n_D^{20} 1·48762, $[\alpha]_D - 7°$.

Eudesmene, $C_{15}H_{24}$, obtained when eudesmol is heated with 90% formic acid, has b. p. 129—132°/10 mm., D^{20} 0·9204, n_D^{20} 1·50738, $[\alpha]_D^{20} + 49°$, and is thus apparently a member of the sesquiterpenes derived from hydrogenated naphthalenes. It yields a characteristic *dihydrochloride* and *dihydrobromide*. The former, m. p. 79—80°, is obtained either by treatment of eudesmol with a saturated solution of hydrogen chloride in glacial acetic acid or by passing hydrogen chloride into eudesmene dissolved in the same solvent. The hydrocarbon is regenerated when the dihydrochloride is boiled with alcoholic potassium hydroxide. The dihydrobromide, m. p. 104—105°, can be prepared by precisely similar methods, and also gives eudesmene when acted on by alcoholic potassium hydroxide.

When treated with zinc dust, eudesmol gives a small quantity of the hydrocarbon, $C_{15}H_{26}$, but is mainly converted into eudesmene. The latter substance is also obtained when phosphorus pentachloride reacts with eudesmol. Oxidation with ozone or potassium permanganate did not lead to definite results.

Globulol, $C_{15}H_{26}O$ (compare A., 1904, i, 604), has b. p. 283°/755 mm. It differs physically from eudesmol, but, possibly, similar relationships exists between the two alcohols as between borneol and *iso*borneol; otherwise they are chemically different. When treated with dehydrating agents, globulol yields a l-*sesquiterpene*, $C_{15}H_{24}$, b. p. 102—103°/6 mm., 247—248°/748 mm., $[\alpha]_D - 55°48'$, n_D^{20} 1·49287, D^{15} 0·8956, and a d-*sesquiterpene*, $C_{15}H_{24}$, b. p. 265·5—266°/750 mm., $\alpha_D + 58°40'$, n_D^{20} 1·50602, D^{15} 0·9236. The latter is possibly identical with eudesmene. H. W.

Determination of Constitutions in the Camphene Group. V. OSSIAN ASCHAN (*Annalen*, 1913, **398**, 299—313).—Since Auwers has recently upheld, on refractometric evidence, Wagner's formula for camphene, the author has examined two carefully purified specimens of the hydrocarbon. These have been obtained from American and Grecian turpentines respectively, through the pinene hydrochlorides. Each has been twice recrystallised from methyl alcohol (whereby the m. p. is constant), and finally distilled over sodium in a vacuum. The camphene from American turpentine has b. p. 158—158·5°, m. p. 43—43·5°, D_4^{50} 0·8486, n_α^{50} 1·46048, and $[\alpha]_D^{16} + 17·95°$ in benzene. The camphene from Grecian turpentine has b. p. 157·2—157·9°/742 mm., m. p. 46—47°, D_4^{50} 0·8446, n_D^{50} 1·45641, and $[\alpha]_D^{20} + 74·55°$ in benzene. The molecular refractions, 43·98 and 43·85 respectively, are in close agreement with the value, 43·91, calculated for the semicyclic formula.

The formula $\begin{matrix} CH_2\cdot CH_2 \\ | \qquad\quad \\ CO\text{——}O \end{matrix}\!\!>C(CO_2H)\cdot CMe_2\cdot CO_2H$ previously assigned by the author (A., 1910, i, 710) to the lactone-dicarboxylic acid, m. p. 256°, obtained from dehydrocamphenic acid, is now proved to be incorrect. The lactone-dicarboxylic acid is reduced to *iso*camphoronic

acid by hydriodic acid, b. p. 127—128°, at 170—180°. Since the constitution of *iso*camphoronic acid is

$$CO_2H\cdot CH_2\cdot CMe_2\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H,$$

and the lactone-dicarboxylic acid yields formic, succinic, and *iso*butyric acids by fusion with potassium hydroxide, it follows that the hydroxy-acid from which the lactone-dicarboxylic acid is derived must be

$$CO_2H\cdot CH(OH)\cdot CMe_2\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H.$$

By boiling with hydriodic acid, by heating with 40% hydrogen bromide in glacial acetic acid, or with concentrated sulphuric acid at 100°, or with hydrochloric acid at 170—180°, the lactone-dicarboxylic acid is changed into a stereoisomeric *lactone-dicarboxylic acid*, $C_9H_{12}O_6$, m. p. 185—186°, large prisms. Such stereoisomerism is possible only when at least two side-chains are present attached to different carbon atoms of the lactone ring. Hence the constitutions of the two lactone-dicarboxylic acids are represented by

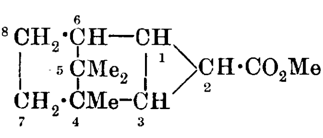
$$CO_2H\cdot CH_2\cdot CH\Big<\begin{matrix}CO\text{---}O\\ CMe_2\cdot CH\cdot CO_2H\end{matrix}.$$

On account of its sparing solubility, the isomeride, m. p. 256°, is regarded as having the trans-configuration.

The author is of opinion that Wagner's formula correctly represents the constitution of camphene. If this is the case, it follows from the preceding work that a transformation must have occurred in the carbon skeleton during the oxidation of camphene by alkaline potassium permanganate. C. S.

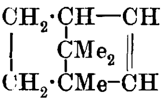
Bornylene and Ethyl Diazoacetate (with a Nomenclature for Tricyclic Carbon Ring Systems). EDUARD BUCHNER and WILHELM WEIGAND (*Ber.*, 1913, **46**, 2108—2117).—The constitution of camphene has recently been demonstrated in a purely chemical manner by the action of ethyl diazoacetate, and the same method is now applied to bornylene (this vol., i, 376). The results indicate that this reagent is of especial value for distinguishing between hemicyclic and endocyclic ethylenic linkings in terpene molecules.

The bornylene applied in this investigation, obtained from borneol through the corresponding methyl xanthate compound, was possibly not quite pure, as its optical activity was somewhat lower than that recorded in the literature; the impurities, however, could not be of such a nature as to affect the trustworthiness of the reaction with ethyl diazoacetate. A solution of ethyl diazoacetate in a little borneol was gradually introduced into a mixture of borneol with a little copper powder at 150°; the reaction is more sluggish than with camphene, but fractional distillation of the product separated *methyl* 4 : 5 : 5-*tri-methyl*tricyclo-[0,1,3 ^{4,6}, 2]-*octane*-2-*carb-oxylate* (annexed formula), a colourless oil, b. p. 136—137°/22 mm., D_4^{20} 1·0283, n_D 1·48337, $[\alpha]_D^{21\cdot5}$ −8·72°.



By hydrolysis with alcoholic potassium hydroxide, the corresponding *acid* is obtained, leaflets, m. p. 137°; *calcium*, *barium*, *lead*, and *silver* salts, colourless, insoluble substances; *amide*, needles, m. p. 174°.

When the acid is heated with an acid solution of potassium permanganate, oxidation slowly occurs with formation of an oily substance, *trans-cyclo*propane-1 : 2 : 3-tricarboxylic acid, which very gradually crystallised. The identity of this acid was confirmed by the preparation of the silver and calcium salts and of the methyl ester, the m. p., 56—57°, of which was unaffected by admixture with a specimen of synthetic origin. These results are in accord with the annexed usual formula for bornylene.



The paper includes an authorised extension of von Baeyer's scheme of nomenclature for dicyclic systems to tricyclic ones. Each tricyclic system contains two tertiary or quaternary carbon atoms in the ring, which are linked by bridges of carbon chains; these bridges, of which there are four in each tricyclic system, are represented by numbers which represent the number of atoms in each; the grouping of these 4 numbers constitutes the "characteristic"; if these bridges do not extend between the same carbon atoms in each case, the numbers representing the carbon atoms which act as origin and extremity of the bridge must be appended to the corresponding number in the characteristic. The application of this scheme can be seen in the above description of the condensation product of bornylene and ethyl diazoacetate.

D. F. T.

The Synthesis of the Glucosides of the Terpene Alcohols by means of Emulsin. JUHO HÄMÄLÄINEN (*Biochem. Zeitsch.*, 1913, **52**, 409—411).—The author has shown (this vol., i, 497, 639) that certain glucosides of the terpene alcohols are readily hydrolysed by emulsin. It seemed therefore possible that synthesis could be effected by the same agency. He has succeeded in obtaining in small quantities synthetically the following glucosides, by allowing the alcoholic solutions of dextrose and the alcohol to react in the presence of emulsin in ethyl alcoholic solutions: *l*-fenchyl-*d*-glucoside, *r*-*iso*borneol-*d*-glucoside, and *l*-borneol-*d*-glucoside. The formation of these glucosides can explain the action of emulsin in producing glycuronates of terpene-alcohols when injected into animals. A synthetic action of the ferment seems more probable than the formation of an anti-substance, as suggested by various investigators.

S. B. S.

Synthesis of β-Geranylglucoside by means of Emulsin; Its Presence in Plants. ÉMILE BOURQUELOT and MARC BRIDEL (*Compt. rend.*, 1913, **157**, 72—74).—*β-Geranylglucoside* is obtained by the action of emulsin on a suspension of dextrose in geraniol saturated with water, or, better, by its action on a solution of the alcohol and sugar in acetone and water. It was separated by the usual method (compare this vol., i, 663), and obtained as a colourless liquid, $[\alpha]_D -25°49'$, not reducing Fehling's solution, precipitated by basic lead acetate, and rapidly hydrolysed in aqueous solution by emulsin. A glucoside similarly hydrolysed by emulsin to dextrose and geraniol and precipitated by basic lead acetate can be extracted by alcohol from *Pelargonium odoratissimum*.

W. G

Cerebronic Acid. III. Its Bearing on the Constitution of Lignoceric Acid. PHŒBUS A. LEVENE and C. J. WEST (*J. Biol. Chem.*, 1913, **15**, 193—195).—Cerebronic acid yields a normal acid of 24 carbon atoms which is identical with lignoceric acid. W. D. H.

Azafrin. II. CARL LIEBERMANN and W. SCHILLER (*Ber.*, 1913, **46**, 1973—1986. Compare A., 1911, i, 391).—Although azafrin and bixin (Hasselt, A., 1911, i, 550) both give blue solutions in concentrated sulphuric acid, they are not identical. This is now shown by the fact that azafrin and methylazafrin give very characteristic colour reactions with a large number of other strong mineral or organic acids, with which bixin gives, at most, only transient and poor effects. One, two, or three molecules of an acid may enter into combination, but the compounds are not simple salts, since azafrin cannot be regenerated from them. Oxidation, reduction, substitution, hydroxyl and ketone reactions have either failed or led to still more complicated substances, but, from the analysis of the above compounds, it seems certain that azafrin has the formula $C_{31}H_{42}O_5$.

It is advisable not be prolong the extraction of azafranillo roots and stems, since benzene dissolves a small amount of a resin which hinders the crystallisation of the desired azafrin. The latter is purified by precipitation from alkaline solution, has m. p. 208°, and yields *methylazafrin*, $C_{32}H_{44}O_5$, in sparkling, reddish-yellow leaflets or needles, m. p. 191°, when treated with methyl sulphate. The following *compounds* with acids have been isolated: $B_3,2H_2SO_4$, B,3HI, B,2HBr, B,HCl, $B,HClO_4$, and $B,3CCl_3 \cdot CO_2H$, where B = azafrin or methylazafrin. They are blue or violet in colour, and dissolve in alkalis with never more than partial loss of acid. Phosphoryl chloride, metaphosphoric acid, and nitric acid also give coloured solutions, but especially characteristic is the reaction with hot anhydrous formic acid, which gives a deep violet solution which may be diluted with water to a stable permanganate-coloured liquid. Glacial acetic acid is a useful indifferent solvent for azafrin, but after boiling the solution for a long time, water procipitates an entirely different substance.

Reduction of azafrin and methylazafrin with zinc dust and acids yields white, amorphous *products*, $C_{31}H_{46}O_4$ and $C_{32}H_{48}O_4$ respectively, whilst hydriodic acid and red phosphorus give rise to compounds which contain phosphorus. Ammonium persulphate yields a white, flocculent acid. J. C. W.

The Hydrogenation of Pyromucic Acid. HEINRICH WIENHAUS and HERMANN SORGE (*Ber.*, 1913, **46**, 1927—1931).—Only in a few cases in the furan group have reductions been effected by hydrogen. The author, in this preliminary announcement, describes tetrahydropyromucic acid obtained by the reduction of pyromucic acid with hydrogen and colloidal palladium.

Tetrahydropyromucic acid, $\begin{matrix} CH_2 \cdot CH_2 \\ | \\ CH_2 \text{——} O \end{matrix} \!\!>\! CH \cdot CO_2H$, was prepared by adding to the aqueous solution of pyromucic acid a little palladious

chloride solution and gum arabic, and shaking with hydrogen. The acid was purified by distillation, b. p. 131°/14 mm., and then crystallises in rhombohedra, m. p. 21°. It is much more stable than pyromucic acid towards potassium permanganate. The *sodium* salt crystallises in thin tablets; the *potassium*, *ammonium*, *barium*, and *silver* salts are all crystalline. When treated with phosphorus trichloride, the free acid is converted into the *chloride*, which reacts with strong ammonia solution, producing the *amide*, leaflets, m. p. 80°, b. p. 135—140°/20 mm. The same amide is formed when the ammonium salt is heated at 200° under pressure. D. F. T.

A New Chromone Synthesis. ERNST PETSCHEK and HUGO SIMONIS (*Ber.*, 1913, **46**, 2014—2020).—When phenols are condensed with β-ketonic acid esters in presence of sulphuric acid, the products are coumarin derivatives (1:2-benzopyrones), but when phosphoric oxide is used, chromones (1:4-benzopyrones) are obtained. Ethyl acetoacetate itself has not yet led to definite products, but the method is being extended, particularly with a view to the synthesis of flavone from ethyl benzoylacetate and phenol.

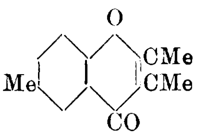
For the preparation of 2:3-*dimethylchromone*, $C_6H_4<\begin{matrix}O-CMe\\CO\cdot CMe\end{matrix}$, the dark mass obtained by mixing a solution of dry phenol in ethyl methylacetoacetate with phosphoric oxide is diluted with water, treated with half the quantity of sodium hydroxide required to neutralise the acid, saturated with salt, and extracted with ether. The extract is washed with alkali, dried, and evaporated. The yield is 25%. The compound forms large, transparent, yellow, monoclinic crystals [$a:b:c=1\cdot5201:1:1\cdot5681$, $\beta=73°19\cdot5'$], m. p. 97°. One litre of water dissolves 0·5 gram at 0°, 1·5 grams at 15°, and 4·5 grams at 100°, and the substance is volatile in steam. It forms a *dibromide*, $C_{11}H_{10}O_2Br_2$, in unstable, orange-yellow needles, m. p. 130°, and an *oxime*, $C_{11}H_{10}O\colon N\cdot OH$, by the direct action of hydroxylamine, in colourless, silky needles, m. p. 158·5°. The isomeric 3:4-*dimethylcoumarin oxime*, prepared from 3:4-*dimethylthiocoumarin*, m. p. 142°, has m. p. 222°. The oxime of the dimethylchromone yields a *dibromide*, m. p. 180—184°, which readily parts with one molecule of hydrogen bromide to form 2-*bromo*-4-*nitroso*-2:3-*dimethylcoumaran*, $C_6H_4<\begin{matrix}C(NO)\colon CMe\\O——CBrMe\end{matrix}$, in colourless needles, m. p. 205°.

2:3-Dimethylchromone is easily oxidised by permanganate or hydrolysed by 3% sodium hydroxide, yielding salicylic acid. When heated with sodium ethoxide (compare Heywang and Kostanecki, A., 1902, i, 816) it is hydrolysed to *o*-*hydroxypropiophenone*,

$$OH\cdot C_6H_4\cdot COEt,$$

which forms a colourless, mobile, unpleasant smelling oil, b. p. 150°/80 mm. It is sparingly soluble in water, and the solution gives an intense reddish-violet coloration with ferric chloride. The *hydrochloride* of dimethylchromone, $C_6H_4<\begin{matrix}O(HCl)\cdot CMe\\CO——CMe\end{matrix}$, is a white, crystal-

line substance, m. p. 88—92°. On nitration with fuming acid in cold concentrated sulphuric acid, 6-*nitro*-2 : 3-*dimethylchromone*, $NO_2{\cdot}C_6H_3{<}\begin{matrix}O{-}CMe\\ \Vert\\ CO{\cdot}CMe\end{matrix}$, is obtained in colourless prisms, m. p. 163°, which dissolve in potassium hydroxide with intense yellow colour. The isomeric 6-*nitro*-3 : 4-*dimethylcoumarin*, $C_{11}H_9O_4N$, from 3 : 4-dimethylcoumarin has m. p. 172°. Both compounds yield 5-nitrosalicylic acid on oxidation. 7(?)-*Chloro*-6-*amino*-2 : 3-*dimethylchromone*, $C_{11}H_{10}O_2NCl$, is obtained when the nitro-compound is reduced by means of tin and hydrochloric acid. It has m. p. 245°, absorbs bromine, and yields a dark red chlorohydroxydimethylchromone.



p-Cresol and ethyl methylacetoacetate condense to form 2 : 3 : 6-*trimethylchromone* (annexed formula) in long, colourless, sparkling needles, m. p. 107°, which yield 5-methylsalicylic acid on hydrolysis with dilute alkali. Similarly, *m*-cresol yields 2 : 3 : 7(or 5)-*trimethylchromone*, in clusters of colourless needles, m. p. 96°. The oxidation to a methylsalicylic acid has met with difficulties. J. C. W.

A Simple Process for the Preparation of Flavones. Synthesis of Thioflavone. SIEGFRIED RUHEMANN (*Ber.*, 1913, **46**, 2188—2197).—The author has succeeded in condensing β-oxyarylcinnamic acids to flavones by heating their chlorides with aluminium chloride. Flavones which are substituted in position 8, ortho to the pyrone oxygen, do not show the fluorescence in concentrated sulphuric acid which is characteristic of these compounds in general. In the case of the hydroxyflavones, the removal of the hydroxyl group from the pyrone oxygen is accompanied by a constant depression of the melting point.

The condensation is carried out by adding phosphorus pentachloride to a suspension of the acid in dry benzene and warming until solution takes place, when aluminium chloride is introduced into the product. In this way β-phenoxycinnamic acid (T., 1900, **77**, 986) gives an almost theoretical yield of flavone; β-*o*-tolyloxycinnamic acid (*loc. cit.*, 988) forms 8-*methylflavone*, $C_6H_3Me{<}\begin{matrix}CO{\cdot}CH\\ \Vert\\ O{-}CPh\end{matrix}$, in colourless needles, m. p. 170°, which are gradually decomposed by boiling concentrated potassium hydroxide into acetophenone; β-*m*-tolyloxycinnamic acid (*loc. cit.*, 1120) yields a mixture of 5- and 7-methylflavones; β-*p*-tolyloxycinnamic acid (*loc. cit.*, 989) gives 6-*methylflavone*, in colourless needles, m. p. 122—123°, and β-thymoxycinnamic acid (T., 1901, **79**, 918) forms 5-*methyl*-8-iso*propylflavone*, $C_{19}H_{18}O_2$, which crystallises in colourless needles, m. p. 143—144°. For the preparation of the isomeride of the latter, ethyl phenylpropiolate was added to a solution of sodium in excess of carvacrol, the resulting yellow, viscous *ethyl β-carvacroxycinnamate*, $C_6H_3MePr{\cdot}O{\cdot}CPh{:}CH{\cdot}CO_2Et$, b. p. 225°/12 mm., was hydrolysed to *β-carvacroxycinnamic acid*, $C_{19}H_{20}O_3$, which formed well-defined, rhombic crystals from light petroleum, and lost carbon dioxide on heating above 103°, and this acid was treated as

above. 8-*Methyl*-5-iso*propylflavone* forms colourless prisms, m. p. 149—150°.

Similarly, β *o*-methoxyphenoxycinnamic acid (T., 1900, **77**, 1181) was converted into 8-*methoxyflavone*, $C_{16}H_{12}O_3$, which crystallised in colourless, silky needles, m. p. 199—200°, and formed 8-*hydroxyflavone*, $C_{15}H_{10}O_3$, in colourless needles, m. p. 249—250°, by hydrolysis with concentrated hydriodic acid in a sealed tube. Finally, β-phenylthiolcinnamic acid (*ibid.*) was condensed in the same way to *thioflavone*, $C_6H_4<\begin{matrix}CO\cdot CH\\ S—\overset{||}{C}Ph\end{matrix}$, which forms white needles, m. p. 129—130°, and dissolves in warm, concentrated hydrochloric acid. The sulphonium salt and the platinichloride are, however, decomposed by water.

J. C. W.

Thiotetronic Acid and Derivatives. ERICH BENARY (*Ber.*, 1913, **46**, 2103—2107. Compare A., 1910, i, 434, 579).—The results of Anschütz and Bertram (A., 1903, i, 271) suggest that the hitherto unknown thiotetronic acid might be obtained through the interaction of ethyl sodiomalonate and acetylthiolacetyl chloride.

Acetylthiolacetic acid, $SAc\cdot CH_2\cdot CO_2H$, is obtained by mixing thioglycollic acid and acetyl chloride, when a vigorous reaction ensues; the acid, b. p. 158—159°/17 mm., which can also be obtained by the interaction of thioacetic acid and chloroacetic acid in alkaline solution, gives a deep blue colour with ferric chloride solution, and is converted by phosphorus pentachloride into *acetylthiolacetyl chloride*, a pungent liquid, b. p. 93—95°/20 mm. The chloride cooled in ethereal solution reacts with ethyl sodiocyanoacetate, yielding *ethyl acetylthiolacetylcyanoacetate* [*a-cyano-β-hydroxy-γ-acetylthiol*-Δ^{a}-*butenoate*],

$$SAc\cdot CH_2\cdot C(OH){:}C(CN)\cdot CO_2Et,$$

colourless needles, m. p. 70—71°, which indicates its enolic character by a red coloration with ferric chloride and by its acidity. Under similar conditions with ethyl sodioacetoacetate, the *sodium* derivative of *ethyl acetylthiolacetylacetoacetate* is obtained; the free ester is a heavy, yellow oil which passes very readily with elimination of alcohol into *a-acetylthiotetronic acid*, $\begin{matrix}CH_2\cdot C(OH)\\ |\qquad\quad\\ S———CO\end{matrix}>CAc$, an acidic substance, needles, m. p. 86—88°; *phenylhydrazone*, yellow needles, m. p. 173—174°, of feeble acid properties. In an analogous manner the interaction of acetylthiolacetyl chloride with ethyl sodiomalonate yields oily *ethyl acetylthiolacetylmalonate*, which on dissolving in sodium hydroxide solution and reprecipitation by acid eliminates a molecule of alcohol with formation of *ethyl thiotetron-a-carboxylate*, $\begin{matrix}CH_2\cdot C(OH)\\ |\qquad\quad\\ C———CO\end{matrix}>C\cdot CO_2Et$, needles, m. p. 122—123°; this reacts acid and gives a blood-red coloration with ferric chloride. On boiling with water for an hour, the ester is converted into *thiotetronic acid*, $\begin{matrix}S—CH_2\\ |\quad\\ CO\cdot CH\end{matrix}>C\cdot OH$, colourless needles, m. p. 115—117°, which behaves as a monobasic acid and gives a deep red coloration with ferric chloride;

the *silver* salt was prepared. With sodium nitrite, its aqueous solution produces a deep violet coloration. D. F. T.

Isomerism with Diacid Quaternary Ammonium Bases of the Coniine Group. Asymmetric Nitrogen 46. EDGAR WEDEKIND and F. NEY (*Ber.*, 1913, 46, 1895—1899. Compare Wedekind, A., 1912, i, 509, 948).—Although many investigations have been made, in only one case (E. and O. Wedekind, A., 1910, i, 834) have the two isomeric forms of a diquaternary ammonium salt, in which the nitrogen atoms are asymmetric, been isolated. Endeavours have now been made to effect this isolation of the isomerides by using compounds containing an active asymmetric carbon atom. The addition of menthyl indoacetate to ditertiary bases is not satisfactory. It was found, however, that the aim could be achieved by the application of diacid bases derived from coniine.

*Ethylene-bis-*d*-coniine,*

$$CH_2{<}{\begin{matrix}CH_2\cdot CHPr^{\alpha}\\ CH_2\text{—}CH_2\end{matrix}}{>}N\cdot CH_2\cdot CH_2\cdot N{<}{\begin{matrix}CHPr^{\alpha}\cdot CH_2\\ CH_2\text{—}CH_2\end{matrix}}{>}CH_2,$$

b. p. 200—203°/19 mm., $[\alpha]_D$ +81·09°, obtained by warming together for three hours a mixture of ethylene bromide with a quadrimolecular proportion of *d*-coniine, reacts with benzyl bromide, producing a mixture of diquaternary ammonium salts with an amine-ammonium salt, but the solubility differences in the products are too small to permit separation. With benzyl iodide the chief product, when the reaction occurs unassisted, is the amine-ammonium salt, decomp. at 178°, but if excess of warm molten benzyl iodide is introduced into the warm ditertiary base the product consists mainly of two diquaternary ammonium salts which can be separated by extraction with a mixture of alcohol and acetone; the more soluble and more abundant isomeride (termed α-), prisms, decomp. at 130—131°, has $[\alpha]_D$ +40·42°, whilst the β-isomeride, cubical crystals, decomp. at 214°, has $[\alpha]_D$ +15·42°, the solutions in both cases being observed in methyl alcoholic solution.

From theoretical reasons, three isomerides might be expected, represented by the schemes (N+,C+) . . . (N+,C+), (N−,C+) . . . (N−,C+), and (N+,C+) . . . (N−,C+). The α- and β-forms isolated are believed to be represented by the first two structures, the isomeride of the third configuration being too unstable to exist under the conditions of the experiment and so passing into the first form. This view is confirmed by the fact that the isomeride of higher rotation, and therefore of the first configuration, preponderates in the reaction product.

*Trimethylene bis-*d*-coniine,* obtained in an analogous manner from coniine and trimethylene bromide, has b. p. 200—201°/17 mm.; unfortunately, its diquaternary salts with benzyl bromide, benzyl iodide, and methyl iodide are amorphous, whilst with allyl iodide the product, which is at first amorphous, on keeping under ether becomes partly crystalline, but very easily undergoes decomposition. That the last substance is the expected *trimethylene*bis*allylconiinium iodide* was proved by analysis of the corresponding *platinichloride*. D. F. T.

The Behaviour of 2-Methylindole towards Aldehydes and Formic Acid. MAX SCHOLTZ (*Ber.*, 1913, 46, 2138—2146).—The

interaction of 2-methylindole with aldehydes in alkaline media is strikingly different from its behaviour in acid or neutral solution (Fischer, A., 1887, 265; Freund and Lebach, A., 1905, i, 663).

If equimolecular quantities of 2-methylindole and benzaldehyde are treated with sodium hydroxide solution, a reaction occurs in which the solvent is implicated, for the product is *ethoxyphenyl-2-methylindolylmethane*, $OEt\cdot CHPh\cdot C\ll\genfrac{}{}{0pt}{}{C_6H_4}{CMe}\gg NH$, colourless leaflets, m. p. 123°.

A similar reaction with *p*-tolualdehyde in place of benzaldehyde yields *ethoxy-*p*-tolyl-2-methylindolylmethane*, $C_6H_4Me\cdot CH(OEt)\cdot C_9H_8N$, colourless prisms, m. p. 101°. If methyl alcohol is applied as solvent instead of ethyl, the product is *methoxy-*p*-tolyl-2-methylindolylmethane*, $C_6H_4Me\cdot CH(OMe)\cdot C_9H_8N$, colourless prisms, m. p. 153°.

Furfuraldehyde, 2-methylindole, and ethyl alcohol under similar conditions yield *ethoxyfuryl-2-methylindolylmethane*,

$$C_4OH_3\cdot CH(OEt)\cdot C_9H_8N,$$

colourless needles, m. p. 158°. With methyl alcohol as solvent, *methoxyfuryl-2-methylindolylmethane*, $C_4OH_3\cdot CH(OMe)\cdot C_9H_8N$, grey prisms, m. p. 108°, is obtained.

The product from anisaldehyde, 2-methylindole, and ethyl alcohol is *ethoxy-*p*-anisyl-2-methylindolylmethane*, $OMe\cdot C_6H_4\cdot CH(OEt)\cdot C_9H_8N$, colourless tablets, m. p. 133°; with methyl alcohol the product is *methoxy-*p*-anisyl-2-methylindolylmethane*, colourless leaflets, m. p. 151°.

o-Chlorobenzaldehyde, 2-methylindole, and ethyl alcohol yield *ethoxy-*o*-chlorophenyl-2-methylindolylmethane*, $C_6H_4Cl\cdot CH(OEt)\cdot C_9H_8N$, tablets, m. p. 122°; methyl alcohol gives *methoxy-*o*-chlorophenyl-2-methylindolylmethane*, needles, m. p. 91°.

m-Nitrobenzaldehyde, 2-methylindole, and ethyl alcohol produce *ethoxy-*m*-nitrophenyl-2-methylindolylmethane*,

$$NO_2\cdot C_6H_4\cdot CH(OEt)\cdot C_9H_8N,$$

yellow leaflets, m. p. 130°; methyl alcohol gives *methoxy-*m*-nitrophenyl-2-methylindolylmethane*, yellow, rhombic prisms, m. p. 155°.

Nearly all the above products have a tendency to redden if kept in a moist condition.

The behaviour of *o*-nitrobenzaldehyde is curiously abnormal, for, whether methyl or ethyl alcohol is used as solvent, and sodium hydroxide or piperidine as alkali, the one product is *o-nitrophenyl-2-methylindolylcarbinol*, $NO_2\cdot C_6H_4\cdot CH(OH)\cdot C_9H_8N$, orange-red leaflets, m. p. 138°.

Salicylaldehyde also failed to react in the above general manner with methylindole and alcohol, for under the usual conditions the sodium salt of salicylaldehyde is deposited, whilst if water is added to retain this, *o*-hydroxyphenyldi-2-methylindolylmethane (Freund and Lebach, *loc. cit.*) separates. If, however, the mixture of salicylaldehyde and methylindole in alcohol is made alkaline by piperidine in place of sodium hydroxide, the piperidine nucleus enters into the reaction product, which is *piperidino-*o*-hydroxyphenyl-2-indolylmethane*, $C_5H_{10}N\cdot CH(C_6H_4\cdot OH)\cdot C_9H_8N$, colourless prisms, m. p. 201°. *p*-Homosalicylaldehyde with piperidine and methylindole in alcoholic solution behaves similarly to salicylaldehyde, producing *piperidino-*

o-*hydroxy*-m-*tolyl-2-methylindolylmethane*,

$$OH\cdot C_6H_3Me\cdot CH(C_5H_{10}N)\cdot C_9H_8N,$$

colourless needles, m. p. 132°. These two piperidino-compounds were the only ones obtainable in a crystalline condition, the products from other aldehydes being oily.

That the 3-carbon atom of the pyrrole nucleus is not entirely deprived of its activity in alkaline media is evidenced by the occasional occurrence of traces of di-indolyl derivatives in the reaction product; indeed, with *p*-hydroxybenzaldehyde and cinnamaldehyde the products are entirely of this type. The former aldehyde with piperidine and 2-methylindole in alcoholic solution gives rise to p-*hydroxyphenyl-bis-2-methylindolylmethane*, $OH\cdot C_6H_4\cdot CH(C_9H_8N)_2$, a crystalline powder, m. p. 237°; in a similar manner, by condensation of one molecule of aldehyde with two molecules of 2-methylindole, cinnamaldehyde produces *styryl-bis-2-methylindolylmethane*,

$$CHPh{:}CH\cdot CH(C_9H_8N)_2,$$

yellow needles, m. p. 226°.

A solution of 2-methylindole in formic acid in a short time becomes deep red, and the addition of water then causes the separation of 2-*methylindolyl*-2-*methylindolidenemethane*,

$$N{\lessdot}\begin{matrix}C_6H_4\\CMe\end{matrix}{>}C{=}CH{-}C{\lessdot}\begin{matrix}C_6H_4\\CMe\end{matrix}{>}NH,$$

as the *formate*, red needles, m. p. 104°, from which the free *base*, an orange-yellow powder, m. p. 230°, is liberated by ammonium hydroxide; *hydrochloride*; *hydrobromide*, fiery-red needles, m. p. 236°; *perchlorate*, red needles, decomp. at 260°. D. F. T.

Colours of the Second Order: *holo*- and *meri*-Quinonoid Salts. JEAN PICCARD (*Ber.*, 1913, **46**, 1843—1860).—The author has systematically examined the *holo*- and *meri*-quinonoid salts derived from a number of *N*-methyl- and *N*-phenyl-substituted benzidines and *p*-phenylenediamines, and comes to the conclusion that Nietzki's well known rule connecting the increase in the complexity of the molecule with the deepening of the colour from yellow through red and blue to yellowish-green requires modification.

Whereas the *meri*-quinonoid salts derived from benzidine and its diphenyl derivative are coloured respectively blue and yellowish-green, the *meri*-quinonoid salts of tetraphenylbenzidine are yellow.

The author explains this apparent exception as follows: When the complexity of the molecule has been gradually increased to such an extent that the colour has passed successively from yellow to red, blue, bluish-green, and finally yellowish-green, the further increase in the complexity causes a repetition of these colours in the same order; and from analogy with the interference colours the second series are termed colours of the second order.

The *meri*-quinonoid salts of tetraphenylbenzidine thus have a yellow colour of the second order.

Aqueous solution of *meri*-benzoquinonephenyldi-imonium salts are formed by the oxidation of *p*-aminodiphenylamine. The salts are bluish-red and are very unstable, decomposing rapidly in concentrated solution

with the formation of emeraldine. The yellow *holo*-quinonoid salts are still less stable.

Solutions of meri-*benzoquinonephenyldimethyldi-imonium* salts are obtained by oxidising *p*-dimethylaminodiphenylamine in acetic acid solution by means of ferric sulphate. They have a blue colour, whilst those of the *holo*-quinonoid salts are red or reddish-yellow according as they are formed by the union of the base with one or two molecules of the acid ; a blue *ferricyanide* was prepared by methods similar to those employed by Willstätter and Kalb (A., 1908, i, 475).

Benzoquinonediphenyldi-imine (Bandrowski, A., 1888, 269) combines with NN′-diphenyl-*p*-phenylenediamine to form a quinhydrone *base*, crystallising in yellow leaflets, m. p. 130—135° ; the *holo*-quinonoid salts give red solutions, the *meri*-quinonoid salts greenish-blue ; the *holo*-quinonoid *picrate*, $C_{18}H_{14}N_2,C_6H_3O_7N_3$, forms dark red prisms, the *meri*-quinonoid *picrate*, $C_{36}H_{30}N_4,2C_6H_3O_7N_3$, long, green needles.

Solutions of the *meri*-quinonoid salts derived from tetraphenyl-*p*-phenylenediamine are green, whilst those of the *holo*-quinonoid salts are blue ; the salts were not isolated.

On account of their instability, *holo*-diphenoquinonedi-imonium salts, which are yellow in colour, have hitherto not been isolated (compare Willstätter and Kalb, A., 1908, i, 986) ; the *picrate*,

$$C_{12}H_{10}N_2,2C_6H_3O_7N_3,$$

is obtained in pointed, brownish-yellow needles by oxidising benzidine dissolved in glacial acetic acid with aqueous chromium trioxide, and adding picric acid to the resulting solution.

The *holo*-quinonoid base derived from diphenylbenzidine is precipitated in an impure condition by the addition of sodium carbonate to aqueous solutions of the salts, which have been described by Kehrmann and Micewicz (A., 1912, i, 1020).

The green *holo*-quinonoid and yellow *meri*-quinonoid salts derived from tetraphenylbenzidine are obtained by oxidising the base with the requisite amount of chromium trioxide in glacial acetic acid solution ; addition of water and picric acid to these solutions precipitates a very unstable green holo- and a yellow meri-*diphenoquinonetetraphenyldi-imonium picrate*,

$$\begin{array}{c} C_6H_2O_7N\cdot NPh_2{:}C_6H_4{:}C_6H_4{:}NPh_2\cdot C_6H_2O_7N \\ \vdots \qquad\qquad\qquad \vdots \\ NPh_2\cdot C_6H_5\cdot C_6H_5\cdot NPh_2 \end{array},$$

which crystallises in prisms, m. p. 130—134°. F. B.

holo- and *meri*-**Quinonoid Salts of Benzidine.** JEAN PICCARD (*Ber.*, 1913, **46**, 1860—1862).—A reply to Madelung (A., 1911, i, 678). The author maintains that the *holo*-quinonoid salts of benzidine are yellow and not blue or violet as stated by Madelung. F. B.

Hippenyl *iso*Cyanate [Benzoylaminomethylcarbimide]. THEODOR CURTIUS (*J. pr. Chem.*, 1913, [ii], **87**, 513—541).—A recapitulation and extension of earlier work (A., 1896, i, 36). The dibromide of phenylcarbimide, $NPhBr_2{:}CO$, which has been previously obtained in an impure condition by boiling benzoylazoimide with bromine in chloroform solution, is prepared by the direct union of bromine and

phenylcarbimide in chloroform solution at a low temperature. It has m. p. 144°, and if carefully heated sublimes undecomposed. When strongly heated, it loses hydrogen bromide, yielding *p*-bromophenylcarbimide. Benzoylaminomethylcarbimide, $COPh\cdot NH\cdot CH_2\cdot N{:}CO$, prepared by heating hippurylazoimide in benzene, chloroform, or carbon tetrachloride solution, has m. p. 96—98° according to the rapidity of heating, combines with methyl and ethyl alcohols to form the urethanes previously described (*loc. cit.*), and when boiled with water yields *s*-dibenzoylaminodimethylcarbamide together with a *substance*, m. p. 130°. It combines with benzamide to form *s-benzoylaminomethylbenzoylcarbamide*, $COPh\cdot NH\cdot CH_2\cdot NH\cdot CO\cdot NH\cdot COPh$, which has m. p. 221°, and has also been obtained by heating hippurylazoimide with benzamide in xylene solution.

p-Bromohippurylazoimide, prepared from *p-bromohippurylhydrazide* (needles, m. p. 226°) in a similar manner to that employed in the preparation of hippurylazoimide from hippurylhydrazide, crystallises in long, lustrous, silky needles, m. p. 98°, and is converted by boiling in benzene solution into *p-bromobenzoylaminomethylcarbimide*, $C_6H_4Br\cdot CO\cdot NH\cdot CH_2\cdot N{:}CO$, which crystallises in broad needles, m. p. 114°, unites with hydrogen chloride in benzene solution yielding a *hydrochloride*, m. p. 235° with previous sintering, and combines with ethyl and methyl alcohols to form the corresponding *urethanes* of m. p. 174° and 214° respectively.

When boiled with water, benzoylazoimide yields only carbanilide, whilst hippurylazoimide gives rise to the following products: carbon dioxide, nitrogen, formaldehyde, hydrazoic acid and its ammonium salt, benzamide, benzoic acid, methylenediamine, ammonium hydrogen hippurate, *s*-dibenzoylaminodimethylcarbamide, and *s-benzoylhippurylmethylenediamine*, $COPh\cdot NH\cdot CH_2\cdot NH\cdot CO\cdot CH_2\cdot NH\cdot COPh$, which crystallises in slender, silky needles, m. p. 234°, and is hydrolysed by boiling dilute sulphuric acid to benzoic acid, glycine, ammonia and formaldehyde. In aqueous alcoholic solution, the decomposition of hippurylazoimide is much simpler, the sole products being dibenzoylaminodimethylcarbamide and the urethane,

$$COPh\cdot NH\cdot CH_2\cdot NH_2\cdot CO_2Et.$$

When boiled with water, *p*-bromohippurylazoimide yields di-*p*-bromobenzoylaminodimethylcarbamide (Heil, *Diss*, *Heidelberg*, 1911), hydrazoic acid and its ammonium salt, formaldehyde, *p*-bromobenzamide, and *p*-bromohippuric acid. F. B.

Benzoylhydrazicarbonyl. OTTO DIELS and HARUKICHI OKADA (*Ber.*, 1913, **46**, 1870—1876. Compare A., 1912, i, 511, 918).—Benzoylhydrazicarbonyl reacts with acid chlorides, yielding compounds which are undoubtedly derivatives of the type

$$CO<\genfrac{}{}{0pt}{}{N\cdot COPh}{N\cdot R},$$

although the formation of metallic salts is best represented on the assumption that the hydrazi-compound has the tautomeric formula $OH\cdot C\lessgtr\genfrac{}{}{0pt}{}{N\cdot COPh}{N}$ Thus, with benzoyl chloride and aqueous potassium

hydroxide it yields dibenzoylhydrazicarbonyl (Stollé and Krauch, this vol., i, 97), which is hydrolysed by fuming hydrochloric acid to benzoic acid and benzoylhydrazicarbonyl, and by dilute sodium hydroxide to s-*dibenzoylhydrazide*, crystallising in lustrous, white needles, m. p. 238°.

Ethyl benzoylhydrazicarbonylcarboxylate, $CO<\begin{matrix}N\cdot COPh \\ | \\ N\cdot CO_2Et\end{matrix}$, prepared from benzoylhydrazicarbonyl and ethyl chloroformate, forms colourless crystals, m. p. 94°, and is hydrolysed by warm aqueous sodium hydroxide to *ethyl benzoylhydrazinecarboxylate*, $NHBz\cdot NH\cdot CO_2Et$, which forms lustrous, white plates, m. p. 127°.

On nitration with sulphuric acid and ethyl nitrate, benzoylhydrazicarbonyl is converted into p-*nitrobenzoylhydrazicarbonyl*. This crystallises in pale yellow leaflets, m. p. 248°, and is reduced by zinc dust and formic acid to p-*aminobenzoylhydrazicarbonyl*, which forms lustrous, silky, colourless leaflets, m. p. 144°, and yields a *sulphate* (decomp. 238°), *hydrochloride*, and *nitrate*. The amino-compound is decomposed by fuming hydrochloric acid at 130° into aniline and hydrazine hydrochloride, and when heated with hydrazine hydrate is transformed into p-*aminobenzoylcarbohydrazide*,

$$NH_2\cdot C_6H_4\cdot CO\cdot NH\cdot NH\cdot CO\cdot NH\cdot NH_2,$$

which crystallises from water in lustrous, white leaflets (decomp. 198°), is hydrolysed by hydrochloric acid to *p*-aminobenzoic acid and carbohydrazide, and may also be obtained directly from *p*-nitrobenzoylhydrazicarbonyl by the action of hydrazine hydrate at 80°.

F. B.

Constitution of Benzoylhydrazicarbonyl. ROBERT STOLLÉ (*Ber.*, 1913, **46**, 1993—1994).—The reactions of dibenzoylhydrazicarbonyl (this vol., i, 97) agree with either the hydrazicarbonyl formula (I), which has been assigned by Diels and Okada to benzoylhydrazicarbonyl (preceding abstract), or with the dihydro-oxadiazole formula (II).

$$\text{(I)}\ CO<\begin{matrix}NBz \\ | \\ NBz\end{matrix} \qquad \text{(II)}\ \begin{matrix}NBz\cdot N \\ | \\ CO—O\end{matrix}\!\!>CPh.$$

The author proposes to combine nitrobenzoylhydrazicarbonyl with benzoyl chloride and benzoylhydrazicarbonyl with nitrobenzoyl chloride, when the compounds should be identical if formula (I) is correct.

J. C. W.

New Series of *iso*Pyrazolones. GEORGES FAVREL (*Compt. rend.*, 1913, **156**, 1912—1914).—It has been shown previously that the γ-chloroacetoacetates react with diazo-chlorides to give the α-alkylhydrazones of γ-chloro-$\alpha\beta$-diketobutyrates (A., 1907, i, 796). The latter are now shown to be converted by the action of aqueous solution of sodium hydroxide into alkyl*iso*pyrazolonecarboxylates.

*Ethyl phenyl*iso*pyrazolonecarboxylate*, $NPh<\begin{matrix}N=C\cdot CO_2Et \\ | \\ CH_2\cdot CO\end{matrix}$, m. p. 258—260°, obtained by the action of aqueous sodium hydroxide solution on the α-phenylhydrazone of ethyl γ-chloro-$\alpha\beta$-diketo-

butyrate, $CH_2Cl\cdot CO\cdot C(N_2HPh)\cdot CO_2Et$, crystallises in long, brilliant, faintly yellow needles from boiling alcohol. The *methyl* ester, m. p. 85—87°, forms small, colourless needles.

Ethyl o-*tolyl*iso*pyrazolonecarboxylate*, m. p. 66—68°, forms feebly yellow crystals with difficulty from alcohol. The *methyl* ester, m. p. 178°, forms whitish crystals soluble in methyl alcohol.

Ethyl p-*tolyl*iso*pyrazolonecarboxylate*, m. p. 111—112°, forms yellow needles, and the *methyl* ester is a crystalline, yellow powder, m. p. 218—220°. All these products in alcoholic solution give intense blue colorations with ferric chloride, which are dissipated by acids. They are soluble in weakly alkaline or strongly acid, but not in dilute acid, solutions. T. A. H.

The Benzoylation of Iminazole [Glyoxaline] Derivatives. Otto Gerngross (*Ber.*, 1913, **46**, 1908—1913).—The author finds that the introduction of acyl groups into iminazole and its homologues, which has hitherto been found impossible, can be affected by mixing the acyl chloride with a bimolecular proportion of the base in ether or benzene solution and shaking for a day or so. The hydrogen chloride formed separates in combination with the excess of base and the acylation proceeds smoothly. If necessary the excess of base can frequently be replaced by the corresponding quantity of pyridine. The benzoyl derivatives are very unstable, and in the course of the preparation great care must be taken for the exclusion of traces of moisture.

1-*Benzoylglyoxaline*, $\begin{matrix}CH\!:\!CH\\ \vert \\ N{=\!=}CH\end{matrix}\!\!>\!NBz$, obtained by evaporation of the benzene solution after the above procedure, slowly crystallises in colourless needles, m. p. 19—20°; when exposed to the air it is rapidly converted by moisture into glyoxaline benzoate, plates, m. p. 99·5°.

1-*Benzoyl*-4(5)-*methylglyoxaline*, obtained in a similar manner, forms needles, m. p. 54—55°; when treated in alcoholic solution successively with silver nitrate and ammonium hydroxide solutions, a *substance* crystallising in needles is precipitated. On exposure to the atmosphere, the benzoyl compound is gradually converted into 4(5)-methylglyoxaline benzoate, plates, m. p. 92—93°.

1-*Benzoyl*-4 : 5-*dimethylglyoxaline*, prepared similarly, forms hexagonal plates, m. p. 74—75°. It is affected by the atmosphere.

Ethyl 1-*benzoyl*-4(5)-*methylglyoxaline*-5(4)-*carboxylate* forms needles, m. p. 43—45°.

1-Benzoylbenziminazole is obtainable in a similar manner to the previous compounds. Although the simultaneously produced benziminazole hydrochloride can be quantitatively re-converted into the original base, if it is preferred the excess of benziminazole can be replaced by pyridine. The benzoyl derivative is more stable than the preceding ones, for although it is hydrolysed by potassium hydroxide solution, it resists sodium carbonate; it gives a *benzoate*, prisms, m. p. 100°, when mixed in ethereal solution with benzoic acid. The precipitate observed by Bamberger and Berlé (A., 1892, 632) in the action of potassium hydroxide on the benzoyl compound was due to the presence of the alcoholate of 1 : 3-dibenzoylbenziminazole as impurity.

Benziminazole can be converted into 1-acetylbenziminazole (Bistrzycki and Przeworski, this vol., i, 103) in the same manner.

D. F. T.

The Mechanism of the Scission of Iminazole [Glyoxaline] Derivatives by Benzoyl Chloride and Alkali. OTTO GERNGROSS (*Ber.*, 1913, **46**, 1913—1924).—The action of benzoyl chloride and an alkali hydroxide on glyoxaline, benziminazole, and their homologues in which the imino-group is unsubstituted, even at 0°, causes scission of the ring with formation of an aliphatic acid and a dibenzoylated diamine (Bamberger and Berlé, A., 1892, 632). If sodium carbonate is used in place of the hydroxide with benzoyl chloride and benziminazole, a formyldibenzoyl-*o*-phenylenediamine can be obtained, and with benzoyl chloride and water in solution in a mixture of benzene and ether, benziminazole gives a dibenzoylbenziminazole-2-ol; these two new products are evidently to be regarded as intermediate steps in the above scission, and the former compound is easily produced from the latter. It is therefore probable that the mechanism of the scission is similar to that of the scission by alkyl haloids and alkali (compare Meldola and Kuntzen, T., 1911, **99**, 1283), namely:

$$\begin{array}{ccccc} C_6H_4{<}\begin{matrix}NBz\\N\end{matrix}{>}CH & \longrightarrow & C_6H_4{<}\begin{matrix}NBz\\N\end{matrix}{>}CH & \longrightarrow & C_6H_4{<}\begin{matrix}NBz\\NBz\end{matrix}{>}CH\cdot OH \\ \text{(I.)} & & \begin{matrix}\text{(II.)}\\ Cl\quad Bz\end{matrix} & & \text{(III.)} \\ & & & & \downarrow \\ & NHBz\cdot C_6H_4\cdot NHBz & \longleftarrow & NHBz\cdot C_6H_4\cdot NBz\cdot COH & \\ & \text{(V.)} & & \text{(IV.)} & \end{array}$$

for the last three stages can thus be experimentally realised.

When benzoyl chloride is gradually added to an agitated and cooled aqueous solution of sodium carbonate and 4(5)-methylglyoxaline, a *substance*, tetragonal plates, m. p. 144° (decomp.), probably dibenzoylformyl-$\alpha\beta$-diaminopropylene, is obtained, which, when boiled with water or treated with cold sodium hydroxide solution, undergoes fission into dibenzoyldiamino-$\alpha\beta$-propylene and formic acid.

Experiments devoted to the isolation of the hypothetical additive compound (formula II above) of benzoylbenziminazole and benzoyl chloride were fruitless, the only new product being a small quantity of *benzoylbenziminazole hydrochloride*, needles, m. p. 195—200°, which is converted by alkali hydroxides into benziminazole.

1 : 3-*Dibenzoylbenziminazole*-2-*ol* (formula III above) is obtained by vigorously shaking for several hours an equimolecular mixture of benzoylbenziminazole and benzoyl chloride with a half-molecular proportion of water in a mixture of benzene and ether; the substance crystallises in cubes, and above its m. p., 135—140°, gradually resolidifies to needles of *formyldibenzoyl*-o-*phenylenediamine* (formula IV), m. p. 157°; this substance on further heating also solidifies with evolution of carbon monoxide and formation of dibenzoyl-*o*-phenylenediamine, which finally melts at 306° (decomp.), due to the last stage in the series of changes. The opening of the ring expressed by the formulæ III—IV, which is thus caused by heat, can be effected more readily by merely shaking with cold water or warming with methyl

alcohol. Dibenzoylbenziminazole-2-ol when boiled with alcohol or mixed in the cold with alcohol containing hydrogen chloride or even a little benzoyl chloride is converted into the corresponding *ethyl ether*, $C_6H_4{<}{}^{NBz}_{NBz}{>}CH{\cdot}OEt$; when heated with propyl alcohol the ethyl radicle is displaced with formation of the propyl ether. Above its m. p., 139°, the ethyl ether undergoes conversion into an *isomeride*, needles, m. p. 152°, which regenerates the original form on mere recrystallisation. In addition to the above-mentioned method, 1 : 3-*dibenzoylbenziminazolol propyl ether*, prisms, m. p. 135—136°, can also be obtained by heating the parent hydroxy-compound with propyl alcohol containing a trace of hydrogen chloride; in the absence of the hydrogen chloride the iminazole ring is forced open.

The action of benzoyl chloride and sodium carbonate solution on benziminazole yields a mixture of formyldibenzoyl-*o*-phenylenediamine and dibenzoyl-*o*-phenylenediamine, which can be separated by making use of the greater solubility of the former in light petroleum or benzene. The formyldibenzoyl-*o*-phenylenediamine on prolonged boiling with water or more quickly with acids or alkalis is converted into formic acid and dibenzoyl-*o*-phenylenediamine.

It is suggested that the opening of the quinoline and benzothiazole rings by benzoyl chloride and alkali (Reissert, A., 1905, i, 925) may be due to a similar series of changes. D. F. T.

isoHydantoin, 2-Imino-4-ketotetrahydro-oxazole, and its Homologues. WILHELM TRAUBE and RICHARD ASCHER (*Ber.*, 1913, **46**, 2077—2084).—The reaction of guanidine with esters of α-amino- and α-hydroxy-acids is more complex than with esters of halogen substituted aliphatic acids (Traube, A., 1911, i, 115), in that not only alcohol but ammonia is eliminated, for example, glycine ester yields glycocyamidine, whilst the esters of the hydroxy-acids yield a reduced oxazole derivative.

When ethyl glycollate is mixed with guanidine in alcoholic solution, heat is developed, and there shortly separates *2-imino-4-ketotetrahydro-oxazole*, $NH{:}C{<}{}^{NH\cdot CO}_{O\text{---}CH_2}$, prisms, m. p. 246—247° (decomp.); *hydrochloride*, rhombic tablets, m. p. 164° (decomp.); *silver* salt; *copper* salt, bright blue. The similarity of this substance to ψ-thiohydantoin, for example, in its hydrolysis by alcoholic hydrogen chloride to 2 : 4-*diketo-tetrahydro-oxazole*, $CO{<}{}^{NH\cdot CO}_{O\text{---}CH_2}$, tablets, m. p. 89—90°, b. p. 173°/11 mm., and by barium hydroxide solution to ammonia, carbon dioxide and glycollic acid, causes the authors to suggest the name ψ- or *iso*-hydantoin for it.

Ethyl lactate also readily reacts with an alcoholic solution of guanidine, giving *methyl*iso*hydantoin* (*2-imino-4-keto-5-methyltetrahydro-oxazole*), leaflets, m. p. 226°; *hydrochloride*, needles. In a manner analogous to the last, this substance undergoes hydrolysis to 2 : 4-*diketo-5-methyltetrahydro-oxazole*, a hygroscopic solid, m. p. 44—45° (decomp.), b. p. 156—161°/15 mm.

By an analogous reaction, ethyl mandelate yields *phenyl*iso*hydantoin* (*2-imino-4-keto-5-phenyltetrahydro-oxazole*), crystals, m. p. 256—257° (decomp.); *nitrate*, prismatic crystals, decomp. at 133°; this on warming with dilute hydrochloric acid becomes hydrolysed, producing 2:4-*diketo-5-phenyltetrahydro-oxazole*, leaflets, m. p. 108°, which is hydrolysed by barium hydroxide solution to mandelic acid, ammonia, and carbon dioxide.

Methyl glycerate reacts readily with guanidine in methyl alcoholic solution, producing *hydroxymethyl*iso*hydantoin* (*2-imino-4-keto-5-hydroxymethyltetrahydro-oxazole*), $NH{:}C\begin{smallmatrix}NH\cdot CO \\ | \quad\quad \\ —O—\end{smallmatrix}\!\!>CH\cdot CH_2\cdot OH$, prisms, m.p. 197°.

Ethyl aminoacetate and guanidine react vigorously when mixed in equivalent quantities, yielding glycocyamidine.

Ethyl ethoxyacetate and ethyl ethoxypropionate both readily enter into reaction with a concentrated alcoholic solution of guanidine, yielding *ethoxyacetylguanidine*, m. p. 162°, and *ethoxypropionylguanidine*, m. p. 196°, respectively. The formation of these compounds is interesting as an indication of the probable intermediate stage in the formation of the *iso*hydantoin derivatives described above, whilst the absence of the second phase of the condensation serves as a confirmation of the structure assumed for the products obtained from the esters of the hydroxy-acids. D. F. T.

Syntheses of Thiohydantoin. II. SHIGERU KOMATSU (*Mem. Coll. Sci. Eng. Kyōto*, 1912, **5**, 13—18. Compare A., 1911, i, 683).—The author has modified his interpretation of the mechanism of the reaction whereby thiohydantoin and methylthiohydantoin are formed by the action of potassium thiocyanate on the respective α-amino-acids in the presence of acetic anhydride, and agrees with the view of Johnson and Nicolet (A., 1912, i, 53) that acetyl derivatives of the thiohydantoins are first formed which subsequently undergo hydrolysis. An attempt was made to substitute benzoic anhydride for acetic anhydride, but neither thiohydantoin nor benzoylthiohydantoin was formed.

When potassium thiocyanate and phenyl aminopropionic acid are heated on the water-bath in the presence of acetic anhydride, *2-thio-3-acetyl-4-benzylhydantoin*, $CH_2Ph\cdot CH<\begin{smallmatrix}CO—NH \\ NAc\cdot CS\end{smallmatrix}$, white needles, m. p. 165—166°, is formed, which, when treated with concentrated hydrochloric acid, is converted into *2-thio-4-benzylhydantoin*, white needles, m. p. 175—177°. Desulphurisation by means of mercuric oxide in ammoniacal solution or by digestion with chloroacetic acid in aqueous solution transforms this into 4-benzylhydantoin, platy crystals, m. p. 185—186°, the *silver* salt of which was analysed (compare Wheeler and Hoffman, A., 1911, i, 498).

Potassium thiocyanate and tyrosine when similarly heated with acetic anhydride yield a viscous, yellowish-brown *acetyl* derivative from which, on hydrolysis, *2-thio-4-*p*-hydroxybenzylhydantoin*,

$$OH\cdot C_6H_4\cdot CH_2\cdot CH<\begin{smallmatrix}CO—NH \\ NH\cdot CS\end{smallmatrix},$$

m. p. 203—204° (decomp.), is obtained. Boiling aqueous chloroacetic acid transforms it into 4-*p*-hydroxybenzylhydantoin, m. p. 253—254° (decomp.) [Wheeler and Hoffmann, *loc. cit.*, give m. p. 257—258° (decomp.)]. H. W.

The So-called Quinhydrone Salts of the Phenazonium Group. ARTHUR HANTZSCH (*Ber.*, 1913, **46**, 1925—1927).—Mainly polemical in reply to Kehrmann (this vol., i, 298, 522). The author repeats his statement that the former's view as to a quinhydrone structure for the dark green methylphenazonium iodide is incorrect.

As further evidence he cites the neutral character of the solution of this substance, whilst hydrophenazine salts are almost completely hydrolysed by water; the dilute aqueous alcoholic solution of the iodide has the same greenish-yellow colour as the true phenazonium salts; finally, on grinding with silver nitrate solution or with a suspension of silver sulphate in water, the iodide is converted entirely into a greenish-yellow nitrate or sulphate. These salts from their colour cannot be quinhydrone salts, and they contain no admixed dihydrophenazine salts, because otherwise ether would extract the corresponding dihydro-base from them. D. F. T.

A Condensation Product from Phenylindanone and 1-Phenyl-3-methyl-5-pyrazolone. GEORG ROHDE and M. TENZER (*J. pr. Chem.*, 1913, [ii], **87**, 541—544).—With the object of establishing the constitution of the red acid substance produced by the condensation of 1-phenyl-3-methyl-5-pyrazolone with phthalic anhydride (this vol., i, 297), the authors have attempted to prepare a similar compound, but of simpler constitution, by the condensation of the pyrazolone with benzylidenephthalide. The product formed by fusing the two latter compounds in equimolecular proportions is, however, not a carboxylic acid, but a phenylmethylpyrazolonylidenephenylindanone of the following formula:

$$\begin{array}{l}\mathrm{N{=}CMe} \\ \mathrm{\,|} \\ \mathrm{NPh{\cdot}CO}\end{array}\!\!>\mathrm{C{:}C}<\!\!\begin{array}{l}\mathrm{C_6H_4} \\ \mathrm{CHPh}\end{array}\!\!>\mathrm{CO},$$

its formation being explained by the transformation of the benzylidenephthalide into 2-phenylindanone, which subsequently condenses with the pyrazolone. This view has been confirmed by the formation of the compound by condensing the pyrazolone with 2-phenylindanone in the presence of anhydrous sodium acetate at 130—135°.

3 : 1′-*Phenyl*-3′-*methyl*-4′-*pyrazol*-5′-*onylidene*-2-*phenylindanone* crystallises in red needles, m. p. 272°, dissolves in alkalis with a deep magenta coloration, and yields an *oxime* and *semicarbazone*. With sulphuric acid it develops a dark green coloration. F. B.

Constitution of Anilopyrine. EZIO COMANDUCCI (*Boll. chim. farm.*, 1913, **52**, 436. Compare Comanducci, this vol., i, 296; Zampolli, this vol., i, 296).—Zampolli's criticism is based on errors contained in a preliminary publication of the author, which were corrected before the appearance of Zampolli's paper. R. V. S.

Iminoindigotins. WALTER MADELUNG (*Ber.*, 1913, **46**, 2259—2264. Compare Binz and Lange, this vol., i, 769).—The mono- and di-imines

can be prepared by heating indigotin with the compound of zinc chloride and ammonia.

The monoimine is obtained in almost quantitative yield by gradually introducing indigotin into the ammonia compound fused at 200°, and maintaining at this temperature for half an hour. In the preparation of the di-imine a higher temperature (about 260°) and more prolonged heating are necessary.

Both imines have the same colour as indigotin, but are much more readily soluble in organic solvents. On reduction with alkaline hyposulphite, the monoimine yields a leuco-compound soluble in alkalis, whilst the di-imine is converted into an insoluble diamine. Advantage is taken of this difference in behaviour to separate the di-imine from the product of the fusion. The leuco-compounds resemble the imines in being readily hydrolysed.

When the monoimine is vatted and the resulting solution, after being heated, submitted to oxidation, a mixture of the monoimine and indigotin is produced. From this the author draws the conclusion that the leuco-compound of the monoimine is present in the vat in the following two forms: $C_6H_4<\substack{C(OH)\\NH}>C{\cdot}C<\substack{C(NH_2)\\NH}>C_6H_4$ and $C_6H_4<\substack{C(OH)\\NH}>C{\cdot}CH<\substack{C(NH)\\NH}>C_6H_4$. The monoimine crystallises with acetic acid (1 mol.).

Di-iminoindigotin, $C_{16}H_{12}N_4$, forms rosettes of microscopic crystals which decompose above 200°, giving off ammonia. It is more readily soluble in all solvents, and possesses more pronounced basic properties than the monoimino-compound. With mineral acids it forms sparingly soluble salts. F. B.

The Action of Potassium Cyanide on Pyronine and Acridinium Dyes. PAUL EHRLICH and LUDWIG BENDA (*Ber.*, 1913, **46**, 1931—1951).—If the red aqueous solution of pyronine-*G* (tetramethyldiaminoxanthylium chloride) is mixed with aqueous potassium cyanide at the ordinary temperature, a violet-red precipitate of tetramethyldiaminoxanthylium cyanide,

$$NMe_2{\cdot}C_6H_3<\substack{CH-\\O(CN)}>C_6H_3{\cdot}NMe_2,$$

is obtained, which on warming at 65° for ten minutes becomes converted into *tetramethyldiamino-9-cyanoxanthen*,

$$NMe_2{\cdot}C_6H_3<\substack{CH(CN)\\O}>C_6H_3{\cdot}NMe_2,$$

which the authors designate pyronine-leucocyanide (compare Hantzsch and Osswald, A., 1900, i, 256); this substance forms almost colourless needles, m. p. 183°, which rapidly become green when exposed to light; its alcoholic solution on the addition of potassium hydroxide shows a beautiful violet fluorescence. Oxidation of the leuco-compound in hydrochloric acid solution by ferric chloride or lead dioxide, yields *cyano pyronine hydrochloride*, green crystals of metallic lustre; *nitrate*, green, crystalline powder; *chromate*, obtained by effecting the oxidation with dichromate, forms blue flocks; the salts of the base, which has the formula $C_{18}H_{17}ON_3$, give blue aqueous solutions which dye mordanted

cotton and silk, and are reducible to the leuco-compound. With sodium hydroxide solution or ammonium hydroxide in the cold, the salts give a pale blue precipitate, and on acidifying, hydrogen cyanide is evolved, whilst the colour disappears. When boiled with sodium hydroxide solution, complete loss of colour occurs with formation of a precipitate of tetramethyldiaminoxanthone, yellow needles, m. p. 242° (compare Biehringer, A., 1897, i, 73), which in alcohol gives a colourless solution with a violet fluorescence, and in sulphuric acid colourless with a strong blue fluorescence.

If the above tetramethyldiaminoxanthone is reduced by zinc dust and hydrochloric acid in warm aqueous alcoholic solution, *bispyronine*, olive-green crystals, separates as deep blue flocks of a double *salt* with zinc chloride, from which it is freed by dissolving in very dilute hydrochloric acid and salting out. The free base,

$$OCl{<}{\begin{matrix}C_6H_3(NMe_2)\\C_6H_3(NMe_2)\end{matrix}}{>}C{-}C{<}{\begin{matrix}C_6H_3(NMe_2)\\C_6H_3(NMe_2)\end{matrix}}{>}OCl,$$

which dissolves in alcohol to a violet solution, and in sulphuric acid to a blood-red, dyes mordanted cotton and silk violet; its violet solution in hydrochloric acid becomes colourless on reduction with zinc dust, but the original coloured substance is regenerated by oxidation with ferric chloride ; the base was analysed as the *nitrate*.

3:6-Diamino-10-methylacridinium chloride (compare Benda, A., 1912, i, 651), for which the authors suggest the name *trypaflavin*, when neutralised with sodium carbonate and treated with potassium cyanide in aqueous solution gives an orange-yellow precipitate of the *cyanide* ; on warming the mixture at 75°, the precipitate is converted into pale red 3 : 6-*diamino*-5-*cyano*-10-*methyldihydroacridine* (compare Kaufmann and Albertini, A., 1909, i, 606), which on oxidation in aqueous hydrochloric acid solution by ferric chloride or potassium dichromate passes into 3 : 6-*diamino*-5-*cyano*-10-*methylacridine* (*cyanotrypaflavin*), deep green prisms of metallic lustre which give a magenta-red aqueous solution; the aqueous solution on addition of the required mineral acid precipitates the *nitrate*, *hydrochloride*, and *sulphate* respectively, which crystallise in needles; the solutions can be reduced by zinc dust and acid to a colourless substance which regenerates the coloured base on oxidation. The hydrochloride suspended in dilute hydrochloric acid is converted by sodium nitrite into a blue *diazo*-compound resembling diazosafranine. If 3 : 6-diamino-5-cyano-10-methyldihydroacridine is warmed for forty hours with sulphuric acid, it is oxidised to 3: 6-diamino-10-methylacridinium sulphate, together with a *sulphonic acid* of unknown constitution.

When the above diaminocyanomethylacridine is warmed with sodium hydroxide solution, the solution changes its colour from red to brownish-yellow, and 3 : 6-*diamino*-10-*methylacridone*, colourless needles, when pure, m. p. 308° (decomp.), slowly deposits; this dissolves in hydrochloric acid to a deep yellow solution, and in hot water or alcohol to a colourless solution with a violet fluorescence; the hydrochloric acid solution on diazotisation gives a red *diazo-compound*, which couples with *R*-salt to a sparingly soluble red *substance*. Reduction of diaminomethylacridone with sodium amalgam in alcoholic solution and re-oxidation by ferric chloride in acid

solution produces diaminomethylacridinium chloride in poor yield. Reduction in hydrochloric acid by zinc dust, however, gives the *zinc chloride* double salt, red needles with metallic lustre, of *bistrypaflavin*, $NMeCl{<}{\substack{C_6H_3(NH_2)\\ C_6H_3(NH_2)}}{>}C{\cdot}C{<}{\substack{C_6H_3(NH_2)\\ C_6H_3(NH_2)}}{>}NMeCl$.

The formation of this substance is believed to depend merely on the reduction of the pinacone compound which is previously produced (compare Decker and Dunant, A., 1909, i, 433). The addition of nitric acid to a solution of the zincochloride causes the separation of the *nitrate* of the base, orange-red needles; the orange-red aqueous solution of this yields a blue diazo-compound.

3 : 6-Tetramethyldiamino-10-methylacridinium *p*-toluenesulphonate (used in place of the chloride, that is, acridinium-orange, for convenience) reacts with an aqueous solution of potassium cyanide, giving first an orange-red precipitate of the corresponding *cyanide*, which on warming passes into a black green *substance*; this on oxidation in hydrochloric acid solution by ferric chloride gives *cyanoacridinium-orange*, $NMe_2{\cdot}C_6H_3{<}{\substack{C(CN)\\ NMeCl}}{>}C_6H_3{\cdot}NMe_2$, green crystals soluble in water to a violet colour; *nitrate*, reddish-brown flocks. Reduction of this substance by zinc dust and hydrochloric acid produces a colourless solution, from which oxidation regenerates the original substance as the *chromate* if potassium dichromate is used as oxidising agent. The action of hot potassium hydroxide solution on cyanoacridinium orange causes the formation of *tetramethyldiamino-10-methylacridone*, colourless needles, m. p. 275—276°; *hydrochloride*, yellow needles; the colourless alcoholic solution exhibits a strong violet fluorescence, whilst in sulphuric acid a very strong bluish-green fluorescence is observed. By reduction in dilute hydrochloric acid with zinc dust, tetramethyldiamino-10-methylacridone is converted into *bis-acridinium-orange zincochloride*, red needles with metallic lustre, which, like the previous example, is probably produced by intermediate formation of a pinacone compound; *nitrate*, green crystals with a bronze lustre. The substance is reducible by zinc dust and hydrochloric acid to a yellow solution with green fluorescence, which can be reoxidised to the red solution of the original substance.

Thiopyronine, in an analogous manner, is converted by potassium cyanide into a blue colouring matter.

From a consideration of the colours of the products obtained with potassium cyanide and of the colours of the original pyronine or acridine dye, the conclusion is drawn that the grouping $>C{\cdot}CN$ in orthoquinonoid dyes exerts the same effect as a cyclic nitrogen atom $>N$ on the colour; also, that in the cyano-compounds, a rearrangement occurs with formation of a para-quinonoid structure. The latter view is confirmed by experimental results which are to be published later, for example, a striking colour difference exists between 3 : 6-diamino-10-methylacridinium chloride and its 2 : 7-dimethyl derivative, the latter of which is structurally prevented from any such rearrangement. D. F. T.

Products of the Internal Condensation of Hydrazinedithiocarbophenylamide. MAX BUSCH and WILHELM SCHMIDT (*Ber.*, 1913, **46**, 2240—2248).—The authors have attempted to prepare a derivative of aminocarbodi-imide, $NH:C:N\cdot NH_2$, by the removal of hydrogen sulphide from hydrazinedithiocarbophenylamide (*s*-diphenylthiocarbamylhydrazide), $N_2H_2(CS\cdot NHPh)_2$, by heating with mercuric oxide in alcoholic solution. The product consisted, however, of *tetrahydrothiodiazoledianil* [*diphenyliminotetrahydrothiodiazole*], $\begin{matrix} NH\cdot C(NPh) \\ | \\ NH\cdot C(NPh) \end{matrix}\!\!>\!S$, which crystallises in lustrous, white leaflets, m. p. 240°, and can also be obtained, together with the anilinothiolthiodiazole described below, by maintaining the hydrazide in a fused condition for a few minutes at a temperature not exceeding 200°

The thiodiazole has been previously prepared by Walther (A., 1906, i, 831), who assigned to it the formula $NPh:C:N\cdot NH\cdot CS\cdot NHPh$, whilst Freund and Wischewiansky (A., 1894, i, 97), who obtained it by the action of carbonyl chloride on the hydrazide, considered it to be a phenyliminophenylthiourazole of the constitution

$$\begin{matrix} CS\cdot NPh \\ | \\ NH\cdot NH \end{matrix}\!\!>\!C:NPh.$$

Walther's formula is excluded on account of the absence of additive properties, whilst Freund and Wischewiansky's formula is inadmissible because the substance does not possess distinct acid properties and is not oxidisable to a disulphide.

Evidence in support of the authors' formula is furnished by the behaviour of the thiodiazole on oxidation, whereby a red *azo*-compound, *diphenyliminodihydrothiodiazole*, $\begin{matrix} N\cdot C(NPh) \\ \| \\ N\cdot C(NPh) \end{matrix}\!\!>\!S$, crystallising in stout, lustrous, dark violet to brownish-red needles, m. p. 113°, is produced. The oxidation is best carried out by heating an alcoholic solution of the thiodiazole with hydrochloric acid and amyl nitrite.

On treatment with nitrous acid the thiodiazole forms a *nitrosoamine*, which is converted by boiling with alcohol or benzene into the above azo-compound. That the sulphur atom of the azo-compound is contained in the ring is proved by its stability towards mercuric oxide, no action taking place even at 140°.

When boiled with concentrated hydrochloric acid, *s*-diphenylthiocarbamylhydrazide loses aniline, yielding *anilinothiolthiodiazole*,

$$\begin{matrix} N\text{——}N \\ \| \\ C(SH)\cdot S \end{matrix}\!\!>\!C\cdot NHPh \quad \text{or} \quad \begin{matrix} N\text{—}NH \\ \| \\ C(SH)\cdot S \end{matrix}\!\!>\!C:NPh,$$

which crystallises in white needles, and has been previously described by Freund and Imgart (A., 1895, i, 400) as a phenyldithiourazole, $\begin{matrix} NH\cdot CS \\ | \\ NH\cdot CS \end{matrix}\!\!>\!NPh$.

Anilinothiolthiodiazole reacts with methyl iodide and alcoholic potassium hydroxide, yielding *anilinomethylthiolthiodiazole*,

$$\begin{matrix} N\text{——}N \\ \| \\ C(SMe)\cdot S \end{matrix}\!\!>\!C\cdot NHPh.$$

This crystallises in lustrous, colourless, glassy needles or large columns,

m. p. 127°, and has also been obtained by the removal of hydrogen sulphide from methyl thiocarbanilinodithiocarbazinate,

$$SH\cdot C(NPh)\cdot NH\cdot N:C(SH)\cdot SMe.$$

Anilinobenzylthiolthiodiazole, $C_{15}H_{13}N_3S_2$, prepared in a similar manner, using benzyl chloride, forms pale yellow needles, m. p. 141°. That the above alkyl derivatives contain an imino-group has been shown by the preparation of a *nitrosoamine*, $C_9H_8ON_4S_2$, crystallising in needles, m. p. 84—85°, by the action of nitrous acid on the methyl derivative.

When heated at 100° with benzyl chloride and alcoholic potassium hydroxide, the methyl derivative is converted into *benzylanilinomethylthiolthiodiazole*, $C_{16}H_{15}N_3S_2$, which forms transparent prisms, m. p. 85°, and yields a *hydrochloride*, m. p. 169°.

The diacetyl derivative of anilinothiolthiodiazole, m. p. 252°, described by Freund and Imgart (*loc. cit.*), readily loses one of its acetyl groups on crystallisation of alcohol. The acetyl group which is so readily removed must be attached to the sulphur of the atom, and the monoacetyl derivative, thus formed, accordingly receives the formula $\begin{matrix} N\text{——}N \\ \| \\ C(SH)\cdot S \end{matrix}\!\!>\!C\cdot NPhAc$ or $\begin{matrix} N\text{—}NAc \\ \| \\ C(SH)\cdot S \end{matrix}\!\!>\!C:NPh.$

In view of the above results the dithiourazoles described by Freund and Imgart must be considered as amino- or imino-tetrahydrothiodiazoles, whilst the aminothiourazoles are probably di-iminotetrahydrothiodiazoles. F. B.

Colour Bases of the Quinoneimide Dyes. I. FRIEDRICH KEHRMANN, EM. HAVAS, and EUGÈNÈ GRANDMOUGIN (*Ber.*, 1913, **46**, 2131—2138).—An investigation of the quinoneimide colouring matters, which brings to light certain analogies with the triphenylmethane colours. The occurrence of chemical change was detected spectroscopically.

If a solution of safranine in water is treated with alkali and a layer of ether placed on the surface, the two red layers exhibit quite different absorption spectra; the same difference holds for the two layers in the case of the alkylated safranines, but the colours of the ether-soluble bases are in all cases strikingly similar. As the ammonium bases are insoluble in water, the ethereal solutions must contain the imino-base; on shaking with water partial hydration occurs, and a portion of the imino-base passes from the ether as the azonium base and imparts to the water the colour of the original salt. These azonium bases, which conduct the electric current, precipitate ferric hydroxide from ferric solutions, and are generally more stable than the analogous triphenylmethane bases, can also be obtained by the action of moist silver oxide. The equilibrium $NH_2R + H_2O \longrightarrow NH_3R\cdot OH$ also shows its effect in the action of much potassium hydroxide, when the excess of hydroxyl ion causes practically all the coloured substance to pass into the ethereal layer as the imino-base. To the substance soluble in water is attributed the structure

$$NH_2\cdot C_6H_3<\begin{matrix}\text{——}N\\ NPh(OH)\end{matrix}>C_6H_3\cdot NH_2,$$

corresponding with the salts, for example,

$$NH_2\cdot C_6H_3{<}\genfrac{}{}{0pt}{}{\text{——N}}{NPhCl}{>}C_6H_3\cdot NH_2,$$

and to the base soluble in ether either

$$NH_2\cdot C_6H_3{<}\genfrac{}{}{0pt}{}{\text{——N}}{NPh}{>}C_6H_3\text{:}NH \text{ or}$$

$NH_2\cdot C_6H_3{<}\genfrac{}{}{0pt}{}{\text{——N}}{NPh}{>}C_6H_3\cdot NH$, preferably the former as it better expresses the analogy to the parent substance ammonia in which the valency passes from three to five in salt-formation.

Indamine, the simplest quinoneimide dye, closely resembles safranine in spectrum, thus indicating similarity in constitution, namely, $NH_2\cdot C_6H_4\cdot N\text{:}C_6H_4\text{:}NH$; when shaken with water, however, it does not undergo any appreciable hydration to the corresponding ammonium base, indicating the less basicity of ammonium nitrogen compared with azonium nitrogen.

Tetraethylsafranine, with dilute potassium hydroxide or moist silver oxide, yields only the azonium base, which is insoluble in ether, but as with crystal-violet, on treatment with concentrated alkali, an ethyl radicle is eliminated with formation of triethylsafranine.

With the thiazine dyes, the introduction of successive methyl groups as with safranine, produces an additive effect in the shifting of the absorption band. Methylene-blue like tetraethylsafranine undergoes scission of one and even two methyl groups under the action of potassium hydroxide. The other ethylated thiazines when treated with alkali yield the ether soluble imino-bases, which on shaking with water pass into the thionium bases with simultaneous assumption of the blue colour characteristic of the salts. D. F. T.

Bisthiohydantoins. GEORG FRERICHS and H. HÖLLER (*Annalen*, 1913, **398**, 256—264).—*Bisthiohydantoin*,

$$\begin{array}{l}CH_2\text{—}CO\\ S\cdot C(\text{:}NH)\end{array}{>}N\cdot N{<}\begin{array}{l}CO\text{——}CH_2\\ C(\text{:}NH)\cdot S\end{array},$$

prepared by boiling bisthiocarbamide with aqueous chloroacetic acid, is a colourless, crystalline powder and possesses more pronounced acid properties than thiohydantoin itself. It is easily soluble in alkali hydroxides and carbonates and in aqueous ammonia; the *potassium* salt, $C_6H_6O_2N_4S_2,2KOH$, and *barium* salt, $C_6H_6O_2N_4S_2,Ba(OH)_2$, are crystalline substances. By treatment with methyl or ethyl iodide and *N*/2-potassium hydroxide, an alcoholic solution of bisthiohydantoin is readily converted at the ordinary temperature into NN-*dimethylbisthiohydantoin*, $C_8H_{10}O_2N_4S_2$, m. p. above 270°, colourless needles, or NN-*diethylbisthiohydantoin*, m. p. 224°, neither of which has acidic properties.

Bisthiocarbamide reacts in a similar manner with α-bromopropionic acid and with α-bromobutyric acid. 4 : 4′-*Dimethylbisthiohydantoin*, $\begin{array}{l}CHMe\cdot CO\\ S\cdot C(\text{:}NH)\end{array}{>}N\cdot N{<}\begin{array}{l}CO\text{———}CHMe\\ C(\text{:}NH)\cdot S\end{array}$, m. p. above 280° (decomp.), forms a *barium* salt, $C_8H_{10}O_2N_4S_2,Ba(OH)_2$, an NN-*dimethyl* derivative, m. p.

255—256°, and NN-*diethyl* derivative, m. p. 187°. 4 : 4′-*Diethylbisthiohydantoin*, m. p. 225—226°, forms a *barium* salt,

$$C_{10}H_{14}O_2N_4S_2,Ba(OH)_2,$$

an NN-*dimethyl* derivative, m. p. 216—217°, and NN-*diethyl* derivative, m. p. 154°. C. S.

The Anomalies of Uric Acid Solubility (Colloidal Uric Acid). HEINRICH SCHADE and E. BODEN (*Zeitsch. physiol. Chem.*, 1913, **86**, 238—243. Compare this vol., i, 404).—Polemical in reply to Lichtwitz (this vol., i, 657). W. D. H.

Action of Hydrazine on the 2 : 4-Dichlorophenylhydrazones of Ethyl α-Chloro- and α-Amino-glyoxylates and the Decomposition of Phenylazoacetoacetamide by Chlorine. Formation of the 2 : 4-Dichlorophenylhydrazone of α-Chloroglyoxylamide and its Basic Derivatives. CARL BÜLOW and PETER NEBER (*Ber.*, 1913, **46**, 2032—2045. Compare this vol., i, 207).—The 2 : 4-*dichlorophenylhydrazone* of *α-hydrazinoglyoxylhydrazide*,

$$C_6H_3Cl_2\cdot NH\cdot N{:}C(NH\cdot NH_2)\cdot CO\cdot NH\cdot NH_2,$$

is formed when hydrazine hydrate acts on an alcoholic solution of the 2 : 4-dichlorophenylhydrazone of ethyl α-chloroglyoxylate under definite conditions which are fully described in the original. It forms straw-yellow leaflets, which rapidly decompose on exposure to air and light, which darken at 155°, and have m. p. 160° (decomp.). It gives an orange-red colour with cold concentrated sulphuric acid which becomes pale, dirty yellow on warming. When warmed with benzaldehyde in alcoholic solution, it yields the corresponding *benzylidine* derivative, $C_6H_3Cl_2\cdot NH\cdot N{:}C(NH\cdot N{:}CHPh)\cdot CO\cdot NH\cdot N{:}CHPh$, yellow needles, m. p. 218° (decomp.).

When an alcoholic solution of the 2 : 4-dichlorophenylhydrazone of ethyl α-aminoglyoxylate is warmed with hydrazine hydrate, the 2 : 4-*dichlorophenylhydrazone* of *α-aminoglyoxylhydrazide*,

$$C_6H_3Cl_2\cdot NH\cdot N{:}C(NH_2)\cdot CO\cdot NH\cdot NH_2,$$

is obtained in long, pale brown needles, m. p. 230° (decomp.). In contrast to the "hydrazidrazone hydrazide" described above, this substance only gives a pale yellow colour with concentrated sulphuric acid, from which the conclusion is drawn that the hydrazino-group attached to the α-carbon atom is the cause of the delicate halochromic property. The presence of the hydrazino-group is established by the preparation of the *benzylidine* derivative,

$$C_6H_3Cl_2\cdot NH\cdot N{:}C(NH_2)\cdot CO\cdot NH\cdot N{:}CHPh,$$

yellow needles.

The 2 : 4-*dichlorophenylhydrazone* of *α-aminoglyoxylacetylhydrazide*, $C_6H_3Cl_2\cdot NH\cdot N{:}C(NH_2)\cdot CO\cdot NH\cdot NHAc$, is formed when a mixture of the 2 : 4-dichlorophenylhydrazone of ethyl α-aminoglyoxylhydrazide and acetic anhydride is allowed to evaporate at the ordinary temperature. It forms white crystals, m. p. 233°. Its constitution is established by the fact that it does not yield a benzylidine derivative when boiled with benzaldehyde in alcoholic solution, and that it immediately yields a cloudy solution when sodium nitrite solution is added to a solution of it in dilute acid.

An attempt was made to confirm this conclusion in the following manner. The 2 : 4-*dichlorophenylhydrazone* of *ethyl α-acetylaminoglyoxylate*, $C_6H_3Cl_2 \cdot NH \cdot N:C(NHAc) \cdot CO_2Et$, white needles, m. p. 153° after previous softening, was prepared by the action of cold acetic anhydride on the 2 : 4-dichlorophenylhydrazone of ethyl α-aminoglyoxylate. When an alcoholic solution of this substance was warmed with hydrazine hydrate, a *product*, $C_{10}H_9ON_5Cl$, white needles, m. p. 205°, was obtained, which yielded a *benzylidene* derivative, and had the formula (1) $\begin{array}{l} C_6H_3Cl_2 \cdot NH \cdot N:C \cdot N:CMe \\ \qquad\qquad\qquad\quad | \qquad | \\ \qquad\qquad\qquad\; CO—N \cdot NH_2 \end{array}$, or

$$(2)\ \begin{array}{l} C_6H_3Cl_2 \cdot N \cdot N:C \cdot CO \cdot NH \cdot NH_2 \\ \qquad\qquad\; | \qquad | \\ \qquad\quad MeC{=\!=}N \end{array},$$

and was formed from the intermediate hydrazide,

$$C_6H_3Cl_2 \cdot NH \cdot N:C(NHAc) \cdot CO \cdot NH \cdot NH_2.$$

The 4-*chlorophenylhydrazone* of *ethyl α-aminoglyoxylate*,

$$C_6H_4Cl \cdot NH \cdot N:C(NH_2) \cdot CO_2Et,$$

is formed by the action of alcoholic ammonia on the 4-chlorophenylhydrazone of ethyl α-chloroglyoxylate (*loc. cit.*). It has m. p. 158°, and can be distilled without decomposition.

The 2 : 4-dichlorophenylhydrazone of ethyl α-chloroglyoxylate is best obtained by the action of chlorine on a solution of ethyl phenylazoacetoacetate in acetone. The advantage gained by the substitution of acetone for chloroform (*loc. cit.*) is that the mother liquors from one preparation can be used as solvent for a succeeding preparation, and this procedure has a favourable effect on the yield.

The 2 : 4-*dichlorophenylhydrazone* of *α-chloroglyoxylamide*,

$$C_6H_3Cl_2 \cdot NH \cdot N:CCl \cdot CO \cdot NH_2,$$

m. p. 232°, is obtained when chlorine is passed into a solution of phenylazoacetoacetamide in glacial acetic acid or alcohol. It is readily soluble in potassium hydroxide. Piperidine converts it into a *substance*, m. p. 136—136·5°, which, at a higher temperature, decomposes suddenly with evolution of a volatile oil. With pyridine, it yields pale flesh-coloured *needles*, m. p. 220—221°. Investigation of these compounds is not completed. The 2 : 4-dichlorophenylhydrazone of ethyl α-aminoglyoxylamide, previously described (*loc. cit.*), is more conveniently obtained by the action of cold alcoholic ammonia on the above amide, and has m. p. 176° instead of 170° as previously given. It forms a *platinichloride*, crystallising in small, yellow octahedra, reduces boiling gold chloride solution, and gives a mirror with cold ammoniacal silver nitrate.

The 2 : 4-*dichlorophenylhydrazone* of *α-hydrazinoglyoxylamide*,

$$C_6H_3Cl_2 \cdot NH \cdot N:C(NH \cdot NH_2) \cdot CO \cdot NH_2,$$

is obtained by the action of hydrazine hydrate on an alcoholic solution of the 2 : 4-dichlorophenylhydrazone of α-chloroglyoxylamide. It has m. p. 157°, and gives an orange coloration with concentrated sulphuric acid. With an alcoholic solution of benzaldehyde, it yields the corresponding *benzylidene* derivative,

$$C_6H_3Cl_2 \cdot NH \cdot N:C(NH \cdot N:CHPh) \cdot CO \cdot NH_2,$$

yellow needles, m. p. 205°.

In order to determine which of the two amino-groups in the 2 : 4-di-

chlorophenylhydrazone of α-aminoglyoxylamide is more loosely held, this substance was energetically treated with an excess of hydrazine hydrate, when the 2 : 4-dichlorophenylhydrazone of α-aminoglyoxylhydrazide was obtained, thus showing the amino-group of the $-CONH_2$ radicle to be the more readily replaceable. H. W.

Azo-dyes Derived from 2-Hydroxy-3-naphthoic Acid. ANUKUL CHANDRA SIRCAR and EDWIN ROY WATSON (*J. Soc. Chem. Ind.*, 1913, **32**, 642—644).—In a previous paper (A., 1912, i, 1037) the authors have described attempts to prepare dyes similar in constitution to benzeneazosalicylic acid, which would possess the same all-round fastness as this dye, but with the colour deepened to red, violet, blue or black. These attempts were not, however, successful as the colour was deepened towards maroon and brown, instead of towards violet and blue as desired. Since many azo-dyes of not more complicated structure possess the desired shades, the authors have examined a list of the well-known azo-dyes prepared from naphtholsulphonic acids, from which they are led to the conclusion that the relative position of the hydroxyl- and chromophore-group is the determining factor in the colour of the dye, the *ortho*-position favouring red, violet, and blue shades, and the *para*-position giving brown shades. A series of dyes have therefore been prepared by coupling diazonium salts with 2-hydroxy-3-naphthoic acid, the hydroxyl group thus being in the ortho-position to the azo-group. The shades obtained are very satisfactory, including fiery-red, claret, cherry-red, brownish-purple, bluish-purple and black. The dyeings on chrome-mordanted wool are quite satisfactory as regards fastness to light and acid test, but are not so resistant to soaping, alkalis, and milling as they were expected to be.

Naphthalene-α-1-azo-2-hydroxy-3-naphthoic acid, prepared from diazotised α-naphthylamine and 2-hydroxy-3-naphthoic acid, forms greenish-red, rhombic prisms, m. p. 236°, whereas Mohlau and Kriebel (A., 1896, i, 242) gave m. p. about 182°.

m-*Xylene-1-azo-2-hydroxy-3-naphthoic acid*,

$$C_6H_3Me_2\cdot N:N\cdot C_{10}H_5(OH)\cdot CO_2H,$$

crystallises in deep red needles, m. p. 240—242°.

p-*Ethoxybenzene-1-azo-2-hydroxy-3-naphthoic acid*,

$$OEt\cdot C_6H_4\cdot N:N\cdot C_{10}H_5(OH)\cdot CO_2H,$$

deep red, needle-shaped crystals with green reflex, has m. p. 231° after softening at a somewhat lower temperature.

m-*Nitrobenzene-1-azo-2-hydroxy-3-naphthoic acid*,

$$NO_2\cdot C_6H_4\cdot N:N\cdot C_{10}H_5(OH)\cdot CO_2H,$$

prepared from diazotised *m*-nitroaniline and 2-hydroxy-3-naphthoic acid, separates from nitrobenzene in beautiful red needles, which do not melt at 275°. The corresponding *dye* from *p*-nitroaniline forms fine hair-like, red needles, which do not melt at 285°.

Benzeneazobenzene-1-azo-2-hydroxy-3-naphthoic acid,

$$NPh:N\cdot C_6H_4\cdot N:N\cdot C_{10}H_5(OH)\cdot CO_2H,$$

is formed when a diazotised solution of *p*-aminoazobenzene (Hewitt, T., 1909, **95**, 1394) is dropped into an alkaline solution of 2-hydroxy-3-naphthoic acid. It crystallises in magenta-red needles with a green reflex and does not melt below 275°.

Diazotised disulphonaphthalene-β-azo-α-naphthylamine combines with an alkaline solution of 2-hydroxy-3-naphthoic acid to yield the *sodium* salt of *disulphonaphthalene-β-azonaphthalene-α-*1*-azo-*2*-hydroxy-*3*-naphthoic acid*, $C_{10}H_5(SO_3Na)_2{\cdot}N{:}N{\cdot}C_{10}H_6{\cdot}N{:}N{\cdot}C_{10}H_5(OH){\cdot}CO_2Na$, which could not be converted into the free acid by boiling with any mineral acid, and forms a black powder. Similarly, *sodium benzidine-bis-*1-(*azo-*2*-hydroxy-*3*-naphthoate*), $C_{12}H_8[N{:}N{\cdot}C_{10}H_5(OH){\cdot}CO_2Na]_2$, is prepared by coupling a diazotised solution of benzidine with an alkaline solution of 2-hydroxy-3-naphthoic acid. It forms a green powder from which the corresponding free acid is not obtained by means of boiling mineral acids.

The colorations produced when the dyes are dissolved in alkalis or in concentrated sulphuric acid together with the shades produced on unmordanted or chrome-mordanted wool are also described. H. W.

Azo-colouring Matters of Phenyl*iso*oxazolone. ANDRÉ MEYER (*Compt. rend.*, 1913, **156**, 1992—1995. Compare A., 1911, i, 341).—As the azo-derivatives previously prepared by the author (*loc. cit.*) contained no salt-forming groups and so were unsuited for dyeing purposes, he has now obtained various compounds chemically suitable for dyes, and has compared them with the corresponding pyrazolone compounds.

*Sodium phenyl*iso*oxazoloneazobenzene-*p*-sulphonate*,

$$C_9H_6O_2N{\cdot}N_2{\cdot}C_6H_4{\cdot}SO_3Na,2H_2O,$$

golden-yellow spangles, obtained by applying a diazotised solution of sulphanilic acid, dyes silk golden-yellow in a bath containing acetic acid.

*Sodium phenyl*iso*oxazoloneazo-*m*-xylene-*o*-sulphonate*, an orange, crystalline powder, with $2H_2O$, dyes silk and wool a deep orange-yellow.

*Sodium phenyl*iso*oxazolone-*1*-azonaphthalene-*4*-sulphonate* forms orange-brown spangles with $2H_2O$; it dyes silk and wool a reddish-maroon.

*Sodium phenyl*iso*oxazolone-*8*-azonaphthalene-*2 : 6*-disulphonate*, orange crystals with $2H_2O$.

The following substantive dyes were prepared by combining a molecule of a tetrazotised solution of benzidine with a molecule of phenyl*iso*oxazolone, and subsequently coupling the free diazo-radicle with a molecule of a phenol or an amine.

*Sodium phenyl*iso*oxazoloneazodiphenylazonaphthylaminesulphonate*, $C_9H_6O_2N{\cdot}N_2{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_5(NH_2){\cdot}SO_3Na$, obtained by applying naphthionic acid for the second coupling reaction, has a red colour changing to blue on addition of acid; it dyes cotton a scarlet-red.

*Sodium phenyl*iso*oxazoloneazo-*o*-ditolylazo-*1*-amino-*8*-naphthol-*3 : 6*-disulphonate* is a reddish-violet powder, changed to bluish-violet by a mineral acid, which dyes a deep violet.

*Sodium phenyl*iso*oxazoloneazodianisylazo-*8*-amino-*1*-naphthol-*3 : 5*-disulphonate* dyes fabric violet.

*Sodium phenyl*iso*oxazoloneazodiphenylazosalicylate* is a deep brown powder, which dyes cotton orange.

The above dyes are not nearly as fast to light as the pyrazole analogues, the substantive colours being even less stable than the

acid colours mentioned first; ultraviolet radiation affected the colours much more rapidly than ordinary light. The replacement of the imino-group in such compounds by an oxygen atom evidently provokes a weakening towards photochemical influence according with the lessening in stability towards ordinary chemical agents. D. F. T.

Existence of Phenyldi-imide. STEFAN GOLDSCHMIDT (*Ber.*, 1913, **46**, 2300. Compare this vol., i, 768).—In ethereal solution *p*-bromophenyldi-imide decomposes mainly into *p*-bromobenzene and nitrogen; quinol and a small amount of a colourless, crystalline substance are also produced in the decomposition. F. B.

The Density and Volume of Some Protein Solutions. AMEDEO HERLITZKA (*Zeitsch. Chem. Ind. Kolloid*, 1913, **12**, 309).—Polemical (compare Chick and Martin, this vol., i, 40; Herlitzka, A., 1910, ii, 1013; Gayda, A., 1912, i, 399). J. F. S.

Changes in the Physical Condition of Colloids. XV. Electrochemical Investigations on Acid Protein. KAICHIRO MANABE and JOH. MATULA (*Biochem. Zeitsch.*, 1913, **52**, 369—408).—The investigations are a continuation of those of Pauli. The present authors have been chiefly concerned in the determination of the diminution of hydrogen and chlorine ion concentration when hydrochloric acid is added to carefully dialysed solutions of proteins. The hydrogen ion concentrations were determined in the ordinary manner, with the employment of a shaking electrode devised by Pauli, which is figured in the text. The chlorine ion concentration was determined by shaking the solution under investigation with calomel and mercury, and preparing from this mixture a calomel electrode in the ordinary way. The *E.M.F.* was determined when this was balanced against a calomel electrode containing a definite concentration of potassium chloride ($N/10$ or N). A figure is given in which the *E.M.F.* produced is plotted against the hydrogen ion exponent of the mixture under investigation measured against both N and $N/10$-potassium chloride. The form of vessel used for these investigations is also figured in the text. In the cases of albumins, or ox-serum, the addition of acids up to a concentration of $0{\cdot}03N$ is accompanied by an increased binding of the free hydrogen atoms; there are, however, only a relatively small number of chlorine ions bound at the same time, and an equality between the hydrogen and chlorine ions bound is only reached in higher concentrations of the acids. If the difference between the bound chlorine and hydrogen ions is plotted against the hydrochloric acid concentration, it will be found that it gradually reaches a maximum and then falls. The maximum corresponds with the maximum of viscosity of the mixture. These results are in accordance with the theory of Pauli, according to whom an albumin hydrochloride is formed, which dissociates in solution giving rise to albumin and chlorine ions; the high viscosity of the solutions is due to the former. With the addition of increasing amounts of hydrochloric acid, the ionic dissociation of the albumin salt is depressed, and the viscosity

diminishes; an equality between the bound chlorine and hydrogen ions is then also gradually attained. The whole of the hydrogen ions added are never completely bound, and the amount of hydrolytic dissociation of the albumin salt has therefore also been ascertained. For this purpose, the hydrogen ion concentration was determined in an ox-serum solution containing 0·02*N*-hydrochloric acid in undiluted condition and when diluted with twice and four times its bulk of water. From the numbers obtained, it was calculated that the hydrolytic dissociation amounted to 4·4% in the twice diluted solution, and to 15·3% in the four times diluted solution. The results obtained with gelatin are somewhat different to those obtained with albumins. In this case, there is but little binding of the chlorine ions, even in higher concentrations of acids; the explanation offered in this case is, that the chloride is strongly dissociated even in presence of a large excess of acid. This does not, however, explain the diminution of the viscosity in the higher concentrations; it is suggested that the acid causes, in this case, a degradation of the protein. The effect of the addition of salts to the acid protein solutions was also investigated. This addition causes a small increase in the bound hydrogen ions in low concentrations of acids (0·005*N*-HCl). Such an increase cannot, however, be detected with certainty in the higher concentrations. It is assumed that in this case the salt attaches itself to the acid protein by means of accessory valencies. The actions possible in this case are discussed in some detail. S. B. S.

The Tyrosine Content of Proteins. OTTO FOLIN and WILLEY DENIS (*J. Biol. Chem.*, 1913, **14**, 457—458).—Polemical. A reply to Abderhalden and Fuchs (this vol., i, 409). The authors insist that their tyrosine figures are more correct than those hitherto recorded. W. D. H.

The Factors Concerned in the Solution and Precipitation of Euglobulin. (Miss) HARRIETTE CHICK (*Biochem. J.*, 1913, **7**, 318—340).—Re-determination of the isoelectric point of euglobulin shows that it coincides with the point of most rapid agglutination, namely, at a hydrogen ion concentration of about 3×10^{-4} normal. Solution and dispersion of euglobulin by electrolysis is influenced by the nature (especially the valency) of the constituent ions. There are two general types: (1) electrical type of solution in which the dispersion is accompanied by the acquisition of an electric charge by the protein molecules; and (2) molecular type in which the dissolved protein is electrically neutral.

When euglobulin is denaturated by heat, it no longer possesses the property of forming the molecular type of solution. The reaction of acid and alkaline solutions of euglobulin is greatly affected by the addition of electrolytes; the influence of electrolytes in causing precipitation is affected by changes in reaction. Euglobulin in common with caseinogen and vegetable globulins presents an interesting analogy with heat denaturated protein, but differs from it in its capacity to form solutions with electrolytes in which the protein particles are electrically neutral. W. D. H.

Do Gliadin and Zein Yield Lysine on Hydrolysis? THOMAS B. OSBORNE and CHARLES S. LEAVENSWORTH (*J. Biol. Chem.*, 1913, **14**, 481—487).—Small quantities of lysine (as picrate) were separated from the hydrolytic products of gliadin from wheat which had been prepared with great care. Zein yielded none. W. D. H.

Phonoporphyrin, a New Degradation Product of Hæmin. OSCAR PILOTY and HERMANN FINK (*Ber.*, 1913, **46**, 2020—2026).—In continuation of their work on the molecular size of hæmin and hæmoglobin (A., 1912, i, 923), the authors have further investigated the reduction of hæmin by hydrogen iodide, and have shown that, in addition to mesoporphyrin, a second substance, *phonoporphyrin*, may be isolated, and that the total weight of products thus obtained is 90% of that theoretically derivable from hæmin. Their previous conclusion that the molecular weight of hæmin is 1303 is thus confirmed. The occurrence of phonoporphyrin among the decomposition products of hæmin seems to have been previously observed by Nencki and Zaleski (A., 1901, i, 434), Zaleski (A., 1903, i, 217), and Fischer and Meyer-Betz (this vol., i, 111), but the substance was not further investigated.

When hæmin is boiled with glacial acetic acid, hydriodic acid (D 1·96), red phosphorus and a little water, and the mixture, after removal of phosphorus, poured into a large bulk of water, a mixture of mesoporphyrin and phonoporphyrin is obtained from which the former may be removed by repeated extraction with large quantities of boiling dilute hydrochloric acid. The residual phonoporphyrin, after purification by solution in sodium hydroxide and precipitation with acetic acid, consists of a dark brown, amorphous powder, analyses of which agree most nearly with the formula $C_{34}H_{36}O_7N_4$ or

$$C_{36}H_{40}O_7N_4.$$

It is not obtained when mesoporphyrin is acted on by hydrogen iodide under the above conditions, and hence cannot be formed as an intermediate product of the formation of mesoporphyrin from hæmin.

When boiled with 9% methyl alcoholic hydrochloric acid, phonoporphyrin yields the corresponding *methyl* ester, $C_{36}H_{40}O_7N_4$ or $C_{38}H_{44}O_7N_4$, which forms minute, brown particles showing no distinct crystalline form, and does not soften at 225°. The similarly prepared *ethyl* ester, $C_{38}H_{44}O_7N_4$ or $C_{40}H_{48}O_7N_4$, decomposes at 255°.

Oxidation of phonoporphyrin in sulphuric acid solution with chromic acid gives methylethylmaleinimide and hæmatic acid, $C_8H_9O_4N$.

H. W.

Histone and its Preparation. WALTER H. EDDY (*Biochem. Bull.*, 1913, **2**, 419—440).—Histone, obtained by precipitating aqueous extracts of thymus with ammonia, is different from that obtained by saturation with sodium chloride. The former is not soluble in water, and contains more nitrogen; the latter is soluble in water, and contains combined chlorine.

The preliminary use of alcohol to precipitate histone and the other proteins in the glands is preferable to direct water-extraction. Bang's

contention that ammonia does not precipitate histone in the absence of salts is incorrect; their presence, however, facilitates the process.
W. D. H.

Chondroitin-sulphuric Acid. PHŒBUS A. LEVENE and FREDERICK B. LA FORGE (*J. Biol. Chem.*, 1913, **15**, 155—160).—For the first time all the components of this acid were isolated and identified; they are those assumed on indirect evidence by Schmiedeberg, namely, sulphuric acid, acetic acid, glycosamine and glycuronic acid. Schmiedeberg's view of the molecular structure of the molecule needs revision, and the new formula is set out in full. It assumes a glucosidic union of two chondrosin molecules, which explains the reason why chondrosin is a reducing agent, and chondroitin-sulphuric acid is not.
W. D. H.

Sphingomyelin. I. The Presence of Lignoceric Acid among the Hydrolytic Products of Sphingomyelin. PHŒBUS A. LEVENE (*J. Biol. Chem.*, 1913, **15**, 153—154).—Thudichum considered that the principal fatty acid in sphingomyelin was isomeric with stearic acid. This is not so; the acid in question has the composition $C_{24}H_{48}O_2$, melts at 81°, and forms an ethyl ester melting at 55—56°; hence it is lignoceric acid. W. D. H.

The Components of Sphingomyelin. PHŒBUS A. LEVENE (*J. Exper. Med.*, 1913, **18**, 679—680).—By the hydrolysis of this phosphatide the author has obtained in addition to lignoceric acid (preceding abstract) a base, $C_{15}H_{31}O_2N$, which is isolated in the form of its sulphate, m. p. 225°. S. B. S.

Myokynine. DANKWART ACKERMANN (*Zeitsch. Biol.*, 1913, **61**, 373—378. Compare this vol., i, 181).—Myokynine may be prepared from horse as well as from dog muscle. Myokynine dichloride from the dog muscle has $[\alpha]_D^{20}$ $-11{\cdot}09°$, that from horse muscle has $[\alpha]_D^{20}$ $-13{\cdot}5°$.

Myokynine can be esterified by means of ethyl alcohol and dry hydrogen chloride; it accordingly contains a carboxyl group. It does not give a pyrrole reaction when distilled with zinc dust. Since an unbranched chain of four carbons in presence of basic nitrogen usually forms pyrrole under these conditions, the presence of such a grouping in myokynine is doubtful. E. F. A.

Did Von Wittich Antedate Ostwald in the Definition of Enzyme Action? WILLIAM N. BERG (*Biochem. Bull.*, 1913, **2**, 441—445).—Quotations from von Wittich's writings of 1872–4 show that his conception of enzyme action was much the same as that of Ostwald. He was probably also the first to describe the adsorption of pepsin by solid proteins, such as fibrin. Abderhalden and others who have utilised the method of recent years have not referred to this.
W. D. H.

Amyloclastic Action of Malt and the Reaction of the Medium. HENRI VAN LAER (*8th Inter. Cong. App. Chem.*, 1912, **14**, 203—213).—The influence of the addition of varying quantities of acid and alkali on malt extracts of different origin has been studied.

The inhibition resulting from the presence of an excess of acid or alkali is due to the formation of an inactive compound between the enzyme and the acid or alkali. The diminution in the activity of diastase acting in presence of an excess of hydrogen or hydroxyl ions is due to three principal causes: (1) The destruction of a portion of the enzyme—this is non-reversible; (2) the temporary inactivity of part of the enzyme; (3) the increase in the activity due to the disappearance of some of the ions due to the influence of the steadiers (buffers).

Diastase has an amphoteric character, and its specific properties depend on both the acid and basic groups which it contains.

E. F. A.

The Nature of Diastase (Amylase). HENRI VAN LAER (*Bull. Acad. Roy. Belg.*, 1913, 395—451).—A critical examination of previous work on the nature of diastase leads to the conclusion that the enzyme converting soluble starch into maltose is to be regarded as constituted by the association of a colloidal organic nitrogen compound with electrolytes, so allowing the former to act as a catalytic agent, provided always that the reaction of the medium is defined within narrow limits.

Diastase as it exists in cereals differs from the enzyme as used in solution. In the cereal, it is partly present as an insoluble zymogen in combination with protein substances which are capable of attack by pepsin; in solution, the enzyme is free and unaltered either by papain or pepsin.

The organic complement of diastase is digested by a solution of pepsin in hydrochloric acid. It is also modified by phosphotungstic acid like other proteins.

In solutions of diastase the dissolved matter is the more active as the amount of nitrogen in solution increases. The amount of pentosan present bears no relation to the activity of the enzyme. The conclusions are confirmed by extracting powdered diastase with successive equal amounts of water.

In dried preparations the enzyme slowly becomes inactive.

The nitrogen complement of diastase behaves as an amphoteric substance.

The mineral matter is essential for activity, but there is a maximum in the amount of neutral salts, above which any further increase will not cause increased enzyme activity.

At present all the established facts relative to the dynamics of diastatic action are best interpreted on the basis of the properties of emulsoids.

E. F. A.

The Relationship Between the Active and Inactive Condition of a Ferment and its Surface Tension. M. J. GRAMENIZKI (*Biochem. Zeitsch.*, 1913, **52**, 142—154).—Taka-diastase

solutions, as the author has already shown, partly recover the activity which has been lost by heating when they are kept. It is now shown that the surface-tensions of the solutions diminish on heating, but again increase on keeping. From these facts, the conclusion is drawn, that there is a connexion between the fermentative activity of a solution and its surface tension. S. B. S.

Saccharification of Starch by Koji Diastase in Presence of Acids and Salts. F. ANDO (*8th Inter. Cong. App. Chem.*, 1912, **14**, 13—24).—Experiments made with an extract of Koji diastase and potato starch in presence of a variety of mineral salts and acids are described. The presence of neutral and acid salts, with the exception of acid calcium phosphate, is up to a certain point favourable to the enzyme. Excess of the salts retards action except in the case of manganese salts.

Alkaline salts, with the exception of potassium phosphate, retard the saccharification. Small quantities of mineral acids accelerate action; organic acids uniformly retard it. Action takes place in solutions of 30% alcohol. E. F. A.

Some Conditions Affecting the Activity and Stability of Certain Ferments. JOHN H. LONG and WILLIAM A. JOHNSON (*J. Amer. Chem. Soc.*, 1913, **35**, 895—913).—It is suggested that for diastasic comparisons, the starch paste should be made from starch prepared in the laboratory from sound ripe potatoes, and subsequently well washed. In experiments in which 0·1 gram of sodium chloride was present in each 100 c.c. of digesting mixture, it was found that amylolytic activity is greatest when about 25 mg. of sodium hydrogen carbonate are also added; sodium hydrogen carbonate in larger quantity retards the action without destroying any of the ferment, whilst the addition of sufficient acid to neutralise the hydrogen carbonate destroys the ferment at once. Glycerol extracts of the pancreas are very stable, but rapidly lose amylotic power after dilution, especially if kept at 40°; the presence of traces of sodium chloride exerts a considerable protecting effect. Experiments with the glycerol extract indicate that the pancreatic diastase is exceedingly sensitive towards even traces of mineral acid, such as hydrochloric acid, but that salt again exerts a protecting action; the effect of the acid, which is more marked than that of alkali, is probably due to immediate destruction of the enzyme, as neutralisation fails to restore the original activity. D. F. T.

The Nature of Enzyme Action. III. The Synthetic Action of Enzymes. WILLIAM M. BAYLISS (*J. Physiol.*, 1913, **46**, 236—266).—Reactions in the system glycerol, dextrose, glycerol-glucoside and water, as accelerated by emulsin, follow the laws deduced from mass action for an equilibrium in a reversible system, catalysed by a single enzyme. The equilibrium position is the same from whichever end it is approached; the glucoside produced is the β-form, and the same which is hydrolysed by emulsin. The reaction-rate is directly proportional (not linear, how-

ever) to the concentration of the enzyme. The final equilibrium is independent of this concentration.

Brailsford Robertson's "synthesis of paranuclein by pepsin" is not a synthesis, nor is it produced by pepsin; the substance formed is not paranuclein. It is a colloidal precipitation, and has no connexion with enzyme action.

Apparent deviations from the law illustrated should be properly investigated, and the reasons for divergence sought. It is unwise to invent new enzymes to explain difficulties. W. D. H.

The Lipases Contained in Pancreatic Cysts. KONRAD BOURNOT (*Biochem. Zeitsch.*, 1913, **52**, 155—171).—The lipases from the fluids of pancreatic cysts are similar to other animal lipases. The liquids can be filtered through paper without loss of lipolytic activity. This continually diminishes if the liquid is kept, but the residue obtained by evaporation at 20° preserves its lipolytic activity. Acids inhibit the lipolytic action, but alkalis in very low concentrations accelerate it. With small quantities of fluids (0·05—0·2 c.c.) there is a direct proportionality between the amount of enzyme and the fat saponified. For larger quantities of ferment the formulæ of Schütz and Arrhenius hold good. The Schütz law and Arrhenius' equation also agree with the time relations in fat hydrolysis and the oleic acid-glycerol fat synthesis within certain limits. Still better agreement is obtained, however, with the employment of contents calculated from the adsorption isotherm $K=X/E^m$. The maximal hydrolysis of triolein obtained was 93·5%, and the maximal synthesis in the presence of excess of glycerol was 42% of the oleic acid. S. B. S.

The Lipase of Chelidonium Seeds. KONRAD BOURNOT (*Biochem. Zeitsch.*, 1913, **52**, 172—205).—Like the ricinus lipase, the chelidonium lipase is insoluble in water, but is, to a large extent, soluble in the oils extracted by ether from the seeds. It is also somewhat soluble in a mixture of oleic acid and alcohol. Whereas, however, the ricinus lipase acts most readily on addition of acids, the chelidonium ferment acts best in the presence of water alone. Even $N/50$-acetic acid has an inhibitory effect on its action. The maximal hydrolysis obtained was 92—95%. The lipases of ricinus and chelidonium are similar, in that they do not readily hydrolyse the esters of the monohydroxy-alcohols. As the molecular weights of the fatty acids increase, the esters are more rapidly attacked by the chelidonium lipase; thus, *iso*butyl oleate and amyl palmitate undergo hydrolysis to the extent of 15—33%. The lipase, furthermore, can cause a rapid and almost complete synthesis of the esters of the higher fatty acids, which action is in marked contrast to the less complete hydrolysis of the same esters caused by the ferment. Possibly the larger quantities of water have an inhibitory action when the water of the substrate cannot form an emulsion. The *iso*butyl oleate synthesis accords with a unimolecular reaction, and there is a direct proportionality between the rate and quantity of enzyme present. The maximal synthesis is 92%. The maximal triolein synthesis is 47—50%. In the latter cases, the same final equilibrium is obtained in synthesis and hydrolysis. The final equilibrium here will depend

on the amount of water present. The seeds can be heated for fifteen minutes at 100° without any very marked deterioration of the ferment. S. B. S.

Action of Boric Acid on Zymase; Comparison with the Action of Phosphates. HENRI AGULHON (*Compt. rend.*, 1913, **156**, 1855—1858).—The author has previously shown (A., 1909, i, 621) that boric acid is remarkably inactive towards diastases in general, and has examined its action on zymase. For this purpose, sucrose or dextrose was mixed with a constant quantity of zymase in the presence of varying amounts of boric acid, the course of the reaction being followed by determining from time to time the loss in weight due to the carbon dioxide evolved. The inhibiting action of boric acid is observable even with only 10 mg. of acid per 100 c.c., whilst with one gram of acid per 100 c.c. fermentation is no longer possible. On the other hand, living yeast derived from the same source is capable of fermenting a portion of the sugar supplied to it even in the presence of boric acid of the concentration 2 in 100, from which it appears that the membrane presents contact of the boric acid with the zymase.

The inhibiting action of boric acid cannot be attributed solely to its acidity, since monosodium phosphate, which possesses the same degree of acidity as boric acid, exerts a slight favouring action. The nature of the electronegative radicle is also important. This is shown by a series of comparative experiments with borax, trisodium phosphate, trisodium citrate, and sodium carbonate, in which only the borax is found to have a marked inhibiting effect. This effect is, however, less than that observed with boric acid, so that it appears that the favouring action of the alkali compensates in some measure the inhibiting action of the electronegative radicle. H. W.

Physiological Chemistry.

The Work Done by the Lungs at Low Oxygen Pressures. ARCHIBALD V. HILL (*Proc. physiol. Soc.*, 1913, xxvii—xxviii; *J. Physiol.*, **46**).—By calculation, from known data, of the work done by the lungs in secreting oxygen (if Haldane's views are accepted) it is found that the work done per minute by the lungs is only 0·8 cal. If therefore the lung cells can secrete oxygen at all, and if they be assumed to possess an "efficiency" in performing the mechanical work of oxygen secretion of only 20%, they should, nevertheless, be well able to perform this work with an activity no greater per gram than that of the body as a whole. W. D. H.

Carbon Dioxide Excretion Resulting from Muscular Work following Forced Breathing. GEORGE O. HIGLEY (*Biochem. Bull.*, 1913, **2**, 390—392).—The sudden increase in the excretion of

carbon dioxide after the beginning of work is due to better ventilation of the lungs; the continuation of the increase is due to ventilation of the blood and tissues also. After forced breathing, followed by muscular work, the new rate of excretion is sharply defined; the further increase as the result of work is not so prompt, and comes on gradually. Some differences of detail occur according to the duration of the forced breathing. W. D. H.

The Influence of Barometric Pressure on the Excretion of Carbon Dioxide in Man. G. O. Higley (*Biochem. Bull.*, 1913, **2**, 393—402).—The degree of influence of barometric pressure on the excretion of carbon dioxide differs in different subjects. It is evidently a minor factor, the effect of which is liable to be masked by other influences, diet, exercise, etc. W. D. H.

The Effect of Altitude on Mesectic Curves. Joseph Barcroft (*Proc. physiol. Soc.*, 1913, xxx—xxxi; *J. Physiol.*, **46**).—In subjects at rest living at a high altitude there is a reduced carbon dioxide tension in the blood, and acidosis. These so nearly balance each other that the dissociation curve remains mesectic (that is, normal). This statement is illustrated by the necessary data and calculations. W. D. H.

The Relation of the Blood-salts to Cardiac Contraction. Ernest G. Martin (*Amer. J. Physiol.*, 1913, **32**, 165—183).—Calcium and sodium are not regarded as antagonistic, but each has a definite function. Calcium promotes (as Howell stated) the conversion of stable into unstable energy-yielding material; sodium (as proposed by Lingle) serves as the immediate stimulus to bring about the actual dissociation, and so to initiate the heart-beat. Neither is an exclusive agent; the preparation of dissociable material is much hampered by the accumulation of waste products, and is therefore aided by abundant supplies of oxygen or by sodium carbonate; carbon dioxide in moderate quantities, and perhaps sugar, act as direct stimulants to cardiac tissue much as sodium acts. W. D. H.

Hæmolysis by Silicic Acid. M. Liebers (*Arch. Hygiene*, 1913, **80**, 43—55).—In the system blood + silicic acid + complement, hæmolysis often takes place. The silicic acid cannot, however, always replace an ordinary amboceptor. Certain complements show the same complementing action towards sheep corpuscles charged with silica as towards the same corpuscles charged with an ordinary amboceptor. The more coarsely colloidal or turbid solutions of silica cause agglutination, and the blood does not then lake so readily when treated with the complement. The ordinary immune amboceptor in the original Wassermann reaction cannot be replaced by silica. S. B. S.

Lipolytic Action of the Blood. Francis H. Thiele (*Biochem. J.*, 1913, **7**, 275—286).—Blood and chyle contain an enzyme which can hydrolyse lecithin, but not neutral fat. When blood and chyle fat

are incubated together, the neutral fat forms an absorption compound with the protein, and is then non-extractable by ether. This compound can be broken up by peptic digestion, by alcohol, and by heating. The formation of the complex occurs in the corpuscles; serum has no such effect. It is not due to hæmoglobin, and is probably brought about by an enzyme. W. D. H.

Variations in Glycæmia during Inanition. HENRY BIERRY and (Mlle.) LUCIE FANDARD (*Compt. rend.*, 1913, **156**, 2010—2013).—The authors have already shown (this vol., i, 426) that the injection of adrenaline can induce perturbations in the glycæmia of an animal, and now bring evidence of the considerable effect on the content of sugar in the blood of dogs caused by inanition. The quantity of free sugar is fairly constant for the first twelve days, then may occasionally increase considerably, but finally decreases. The combined sugar, which is liberated on hydrolysis, commences to increase in quantity about the twelfth day and continues to increase until death. D. F. T.

The Action of the Thromboplastic Substance in the Clotting of Blood. F. W. MACRAE and A. G. SCHNACK (*Amer. J. Physiol.*, 1913, **32**, 211—218).—Calcium-free (oxalated) peptone plasma may be made to clot by the addition of calcium-free solutions of thromboplastic substance (kephalin), provided the excess of oxalate is removed by dialysis. The action of the kephalin is demonstrated more easily if some thrombin is added previously to the dialysed oxalate plasma in an amount insufficient in itself to overcome the effect of antithrombin. This result is opposed to the theory of Morawitz that the thromboplastic substance acts as a kinase in conjunction with calcium, but accords with Howell's view that kephalin facilitates clotting by neutralising antithrombin.

W. D. H.

Blood-relationship of Animals as Displayed in the Composition of the Serum-proteins. II. A Comparison of the Sera of Ox, Sheep, Hog, Goat, Dog, Cat, and Guinea-pig with Respect to their Content of Various Proteins. J. HOMER WOOLSEY (*J. Biol. Chem.*, 1913, **14**, 433—439).—The following table summarises the average results obtained:

	Percentage of the total proteins in the sera of						
	Ox.	Sheep.	Hog.	Goat.	Dog.	Cat.	Guinea-pig.
"Insoluble" globulin...	8·1	6·4	6·0	6·5	7·7	6·5	4·2
Total globulin	29·0	17·0	36·0	22·0	18·0	30·0	16·0
Total albumin	70·0	82·0	64·0	75·0	81·0	69·0	84·0

W. D. H.

The Activation of Blood-serum. CORNELIS A. PEKELHARING (*Zeitsch. physiol. Chem.*, 1913, **85**, 341—345).—When blood-serum is kept, its power to coagulate fibrinogen lessens. Morawitz attributes this to a change of thrombin into a metathrombin. Such serum

can be reactivated by adding alkali, and then neutralising; the author advances the view that the loss of activity is due to the development of inhibitory substances, and that these are destroyed by alkali. He also disagrees with Landsberg, who regards the loss of activity as due to adsorption of the thrombin by the serum proteins; and quote experiments to support his view. Among other things proved is the fact that dialysis of the serum removes the inhibitory substance or substances. Activated serum on keeping loses its activity more rapidly than serum which has not been treated with alkali. W. D. H.

The Digestive Enzymes of Cold- and Warm-blooded Animals. I. The Pepsin of the Hake and Dog. A. RAKOCZY (*Zeitsch. physiol. Chem.*, 1913, **85**, 349—371).—The pepsin of hake and dog are not identical, but show the following differences: Hake pepsin digests fibrin, serum protein, and caseinogen well, but it is less active towards edestin, and especially towards egg-albumin and elastin than dog's pepsin. Hake pepsin is adapted to work at a lower acidity than dog's pepsin; there are also differences in milk-curdling power, adsorption by elastin, velocity of action, and in optimum temperature. Hake's pepsin is only slightly inhibited at freezing point. W. D. H.

The Pepsin–Chymosin Question. WILLEM VAN DAM (*Zeitsch. physiol. Chem.*, 1913, **86**, 77—84).—Polemical against Rakoczy's views. W. D. H.

The Influence of Preliminary Heating on Peptic and Tryptic Digestion. A. H. BIZARRO (*J. Physiol.*, 1913, **46**, 267—284).—During peptic digestion, Sörensen's formaldehyde method shows that amino-acid groupings are liberated slowly, and after many days' action the time varies for different proteins. Preliminary heating of egg-white to 120—140° makes subsequent tryptic proteolysis more active; the same is true for fibrin, caseinogen, and beef; but the opposite for gelatin. The amino-acid groupings in tryptic solutions increase after fifteen hours' digestion. W. D. H.

Pancreatic Digestion. (Miss) GERTRUDE D. BOSTOCK (*Zeitsch. physiol. Chem.*, 1913, **85**, 471—492).—A study of the influence of alkali on the partition of nitrogen in the digestion of fibrin by pancreatin shows that the powers to dissolve and to split proteins are two different things. The most favourable degree of alkalinity for protein solution is between 1·2 and 1·8% of sodium carbonate. Protein cleavage is hindered by 0·6% sodium carbonate, but between 0% and 0·3% no differences were noted. An optimum concentration for cleavage was not found. The cleavage during protein tryptic digestion is as unfavourably influenced by 0·6 to 1·2% of sodium carbonate as is protein cleavage during autolysis. W. D. H.

The Influence of Carbon Dioxide on Chlorine Metabolism. ERNST LAQUEUR and J. SNAPPER (*Biochem. Zeitsch.*, 1913, **52**, 44—59).—It has been shown by Hamburger that chlorine passes from the

body fluids into tissue cells when the mixture is treated with carbon dioxide *in vitro*. Experiments carried out with rabbits, which were allowed to inhale air rich in carbon dioxide, failed to reveal a similar action *in vivo*, as no chlorine retention was found to take place after such inhalations, as should be expected if chlorine passed from the blood serum into the formed elements. It is assumed that the body possesses some compensatory mechanism which prevents this from taking place. S. B. S.

The Nitrogen-sparing Action of Salts, Especially of Sodium Acetate, in the Case of Carnivorous Animals. ERNST PESCHECK (*Biochem. Zeitsch.*, 1913, **52**, 275—330).—Numerous experiments are given in detail, in which sodium acetate and other salts were added to basal diets given to dogs, in which the nitrogen balance was, in some cases, complete, in other cases positive, and in still other cases negative. The results of previous experiments were confirmed, which tended to show that sodium acetate causes nitrogen retention, this action being specially marked when the nitrogen balance is a negative one. The salt is without action on the amount of nitrogen excreted in the fœces. Sodium citrate, sodium lactate, and magnesium acetate appear to exert a similar action. The author supposes that the action is due to the alkali added, which can be used for neutralisation of acids in the body, instead of the ammonia set free by the deamidisation of the proteins. S. B. S.

[Nitrogenous Metabolism.] EDUARD GRAFE (*Zeitsch. physiol. Chem.*, 1913, **85**, 347—348).—Polemical. A final reply to Abderhalden and Lampé (compare this vol., i, 547, 671). W. D. H.

The Normal Protein Metabolism of the Rat. OTTO FOLIN and J. LUCIEN MORRIS (*J. Biol. Chem.*, 1913, **14**, 509—515).—The new micro-chemical analytical methods enable small quantities of urine to be dealt with, such as are excreted by the rat. Rat's urine closely resembles that of man. The high percentage of uric acid is remarkable, for the rat's tissues lack the uric acid-forming enzymes, although the liver destroys it. W. D. H.

Intermediary Metabolism of Carbohydrates and Proteins. The Mutual Interconversion of α-Amino-acids, α-Hydroxy-acids, and α-Ketonic Aldehydes. HENRY D. DAKIN and HAROLD W. DUDLEY (*J. Biol. Chem.*, 1913, **14**, 555—561; **15**, 127—143).—By a suitable choice of experimental conditions it is possible to convert α-amino- and α-hydroxy-acids into α-ketonic aldehydes at low temperatures; lactic acid and alanine, for example, yield methylglyoxal. When methylglyoxal is acted on by enzymes (glyoxalases) found in the body, *d*- and *l*-lactic acid are formed. When given to the glycosuric animal, glyoxal and both lactic acids yield dextrose. Methylglyoxal is therefore believed to be an intermediate product in the mutual interconversion of alanine, lactic acid, and dextrose (compare Proc., 1913, **29**, 156). W. D. H.

The Value of Lactose and Galactose after Partial Exclusion of the Liver (Eck's Fistula). Ludwig Draudt (*Arch. expt. Path. Pharm.*, 1913, **72**, 457—474).—After an Eck's fistula the nutritive value of lactose and galactose falls; the liver fails to convert them into glycogen, and the sugars circulate in the blood and leave the body by the urine. W. D. H.

The Formation of Fat from Carbohydrate. Sergius Morgulis and Joseph H. Pratt (*Amer. J. Physiol.*, 1913, **32**, 200—210).—The present observations on dogs confirm the results of others with other animals, that feeding on carbohydrates leads to fat formation with the accompaniment of a high respiratory quotient.
W. D. H.

Fat Absorption. II. Absorption of Fat-like Substances other than Fats. W. R. Bloor (*J. Biol. Chem.*, 1913, **15**, 105—117).—Neither petroleum hydrocarbons nor unsaponifiable esters (wool-fat) are absorbed. Neither class of compounds is reducible to a water-soluble form in the intestine. Hence it is extremely probable that fats can only be absorbed in water-soluble form, and that saponification is a necessary preliminary to absorption. W. D. H.

The Absorption of Nitrogenous Products. Otto Folin and Willey Denis (*J. Biol. Chem.*, 1913, **14**, 453—455).—Polemical. A reply to Abderhalden and Lampé (A., 1912, ii, 1189). W. D. H.

Nutrition of the Embryo-chick III. The Assimilation of Egg-white. Hubert W. Bywaters and W. Barrett Roue (*Proc. physiol. Soc.*, 1913, xxxiii—xxxiv; *J. Physiol.*, **46**).—During incubation the ratio of albumin to ovomucoid in the white of the egg remains constant. Either the two proteins are absorbed at the same rate or the albumin alone is absorbed, and then fresh albumin is formed from the ovomucoid. The ovomucoid contains the same proportion of carbohydrate throughout. Probably the first explanation is the correct one. W. D. H.

An Important Chemical Difference between the Eggs of the Sea Urchin and those of the Star-fish. Albert P. Mathews (*J. Biol. Chem.*, 1913, **14**, 465—467).—Cholesterol is absent or nearly so in the starfish egg. It could not be found in the eggs of *Asterias forbesii*. It is present in considerable amount in the sea urchin eggs. The phosphatide of the starfish contains about 10% of a reducing sugar in firm combination and also sulphuric acid.
W. D. H.

The Influence of Hypertonic Solution on the Rate of Oxidations in Fertilised and Unfertilised Eggs. Jacques Loeb and Hardolph Wasteneys (*J. Biol. Chem.*, 1913, **14**, 469—480).—The unfertilised eggs of sea urchins which have undergone artificial membrane formation die if not treated with a hypertonic solution,

but the solution does not increase the rate of oxidations either in unfertilised or fertilised eggs. Such solutions increase the rate of oxidations in unfertilised eggs if they have not undergone membrane formation. Weak bases added to normal sea-water cause membrane development, and affects the rate of oxidation in unfertilised eggs as when they are added to hypertonic sea-water. Complete cytolysis of the unfertilised eggs by saponin raises the rate of oxidation to the same height as fertilisation, showing that cytolysis of the surface of the egg is the essential feature in fertilisation.

W. D. H.

The Influence of Bases on the Rate of Oxidations in Fertilised Eggs. JACQUES LOEB and HARDOLPH WASTENEYS (*J. Biol. Chem.*, 1913, **14**, 459—464).—Bases influence the rate of oxidations differently in the fertilised and unfertilised eggs of *Strongylocentrotus purpuratus*. Strong bases accelerate this rate in the fertilised egg only if their concentration is over $10^{-3}N$; this suppresses development of the egg. Weak bases accelerate the rate slightly in the fertilised egg. No conclusion as to the seat of oxidation in the egg is warranted. W. D. H.

Biochemistry of Protozoa. II. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1913, **86**, 33—42).—The parasitic protozoon *Goussia gadi*, which lives in the swim-bladder of certain fishes and also in shellfish, was investigated.

The composition and constants of the fatty substances present show them to be different from those in the host. No sugar or related substance was found. The keratin-like protein in the spore-capsules is free from sulphur and phosphorus. After hydrolysis, lysine, histidine, arginine, tyrosine, glycine, and glutamic acid were separated. W. D. H.

The Action of Tissues on Hexoses. PHŒBUS A. LEVENE and GUSTAV M. MEYER (*J. Biol. Chem.*, 1913, **15**, 65—68).—Kidney tissue was obtained aseptically, and in its presence dextrose, *d*-mannose, and *d*-fructose were all converted into *d*-lactic acid. The action is the same, but not quite so powerful as that of leucocytes.

W. D. H.

The Biochemical Conversion of Methylglyoxal into Lactic Acid and the Formation of the Different Lactic Acids in Nature. CARL NEUBERG (*Biochem. Zeitsch.*, 1913, **51**, 484—508).—Animal tissue extracts contain an aldehydomutase, which readily converts methylglyoxal into lactic acid. The reaction takes place best when the reaction mixture contains calcium hydrogen carbonate, which prevents the mixture from becoming too acid. This process is carried out in the following way: 1·40 grams of calcium carbonate are added for each 0·72 gram of methylglyoxal present in solution in the organ extract; the former is added, and the liquid is saturated with carbon dioxide before addition of the aldehyde. After remaining in the incubator, the mixture is heated

and filtered, and an aliquot portion is evaporated to a small bulk. Hot alcohol is added, the precipitated substances were filtered off, the filtrate is again evaporated, treated with alcohol, and again evaporated. These processes are continually repeated until no precipitate is produced on addition of alcohol. The amount of lactic acid formed can be estimated by determining the amount of calcium in an aliquot part of the final filtrate; for determination of the rotation the zinc salt can be made from this liquid. Control estimations should be made with the methylglyoxal and tissue extract separately, both of which yield small quantities of a soluble calcium salt when treated by the above process, and a correction can be thus introduced into the result.

The conversion of methylglyoxal into lactic acid is never quantitative, but reaches sometimes 75%. Certain maceration juices of top yeasts are also capable of producing lactic acid from methylglyoxal, but not aqueous extracts of the same. The lactic acid thus produced is inactive. On the other hand, muscle and liver extracts produce the *l*-acid, which is not the naturally occurring form. The theory of the formation of this active form is discussed by the author in some detail. He assumes that by the addition and scission of the elements of water optically active substances can be produced from forms such as methylglyoxal, which are themselves inactive, and that such active substances are formed as intermediary products in various biochemical changes. These views are illustrated by numerous examples and formulæ. S. B. S.

The Preparation from Animal Tissues of a Substance which Cures Polyneuritis in Birds Induced by Diets of Polished Rice. I. EVELYN A. COOPER (*Biochem. J.*, 1913, **7**, 268—274).—A fraction rich in the anti-neuritic substance can be precipitated by ether from the fats and lipoids (alcoholic extract) of horse-flesh. The substance is insoluble in alcohol, benzene, chloroform, ether, and ethyl acetate, but is moderately soluble in water. It is absorbed to some extent by animal charcoal, and is destroyed readily by alkali. Quinine and cinchonine exert a temporary curative action in these birds, but lose this power after being heated at 125° for six hours; the effect is regarded as due to traces of the anti-neuritic substance from the cinchona bark. Alcohol given to the birds in small doses does not affect the onset of polyneuritis when a diet of polished rice is taken. This suggests that alcoholic neuritis is not due to a lessened capacity of the body to utilise the anti-neuritic substance. W. D. H.

Lipolytic Action of the Tissues. FRANCIS H. THIELE (*Biochem. J.*, 1913, **7**, 287—296).—The tissues possess a true lipolytic enzyme, but, except in the case of the pancreas, it hydrolyses phosphatides and jecorins, but not ordinary fats. It acts in an alkaline or acid medium. There is no evidence of a kinase in the spleen.

W. D. H.

The Influence of Anæsthetics on the Oxydones. FRÉD. BATELLI and (Mlle.) LINA STERN (*Biochem. Zeitsch.*, 1913, **52**, 226—252. Compare Vernon, this vol., i, 220).—The "oxydones" are the insoluble catalysts contained in animal tissues, which accelerate the oxidation of certain substances. Below certain concentrations, anæsthetics have no action on the succinic oxydone; at a certain critical concentration they exert an inhibitory influence, which is not far removed, except in the case of antipyrine, from a limiting concentration at which the ferment becomes quite inactive. Similar phenomena were observed by Vernon in the case of the phenylenediamine oxydone. All anæsthetics have the power of precipitating nucleoproteids from aqueous solution; this precipitation is only marked when a certain critical concentration is reached, and is complete in a slightly higher concentration. These two concentrations, except in the cases of phenol and *o*-cresol, are almost identical with the concentrations necessary for inhibition and complete inactivation of the oxydone. They also vary, in both cases, with the temperature. The influence of the anæsthetics on the activity of the succinic oxydone is not much stronger when they are present during the actual oxidation than when the tissue has been treated by them and then washed. The destruction of the oxydone is therefore an irreversible process. There is, as Vernon has already shown, a parallelism between narcotic action and capacity to destroy oxydones, which is far more marked than the parallelism between the narcotic action and coefficient of distribution between oil and water. There is also a parallelism between the capacity for destroying oxydones and the hæmolytic action, the toxicity, and capillary activity. The authors draw the conclusion that these activities are due rather to actions on the proteins than to the actions on lipoids. S. B. S.

The Influence of Aldehydes on the Oxydones. FRÉD. BATELLI and (Mlle.) LINA STERN (*Biochem. Zeitsch.*, 1913, **52**, 253—270).—The aldehydes are similar in their action on oxydones to the anæsthetics, the method of action of which is described in the preceding paper. There is a critical concentration at which inhibition is effected, which is not far removed from the limiting concentration of total inactivation. Both vary with the temperature; the destructive action on the oxydones, furthermore, is an irreversible one. These critical and limiting concentrations do not coincide, however, with the incipient and complete precipitation of the nucleoproteins in the case of liver extracts, but, as a general rule, they nearly coincide with the capacity of the aldehyde to form a precipitate with the soluble proteins after acidification with acetic acid. Again, the authors draw the conclusion that the destruction of oxydones is due rather to action on the proteins than to action on the lipoids. S. B. S.

The Sympathetic System Does Not Possess the Same Chemical Composition as the Axial Nervous Tissue and the Cranial or Spinal Nerves. N. ALBERTO BARBIERI (*Compt. rend.*, 1913, **157**, 69—72).—By successive extraction with carbon

disulphide, distilled water, alcohol, ether, and boiling alcohol the author has made a comparative analysis of the tissue of the sympathetic system and of the axial nervous tissue and the cranial and spinal nerves, and finds that the first-named differs in chemical composition from the others. Of its total extract 66% is composed of oil and stearin. It is completely void of nervous serum and of cerebroin and cerebrin. W. G.

Carbon Dioxide Production in Nerve Fibres. SHIRO TASHIRO (*Amer. J. Physiol.*, 1913, **32**, 107—136).—All nerve fibres give off carbon dioxide. A nerve of the spider crab at rest produces $6{\cdot}7 \times 10^{-7}$ gram per 10 mg. per ten minutes. The figure for frog's sciatic is $5{\cdot}5 \times 10^{-7}$. The amount is increased in activity to 16×10^{-7} (crab) and $14{\cdot}2 \times 10^{-7}$ (frog). This is due to a vital active process, which is reduced by anæsthetics, both in nerves and seeds. W. D. H.

The Cerebro-spinal Fluid in Nervous Diseases. I. ROBERT V. STANFORD (*Zeitsch. physiol. Chem.*, 1913, **86**, 43—50).—The high specific gravity of the cerebro-spinal fluid in cases of progressive paralysis is regarded as of diagnostic importance. W. D. H.

The Cerebro-spinal Fluid in Nervous Diseases. II. Nitrogen. ROBERT V. STANFORD (*Zeitsch. physiol. Chem.*, 1913, **86**, 219—233).—The amount of nitrogen follows the specific gravity; it is increased in progressive paralysis, and in certain other mental diseases, but not so greatly. In epilepsy this is not the case as a rule.
W. D. H.

The Action of Electrolytes on the Heart. GEORGE R. MINES (*J. Physiol.*, 1913, **46**, 188—235).—The experiments were made on the frog's heart, simultaneous records of the contractions and of their electrical accompaniment being taken. The character of the electrocardiogram and the changes it undergoes are discussed at length. Among the points of interest noted is that the electrical changes may continue after all movements have ceased, as when calcium is absent from the perfusing fluid. This has already been noticed in the mammal's heart by Locke and Rosenheim.
W. D. H.

The Action of Pituitrin and β-Amino-4 ethylglyoxaline (Histamine) on the Action of the Heart. W. EINIS (*Biochem. Zeitsch.*, 1913, **52**, 96—117).—The experiments were made on the isolated hearts of frogs and rabbits. In the rabbit's heart single small doses of pituitrin cause a slight increase in the frequency, larger doses a diminution. Repeated doses also cause a diminution. In hearts brought to a standstill by want of oxygen, pituitrin causes a transient activity. β-Amino-4-ethylglyoxaline causes a diminution of frequency by inhibition of the stimulus. On the mammalian heart pituitrin causes a diminution of frequency, followed by a more or less marked rise; there is a diminution in

the height of contraction, followed by a recovery to the normal, or even higher than the normal. The diminution in the frequency and height of contraction may be ascribed to the chloretone contained in the preparation used. β-Amino-4-ethylglyoxaline causes an increase in the frequency in the mammalian heart to two or three times the normal after a slight preliminary transient diminution. The final value is below normal. It also causes a marked increase in the height of contraction. S. B. S.

The Action of the Diastatic Ferment on Glycogen within the Cell. III. ERNST J. LESSER (*Biochem. Zeitsch.*, 1913, **52**, 471—485).—During the winter months glycogen does not disappear quickly from the liver during incubation of the intact organ. If, however, the organs are ground up so as to destroy the structure, the glycogen rapidly disappears; in fact, it is hydrolysed as rapidly as it is in the intact organs taken from animals during the months of May and June, when the glycogen is labile. The difference is probably due to the difference of the diffusibility of the ferment through the cells, which enables it to come into contact with the glycogen, and not to the presence of blood-diastase, as the same results are obtained with the organs which have been perfused and rendered blood-free, as with the organs directly removed from the body (compare Ivar Bang, this vol., i, 552, 553). S. B. S.

The Action of Antiglycosuric Medicaments and Liver Glycosuria. III. The Perfusion of the Liver with Blood under the Influence of Different Reagents. ERNST NEUBAUER (*Biochem. Zeitsch.*, 1913, **52**, 118—141. Compare A., 1912, ii, 962).—The results were obtained by oncometric experiments on rabbits' livers. An increase of volume of the organ follows the intravenous or subcutaneous injection of adrenaline, and the intravenous injection of the infundibular portion of pituitary body, of strophanthin, of cocaine (after subcutaneous injection of adrenaline), after asphyxia produced by stoppage of the trachea, after faradic stimulation of the central end of the vagus in the neck and the stimulation of the splanchnic. There is contraction or inhibition of expansion of the liver, after intravenous injection of the glandular portion of the pituitary body, after veronal, chloral hydrate, ergotoxin, after venesection, and after stimulation of various kinds of the peripheral end of the vagus. Phloridzin and cocaine have no specific action on the liver volume. Caffeine and diuretin cause repeated alterations in the kidney volume. The liver volume changes run as a rule parallel with the height of the blood-pressure, behaving in this respect like the limbs, but unlike the spleen. Those treatments of the animals which produce hyperglycæmia in the liver through vaso-constriction in the splanchnic vessel system cause, generally, expulsion of the sugar, whereas those treatments which antagonise this stasis in the liver, antagonise also glycosuria. The rule is, however, not absolute; diminution of the liver volume produced by insufficient arterial blood supply, for example, can also be accompanied by expulsion of sugar, which also takes place in a stasis produced by anoxybiotic conditions. S. B. S.

The Oxidation Products of Cholesterol in the Animal Organism (Portal and Hepatic Veins). V. ISAAC LIFSCHÜTZ (*Biochem. Zeitsch.*, 1913, **52**, 206—213).—The absence of oxycholesterol from the liver might be explained, either on the assumption that the liver cannot take up this substance, or that it takes it up from the blood-stream and changes it into other products which do not give the oxycholesterol reactions. From analyses of the blood of the portal and hepatic veins, and of blood which had been artificially perfused through the liver, the second of the above explanations seems to be correct, for the hepatic vein contains less oxycholesterol than the portal vein, and unperfused blood less than perfused blood. S. B. S.

The Effect of Changes in the Circulation of the Liver on Nitrogen Metabolism. SAMUEL A. MATTHEWS and E. M. MILLER (*J. Biol. Chem.*, 1913, **15**, 87—104).—After an Eck fistula is established, urea in the urine is largely replaced by ammonia, and toxic effects have been described as the result of increased ammonia in the blood. In the present experiments a large number of the dogs died of inanition, but in some the augmented excretion of ammonia over long intervals did not even produce ill health. Such dogs, however, are susceptible to meat intoxication. In animals which survive a long time the formation of adhesions may bring about a partial return of portal blood to the liver. W. D. H.

Physiology and Pathology of the Kidney Functions. WILHELM BAETZNER (*Archiv expt. Path. Pharm.*, 1913, **72**, 309—315).—In experiments on animals it was found contrary to the statements of Bock that in water diuresis a regularly increasing rise in phosphorus elimination takes place. W. D. H.

Action of Leucocytes on Hexoses. IV. The Mechanism of Lactic Acid Formation. PHŒBUS A. LEVENE and GUSTAV M. MEYER (*J. Biol. Chem.*, 1913, **14**, 551—554).—The present paper confirms the work of Dakin and Dudley (this vol., i, 565; also corroborated by Neuberg, this vol., ii, 564) on the existence of glyoxalases. In the present experiments bacteria were rigidly excluded. Leucocytes and kidney tissues were used, and produced the conversion of methylglyoxal into *dl*- and *d*-lactic acid. This confirms the view that the formation of *d*-lactic acid from the various *d*-hexoses is conditioned by the intermediate formation of methylglyoxal:

$$OH{\cdot}CH_2{\cdot}CH(OH){\cdot}CHO \longrightarrow CH_3{\cdot}CO{\cdot}CHO \longrightarrow CH_3{\cdot}CH(OH){\cdot}CO_2H.$$

W. D. H.

The Physiology of the Thyroid. F. BLUM (*Zeitsch. physiol. Chem.*, 1913, **85**, 428—429).—Introductory to a series of papers to follow later. W. D. H.

Self-digestion of the Thymus. ELI K. MARSHALL, jun. (*J. Biol. Chem.*, 1913, **15**, 81—84).—In self-digestion of the thymus, the

enzymes present are not capable of decomposing all the nucleic acid within any reasonable length of time; the portion left undecomposed appears to be identical with that prepared from the fresh gland. W. D. H.

Physical Chemistry of Muscle-plasma. FILIPPO BOTTAZZI (*Biochem. Bull*, 1913, **2**, 379—385).—Muscle-plasma as seen under the ultra-microscope is full of many brilliant, small particles (myosin) and a small number of coarse particles; the latter are composed of fat, glycogen, and nuclear and sarcoplasmic fragments. The liquid portion contains salts, extractives, and protein in true solution. When freed from the granules, the plasma is optically homogeneous, but on adding acid or heating to 55°, true precipitation of a dissolved muscle protein (myoprotein) occurs.

The fine plasma granules are degradation products from the muscular fibrils. They tend to flocculate spontaneously, and the so-called heat coagulation which occurs between 38° and 54° is due to rapid aggregation. Myoprotein is not completely coagulated by heat even at 80°; it is totally precipitated by dialysis. Tables of the composition and physical constants of muscle plasma are appended. The osmotic pressure is high, and the reaction always acid. The maximum production of acid substances occurs soon after the muscles are separated from the body, and it is these which cause the high osmotic pressure. The surface tension is also higher than that of blood-serum. W. D. H.

Fasting Studies. XI. Composition of Muscle from Fasting Dogs. HENRY C. BIDDLE and PAUL E. HOWE (*Biochem. Bull.*, 1913, **2**, 386—389).—The tables given show an increase in water, and a decrease in nitrogen and creatine as a result of fasting. In the heart (one observation only) the nitrogen falls and the creatine rises. W. D. H.

Carnosine Content of the Muscles of Mammals. MARIE MAUTHNER (*Monatsh.*, 1913, **34**, 883—900).—The present investigation was undertaken with the object of deciding whether carnosine is the sole component of the carnosine fraction obtained by Gulewitsch (A., 1900, i, 516) from the muscles of mammals, and also in the hope of discovering an exact method for the estimation of carnosine. The following are the main conclusions:

(i) If a carnosine fraction is obtained from meat extract by addition of lead acetate and silver nitrate, separation of the precipitated matter, addition of silver nitrate and barium hydroxide to the filtrate and decomposition of the precipitate so obtained by means of hydrogen sulphide, it is frequently possible to separate the carnosine in the form of the sparingly soluble, blue, crystalline copper compound described by Gulewitsch. A quantitative separation is, however, never obtained, and there are many indications that, in addition to carnosine itself, a modification or decomposition product of it is often present which does not possess the power of dissolving copper hydroxide.

(ii) Estimations by the picrolonic acid method of the histidine obtained by hydrolysis of carnosine fractions by hydrochloric or sulphuric acids show that 80—90% of the nitrogen present in the latter is contained in the form of carnosine or of a closely allied compound.

(iii) The same result is obtained by the separation of the base from carnosine fractions in the form of a sparingly soluble, yellow, crystalline *picrolonate*, which, according to ultimate analysis and to the amount of picrolonic acid separable from it by addition of hydrochloric acid, is a mono-sodium compound of carnosinedipicrolonate, $C_{29}H_{29}O_{13}N_{12}Na$. H. W.

The Occurrence of Alcohol-resistant Carmine-red and Brown-red Pigments in the Skin of Bony Fishes. EMIL BALLOWITZ (*Zeitsch. physiol. Chem.*, 1913, **86**, 215—218).—The red pigments referred to occur in the chromatophores, and are distinct from a yellow lipochrome which is soluble in alcohol. W. D. H.

The Presence of Boron in Milk and Eggs. GABRIEL BERTRAND and HENRI AGULHON (*Compt. rend.*, 1913, **156**, 2027—2029. Compare A., 1910, ii, 241; 1912, ii, 854; this vol., i, 423).—From the very frequent occurrence of this element in animals and vegetables the authors raise the question as to whether the element may not play, like iron and manganese, an indispensable part (possibly catalytic) in the living cell. They have extended their investigation to milk (human, ass, goat, and cow) and to eggs (fowl, pigeon, wild duck, turkey, and goose), with distinct positive results in each case. Analysis indicates the presence of 0·08, 0·1, and 0·2 mg. of boron in 1 litre of human, ass's, and cow's milk respectively, and 1 mg. of boron in 1 kilogram of dried material from the egg of the fowl, turkey, or goose. D. F. T.

The Alcohol Content of Milk after Ingestion of Alcohol and under the Influence of Tolerance. WILHELM VÖLTZ and JOHANNES PAECHTNER (*Biochem. Zeitsch.*, 1913, **52**, 73—95).—After a short period of toleration the amounts of alcohol appearing in the milk in the case both of cows, and of a woman, who ingested moderate quantities, are practically negligible. When cows are fed on residues from distillation processes, which seldom contain more than 0·1 to 0·3% alcohol, only, at the outside, a few milligrams of alcohol can be ingested daily by infants fed on the milk from such animals, quantities, in fact, which are absolutely without action. S. B. S.

Action of Hydrogen Peroxide on the Amylase of Human Milk. L. LAGANE (*Compt. rend.*, 1913, **156**, 1941—1943).—Starch paste is not liquefied by cow's or goat's milk before or after boiling, but a slight liquefaction occurs with either of these milks in a fresh state in presence of hydrogen peroxide. Fresh human milk, on the contrary, liquefies starch paste, and this action is greatly accelerated in presence of hydrogen peroxide, although the latter

does not enable boiled human milk to effect liquefaction. Similarly, the saccharification of starch paste by fresh human milk takes place more rapidly in presence of hydrogen peroxide, but this action is less marked than the acceleration of liquefaction. Control experiments of various kinds indicate that the acceleration is due to direct action of the peroxide on the amylase, or possibly to indirect action through peroxydases in the milk. T. A. H.

The Critical Solution Point of Urine. WILLIAM R. G. ATKINS and THOMAS A. WALLACE (*Biochem. J.*, 1913, **7**, 219—230).—In normal urines the rise in critical solution point is about eight times as great as the depression of freezing point. In very dilute urines, and when excess of salts are present, this is greater; in the presence of dextrose or excess of urea it is less. The relationship between the rise of the critical solution temperature and the depression of the freezing point furnishes a useful datum in the examination of urine. W. D. H.

Toxic Bases in the Urine of Parathyroidectomised Dogs. W. F. KOCH (*J. Biol. Chem.*, 1913, **15**, 43—63).—Digested proteins have a very toxic effect after parathyroidectomy; the toxic substances which arise either in intestinal or parenteral digestion pass into the urine, in which secretion several bases were found, among which β-amino-4-ethylglyoxaline, choline, and methylguanidine were identified. In animals in which no feeding occurred, the violent symptoms observed are attributed to disintegration of the body-protein. Histological examination reveals active degeneration of the cell-nuclei. The parathyroid secretion is regarded as concerned with anabolic processes closely related to the building up of nucleins. W. D. H.

The Chemical Composition of the So-called "Colloidal" Nitrogenous Substances obtained from Human Urine by Precipitation with Zinc Salts. H. THAR and J. BENESLAWSKI (*Biochem. Zeitsch.*, 1913, **52**, 435—438).—Salkowski has shown that alcohol produces a precipitation in concentrated human urine which contains nitrogen, is non-dialysable, and was supposed to consist of oxyproteic acid and similar substances. These same substances càn also be obtained by precipitation with zinc sulphate. They have been investigated in greater detail by the authors, who now show that the precipitate contains chiefly uric acid and purine bases, contaminated with small quantities of urea, ammonia, and other constituents of the urine. S. B. S.

Acapnia and Shock. HENRY H. JANEWAY and EPHRAIM M. EWING (*Biochem. Bull.*, 1913, **2**, 403—406).—The conclusion is drawn from experiments on dogs that the reduction of the carbon dioxide of the blood is not an important factor in the production of shock induced by hyper-respiration, but that the essential influence is an interference with the venous return to the heart. In experiments on the intestines, shock is due to manipulation of the gut, and not to

any lessening of carbon dioxide in the blood produced thereby. Aëration of the intestines without the addition of carbon dioxide does not produce shock. W. D. H.

Beri-beri. VII. The Vitamine Fraction from Yeast and Rice Polishings. CASIMIR FUNK (*J. Physiol.*, 1913, **46**, 173—179). —The vitamine fraction from yeast was separated into three substances: (1) with formula $C_{24}H_{19}O_9N_5$, (2) with formula $C_{29}H_{23}O_9N_5$, and (3) nicotinic acid. The first substance mixed with the third is stated to have some curative effect on pigeons suffering from polyneuritis.

The vitamine fraction from rice polishings was separated into two fractions: (1) with formula $C_{26}H_{20}O_9N_4$, and (2) nicotinic acid. The deductions as to their curative power are not yet published. W. D. H.

The Theory of Diabetes. I. Sarcolactic Acid in Diabetic Muscle. ROLLIN T. WOODYATT (*J. Biol. Chem.*, 1913, **14**, 441—451. Compare this vol., i, 559).—Muscles of glycogen-free animals form some sarcolactic acid (about 30% of the normal). This cannot come from glycogen, but must arise from preformed sugar or directly from amino- or fatty acids. The muscles of a severe human case of the disease formed even less than that of fully phloridzinised dogs. This suggests an impaired power to dissociate dextrose on the part of the muscles, as they are bathed in an abnormally high quantity of sugar. With D : N (dextrose : nitrogen) ratios of 3·65 : 1 post-mortem analyses of dog's muscles and livers show no glycogen. With ratios 2·8 or 3·0 : 1 this is not necessarily the case, and it cannot be assumed that with a constant D : N ratio of this magnitude an animal is free from glycogen. W. D. H.

The Part Played by Acids in Carbohydrate Metabolism. II. Starvation Diabetes. HERBERT ELIAS and L. KOLB (*Biochem. Zeitsch.*, 1913, **52**, 331—361. Compare this vol., ii, 215).—The object of the investigation was to ascertain whether the diabetes produced by administration of carbohydrates during starvation is due to acidosis. This, from experiments on young dogs, appears to be the case for the following reasons. The starvation diabetes is accompanied by increased acidity of the blood, as determined by Spiro and Pemsel's method, and by an increased carbon dioxide tension in the alveolar air, as estimated by a modification of Wolffberg's technique. The diabetes is always accompanied also by hyperglycæmia, which indicates that it cannot be ascribed to renal insufficiency; neither is it due to any action of the suprarenals, as it also occurs after bilateral splanchiotomy. Furthermore, the diabetes is depressed by administration of alkali, which also reduces the blood sugar to the normal. The diabetes appears to be due, therefore, to some disturbance in the intermediary metabolism, and is to a great extent to be ascribed to acidosis. S. B. S.

The Sugar Consumption in Normal and Diabetic (Depancreated) Dogs after Evisceration. JOHN J. R. MACLEOD and R. G. PEARCE (*Amer. J. Physiol.*, 1913, **32**, 184—199).—No differences occur in the consumption of sugar in the muscles and heart of depancreated dogs and normal dogs. This is opposed to the statements of Starling and Knowlton. W. D. H.

Gluconeogenesis. III. The Fate of *iso*Butyric, *iso*Valeric, and *iso*Hexoic Acids in the Diabetic Organism, with Consideration of the Intermediary Metabolism of Leucine and Valine. A. I. RINGER, EDWARD M. FRANKEL and L. JONAS (*J. Biol. Chem*, 1913, **14**, 525—538).—In experiments on phloridzinised dogs it was found that *iso*butyric acid and *iso*butyl alcohol give rise to dextrose, probably by undergoing demethylation and so giving rise to normal fatty acids (propionic acid). *iso*Valeric acid does not give rise to dextrose, but to large quantities of acetoacetic acid, acetone, and β-hydroxybutyric acid. *iso*Hexoic acid gives rise to dextrose, probably by demethylation to valeric acid and subsequent oxidation to propionic acid. In certain cases *iso*butyric acid possesses marked antiketogenic properties. It is suggested that *iso*valeric and *iso*butyric acids are normal intermediary products in the katabolism of leucine and valine respectively. W. D. H.

Gluconeogenesis. IV. The Fate of Succinic, Malic, and Malonic Acids in the Diabetic Organism, with Consideration of the Intermediary Metabolism of Aspartic Acid, Glutamic Acid, Proline, Lysine, Arginine, and Ornithine. A. I. RINGER, EDWARD M. FRANKEL and L. JONAS (*J. Biol. Chem.*, 1913, **14**, 539—550).—In phloridzinised dogs, succinic, malic, and perhaps malonic acids give rise to extra dextrose. Succinic acid is an intermediary substance in the metabolism of glutamic acid, ornithine, and proline, which accounts for their conversion into dextrose. Malonic acid may arise in part from the katabolism of aspartic acid; lysine in its catabolism may pass through a glutaric acid stage, which accounts for its non-conversion into dextrose..

W. D. H.

Gluconeogenesis. V. The Rôle of Pyruvic Acid in the Intermediary Metabolism of Alanine. A. I. RINGER, E. M. FRANKEL and L. JONAS (*J. Biol. Chem.*, 1913, **15**, 145—152).—In phloridzinised dogs pyruvic acid is capable of yielding extra dextrose in the diabetic organism. In some cases the amount was much less than arises from similar amounts of alanine and lactic acid. Pyruvic acid cannot therefore be considered a necessary intermediary product in the conversion of alanine into lactic acid, and alanine cannot be considered to undergo oxidative deaminisation. W. D. H.

The Biochemical Relation between Pyruvic Acid and Dextrose. HENRY D. DAKIN and N. W. JANNEY (*J. Biol. Chem.*, 1913, **15**, 177—180).—Results similar to those obtained by Ringer (see preceding abstract). W. D. H.

The Influence of Thyroid- and Parathyroid-ectomy on Carbohydrate Metabolism. SOICHIRO MIURA (*Biochem. Zeitsch*, 1913, **51**, 423—442).—The onset of alimentary galactosuria in cats is not markedly influenced either by unilateral thyroid or parathyroidectomy. Neither does this exert any influence on the sugar and nitrogen excretion in cases of phloridzin diabetes. Even, therefore, in an animal from which the thyroids and accessory glands have been extirpated, phloridzin causes new sugar formation at the expense of the proteins. Some weeks after the extirpation, however, the sugar/nitrogen ratio increases, as the nitrogen excretion sinks, and is not accompanied with a corresponding decrease of sugar formation. Adrenaline-glycosuria is markedly diminished in animals which have been deprived some weeks before of their thyroid glands and have been treated with phloridzin. S. B. S.

The Influence of Chloral Hydrate on Various Experimental Forms of Hyperglycæmia. AAGE TH. B. JACOBSEN (*Biochem. Zeitsch.*, 1913, **51**, 443—462).—In the case of rabbits, chloral hydrate causes hyperglycæmia, and increases hyperglycæmia produced by adrenaline, *piqûre*, and venesection. This increased action is most marked when the chloral exerts a strong narcotising action. In cases where the animals are only slightly influenced by the chloral, it is often impossible to state whether there has been an increase of hyperglycæmia or not. From the results it is impossible to determine whether the *piqûre* hyperglycæmia is due to adrenaline diabetes. S. B. S.

The Influence of Fever on the Elimination of Creatinine. VICTOR C. MYERS and G. O. VOLOVIC (*J. Biol. Chem.*, 1913, **14**, 489—508).—Fever increases creatinine excretion; so also in rabbits does artificial hyperthermia; hence the result is due to the rise of temperature which accelerates the normal metabolic processes. In toxic fevers, creatine is also generally found, but usually after the crisis. W. D. H.

Is Narcosis due to Asphyxiation? JACQUES LOEB and HARDOLPH WASTENEYS (*J. Biol. Chem.*, 1913, **14**, 517—523).—Chloral-hydrate, ethyl urethane, chloroform, and various alcohols produce complete narcosis in the fertilised eggs of the sea urchin, whilst they lower hardly at all the rate of oxidation in the egg. W. D. H.

Transformation of Calomel into Soluble Salts of Mercury in Digestive Media. H. ZILGIEN (*Compt. rend.*, 1913, **156**, 1863—1864).—Aqueous solutions of lactic acid, ammonia, or previously prepared ammonium lactate do not convert calomel into soluble salts of mercury; if, on the other hand, ammonia is added to a suspension of calomel in water containing lactic acid, a considerable quantity of soluble mercury salts is immediately formed, the amount of which does not increase when the mixture is preserved. A similar result is obtained with nascent ammonium

chloride, although the previously prepared substance is inactive. The soluble salt obtained is probably mercuric chloride. Sodium chloride, whether previously prepared or nascent, is inactive. Similar results are obtained with salts of bismuth, etc., so that probably a general principle is here involved.

In the dog the conversion of calomel into soluble salts of mercury occurs in the stomach only, mercuric sulphate being formed in the intestine. Administration of ammonia in suitable quantity causes a considerable increase in the amount of calomel transformed.

H. W.

The Inactivation of the Hæmolytic Action of Ethyl Alcohol by Normal Serum Albumin. ALBERT FISCHER (*Biochem. Zeitsch.*, 1913, **52**, 60—72).—Normal serum inhibits hæmolysis by ethyl alcohol; sodium fluoride serum has a more powerful action in this respect than the serum which separates from a coagulum. Serum albumin also inhibits the hæmolytic action, the process being one of adsorption. Bases are strongly adsorbed by serum albumin, whereas with acids there is a negative adsorption.

S. B. S.

The Mechanism of the Union of Digitalis-like Heart Poisons. VIKTOR WEIZSÄCKER (*Arch. expt. Path. Pharm.*, 1913, **72**, 347).—Merck's digitalin acts twenty-five times more strongly than strophanthin. The difference in activity of various preparations depends largely on the amount of active substances in combination, but the depression of cardiac activity depends on the concentration of the toxic molecules in the cell; combinations are formed in the cells.

W. D. H.

The Distribution and Excretion of Digitoxin when Administered Subcutaneously to Bufo vulg. CAMILL LHOTÁK VON LHOTA (*Biochem. Zeitsch.*, 1913, **52**, 362—368).—In the case of the toad, digitoxin acts in the first instance as a nerve poison, and only as a heart poison when it is administered in large doses. When administered subcutaneously, it is for the most part absorbed, although a certain portion remains for a long time unabsorbed at the place of injection. The absorbed drug can be detected in the muscular tissue, in the cloacal fluid, and in the urine, in which about 10% of the substance administered is slowly excreted. The greater part of the absorbed drug cannot, however, be detected in the body, and appears to be destroyed. Keller's reaction was employed for the estimation of the digitoxin.

S. B. S.

The Action of Ergotoxine. HENRY H. DALE (*J. Physiol.*, 1913, **46**, 291—300).—Ergotoxine does not reverse the motor effects of adrenaline by producing high tonus of plain muscle (blood vessels, uterus); it may even lower tone, and yet replace a motor adrenaline effect by an inhibitory one. Stimulation of the splanchnic nerves, after an adequate dose of ergotoxine, may cause a fall of blood-pressure although the suprarenal glands are removed.

Much of the paper is devoted to a discussion of the detection of sympathetic vaso-dilator nerves. There is no evidence apart from that furnished by the action of ergotoxine for a mixed motor-inhibitory supply to arteries in general. W. D. H.

[Physiological Action of] Certain Derivatives of Quinine. KNUD SCHROEDER (*Arch. expt. Path. Pharm.*, 1913, **72**, 361—386).—Towards Infusoria and Plasmodia, monobromoquinine and dibromoquinine are almost twice as strongly active as quinine; and dehydroquinine has about half the activity; the alkaloid, $C_{19}H_{22}O_3N_2Cl_2$, is inactive. These substances act in a similar relative way on bacteria, but not so strongly. Equimolecular doses of the quinine derivatives mentioned have the same antipyretic effect as quinine. They do not affect nitrogeneous metabolism in rats; subcutaneous injection causes local necrosis, the various substances producing this in varying degrees. Dehydroquinine and quinine differ in so much as the vinyl group, $CH:CH_2$, of the quinine is changed into $C:CH$ in the first-named material; this alteration is believed to be responsible for the change in activity. W. D. H.

Action of Morphine on the Circulation. E. ANDERES (*Arch. expt. Path. Pharm.*, 1913, **72**, 331—346).—In both dogs and rabbits morphine causes the heart to slow, although the arterial pressure may be unaltered or even slightly rise. In dogs this is due to central vagus stimulation; in rabbits there is, in addition, a peripheral stimulation due to decrease in negative intrapleural pressure. Curare produces the same effect in rabbits, but in dogs, where it does not alter the intrathoracic pressure, there is no synergic action if both drugs are given together. W. D. H.

[Physiological Action of] Strophanthidin. A. GRÖBER (*Arch. expt. Path. Pharm.*, 1913, **72**, 317—330).—Strophanthin acts in rabbits about 3·6 times as toxically as strophanthidin when given intravenously. Death is produced by both drugs by central respiratory paralysis. In minimal lethal doses, strophanthidin acts more quickly and instantaneously, whereas in the case of strophanthin death is preceded by dyspnœa, which lasts for some minutes. On the isolated frog's heart, both poisons act in the same concentration (1 in 1,500,000) in causing standstill of the ventricle. W. D. H.

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[Physiological Action of] Certain Derivatives of Quinine. KNUD SCHROEDER (*Arch. expt. Path. Pharm.*, 1913, **72**, 361—386).—Towards Infusoria and Plasmodia, monobromoquinine and dibromoquinine are almost twice as strongly active as quinine; and dehydroquinine has about half the activity; the alkaloid, $C_{19}H_{22}O_3N_2Cl_2$, is inactive. These substances act in a similar relative way on bacteria, but not so strongly. Equimolecular doses of the quinine derivatives mentioned have the same antipyretic effect as quinine. They do not affect nitrogeneous metabolism in rats; subcutaneous injection causes local necrosis, the various substances producing this in varying degrees. Dehydroquinine and quinine differ in so much as the vinyl group, $CH{:}CH_2$, of the quinine is changed into $C{:}CH$ in the first-named material; this alteration is believed to be responsible for the change in activity. W. D. H.

Action of Morphine on the Circulation. E. ANDERES (*Arch. expt. Path. Pharm.*, 1913, **72**, 331—346).—In both dogs and rabbits morphine causes the heart to slow, although the arterial pressure may be unaltered or even slightly rise. In dogs this is due to central vagus stimulation; in rabbits there is, in addition, a peripheral stimulation due to decrease in negative intrapleural pressure. Curare produces the same effect in rabbits, but in dogs, where it does not alter the intrathoracic pressure, there is no synergic action if both drugs are given together. W. D. H.

[Physiological Action of] Strophanthidin. A. GRÖBER (*Arch. expt. Path. Pharm.*, 1913, **72**, 317—330).—Strophanthin acts in rabbits about 3·6 times as toxically as strophanthidin when given intravenously. Death is produced by both drugs by central respiratory paralysis. In minimal lethal doses, strophanthidin acts more quickly and instantaneously, whereas in the case of strophanthin death is preceded by dyspnœa, which lasts for some minutes. On the isolated frog's heart, both poisons act in the same concentration (1 in 1,500,000) in causing standstill of the ventricle. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Oxidation of Petroleum, Paraffin, and Benzene by Bacteria. NICOLAAS L. SÖHNGEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 1145—1151).—Although most of the bacteria which oxidise hydrocarbons are unable to decompose fatty acids, some species

belonging to the mycobacteria are able to split fats by the secretion of lipase. Many species, such as *Bacillus fluorescens liquefaciens*, *B. pyocyaneus*, *Micrococcus paraffinae*, etc., were found in soil and canal water, and when cultivated in a medium containing tap water with 0·05% of ammonium chloride, 0·05% of dipotassium phosphate, and 1·0% of the hydrocarbon were able to oxidise the compound with great rapidity. Plate cultures showed the organisms to be extremely widely distributed, and it may rise to about 50,000 per gram of garden soil.

Pure cultures of the paraffin oxidising organisms decomposed, on an average, about 7·5 mg. of petroleum and 4 mg. of paraffin in twenty-four hours at 28° per square centimetre surface of the culture liquid. H. B. H.

A Comparative Study of the Metabolism of Pneumococcus, Streptococcus, Bacillus lactis erythrogenes, and Bacillus anthracoides. MARY LOUISE FOSTER (*J. Amer. Chem. Soc.*, 1913, **35**, 916—919. Compare this vol., i, 684).—A study of the proteolytic power of the various organisms. Two strains of *Pneumococcus* were very different in their power of affecting the protein molecule; increase of temperature from 37° to 40° favoured the reaction to such an extent that with the more active strain the phosphotungstic acid fraction was more than doubled, whilst the monoamine fraction is increased in the ratio 6:1. When milk was used as culture medium for *Streptococcus*, *Bacillus lactis erythrogenes*, and *B. anthracoides*, the liquid became alkaline and assumed a red colour and glue-like odour; no indication of lactic acid could be observed. The results indicate the probability of chemical similarity between organisms which morphologically are widely different. D. F. T.

Mechanism of the Acclimatisation of Yeasts to Formaldehyde. M. EMMANUEL POZZI-ESCOT (*Compt. rend.*, 1913, **156**, 1851—1852).—According to Effront, the acclimatisation of yeasts to formaldehyde is due to the destruction of the latter by an oxidising agent which develops in the yeast, the requisite oxygen being obtained from the air or from substances contained in the mixture; the substance produced by acclimatisation plays the part of selective catalyst, without which oxidation does not occur. The author considers this view to be improbable, and has carried out a series of experiments, in which he finds that (i) formaldehyde actually disappears, (ii) destruction takes place more readily in a medium rich in complex nitrogenous substances; if a poor barley wort is employed and the nitrogenous matter removed by means of tannin, fermentation becomes more difficult in the presence of a constant amount of formaldehyde; fermentation occurs more readily if a large initial quantity of yeast is used; (iii) combustion of formaldehyde is complete since formic acid cannot be detected; (iv) formaldehyde combines almost quantitatively with a wort rich in nitrogenous matter forming a labile compound, from which it can be recovered by energetic treatment. Fermentation, and conse-

quently acclimatisation, of the yeast are more difficult in proportion as the wort is poorer in organic nitrogen, and, with an artificial wort containing only ammonium phosphate, becomes very difficult.

The author is led to the conclusion that formaldehyde loses its antiseptic properties owing to the extreme ease with which it combines with groups containing nitrogen, and that the disappearance of the aldehyde corresponds simply with the consumption of the amino-compound formed by the yeast. H. W.

The Formation of the Higher Alcohols from Aldehydes by Yeasts. I. The Conversion of Valeraldehyde into Amyl Alcohol. CARL NEUBERG and H. STEENBOCK (*Biochem. Zeitsch.*, 1913, **52**, 494—503).—It has been already shown by Neuberg and his pupils that keto-acids can be converted by a ferment in yeasts into aldehydes. If these two classes of substances are intermediary products in alcoholic fermentation, it should be expected that the yeasts can convert aldehydes into alcohol. This is now experimentally shown to be possible, and yields of over 80% of the theoretical of amyl alcohol have been obtained from valeraldehyde when this aldehyde is present during alcoholic fermentation. The reaction is apparently a direct reduction, and not a conversion of aldehyde into an equal number of molecules of acid and alcohol by Cannizaro's reaction, as only small quantities of acid could be isolated, and the yield, furthermore, of the alcohol was too large to admit of this explanation. The higher alcohol was separated from the ethyl alcohol by fractional distillation. S. B. S.

The Assimilability of Maltose by Yeasts. A. J. KLUYVER (*Biochem. Zeitsch.*, 1913, **52**, 486—493).—It has been shown by Rose that certain yeasts will grow in culture media containing maltose, without producing fermentation, whereas they will not grow in dextrose solutions, although they will produce fermentation with this sugar when added to the medium containing maltose. These results were to a large extent confirmed by more extended researches of Lindner and Saito. The author now shows that certain yeasts will grow in Hayduck's medium containing some preparations of maltose, whereas they will not grow in the presence of maltose obtained from other firms. If, furthermore, the maltose samples which produce growth are purified by recrystallisation, they lose their power of producing growth. The results of Rose, Lindner, and Saito are therefore to be explained by the fact that the maltose they employed was not pure, but contained probably some protein substances derived probably from the diastase used in their preparation. S. B. S.

The Protein Substances of Yeast. PIERRE THOMAS (*Compt. rend.*, 1913, **156**, 2024—2027).—The only earlier work of an exact nature on this subject is that of Kossel (*Zeitsch. physiol. Chem.*, 1879, **3**, 284; 1880, **4**, 290) and of Schröder (A., 1902, i, 730). The author has succeeded, after partial autolysis of yeast, in isolating two protein substances; the first, which from its properties

appears to occupy a position between casein and the vitellin of egg-yolk, contains 16·2% nitrogen, 1·8% phosphorus, and 0·38% sulphur; it is soluble in dilute solutions of the alkali hydroxides and carbonates, but is precipitated by acids; rennet causes its coagulation, but less readily than it does caseinogen. If a solution of the protein in 1% sodium hydroxide is maintained at 37°, the phosphorus passes gradually into the mineral state, the extent of 58% being attained in five days (compare Plimmer and Scott, T., 1908, **93**, 1699).

The second substance, for which the author proposes the name *cerevisin*, closely resembles albumin; it is soluble in water, coagulable by heat, and not precipitable by acetic acid; the substance, which contains 16·3% nitrogen, 0·9% sulphur, and a trace of phosphorus, probably due to impurity, gives the usual precipitation and colour reactions. D. F. T.

Rôle of Reductase in Alcoholic Fermentation. S. D. Lvov (*Bull. Acad. Sci. St. Pétersbourg*, 1913, 501—532).—Further experiments on the lines of those previously carried out by Palladin and the author (see this vol., i, 684) lead to the following results.

The first stage, or one of the first stages, in alcoholic fermentation consists in the activation of two atoms of hydrogen with the aid of reductase. So far as is at present known, this active hydrogen may be formed either directly from the dextrose or as the result of the ionic dissociation of water; in the latter case the dextrose would be oxidised by the hydroxyl ions, whilst in the former this early stage would be represented by the equation

$$C_6H_{12}O_6 + R = (C_6H_{12}O_6 - 2H) + RH_2,$$

where R denotes the reductase. The hydrogen fixed temporarily on the reductase is necessary to the further course of normal fermentation. Failure of the distillate to yield the reaction for aldehydes with magenta and sulphurous acid indicates that the formation of aldehydes during the fermentation of sugar, if it actually occurs, is a more complex process than is assumed in Kostytschev's scheme (A., 1912, ii, 589, 860; this vol., i, 323).

Between the reducing and fermentative capacities of yeast strict parallelism is observed; the reductase gives up the hydrogen it fixes to an amount which stands in equimolecular relation to the diminution in yield of the products of fermentation.

A number of auto-fermentation experiments have also been made. The results of these show that the extraction during the process of reduction, of 2 gram-atoms of hydrogen by 1 gram-mol. of methylene-blue, is accompanied by the evolution of an excess of 1 gram-mol. of carbon dioxide. Hence a fermenting medium contains some substance which, in absence of sugar, is capable of liberating 1 mol. of carbon dioxide when the conditions are such that the substance itself loses 2 atoms of hydrogen. This process is found to be enzymic in character, and is one-sided in that no corresponding excess is observed in the yield of alcohol. The excess of carbon dioxide is regarded as resulting from the decomposition of amino-acids, with parallel formation of aldehydes.

The conclusion is drawn that activation of the hydrogen under the influence of reductase is an all-important factor in the processes of fermentation, which are unable to take place in absence of reductase. T. H. P.

Alcoholic Fermentation of Sugar. EDUARD BUCHNER and KURT LANGHELD (*Ber.*, 1913, **46**, 1972).—Sugar was allowed to ferment with expressed or macerated yeast juice in presence of trisodium phosphate or disodium hydrogen phosphate in an extraction apparatus, through which a flow of ether was maintained. The presence of acetaldehyde in the solvent was detected by the formation of the *p*-nitrophenylhydrazone. A similar result was obtained by Kostytschev in the presence of zinc chloride (A., 1912, ii, 589). J. C. W.

Alcoholic Fermentation. IV. Decomposition of Sugar by Dry Yeast in Presence of Zinc Chloride. S. KOSTYTSCHEV and A. SCHELOUMOV (*Zeitsch. physiol. Chem.*, 1913, **85**, 493—506. Compare A., 1912, ii, 589, 860; 1913, i, 323, 434).—When sugar is fermented by yeast preparations in the presence of zinc chloride, the normal series of changes is disturbed and acetaldehyde formed. Parallel with this there is a marked restriction of the production of carbon dioxide. Various zinc salts act in a similar manner, most acetaldehyde being produced in presence of zinc iodide, bromide, or chloride, and less when zinc acetate, carbonate, or phosphate is used.

In the absence of zinc chloride, equal quantities of carbon dioxide and alcohol are obtained on fermentation, but after twenty-four hours about 25% of the sugar decomposed has not been converted into these products; it has probably been used to form hexose phosphate. After forty-eight hours' action, the whole of the sugar is converted into alcohol and carbon dioxide. In parallel experiments in which 0·15 gram of zinc chloride was added per 10 grams of yeast, the sugar is more rapidly decomposed, the fermented part of it being used to form other products. At first the amounts of carbon dioxide and alcohol are equal; after forty-eight hours the production of carbon dioxide is in excess.

When the amount of zinc chloride is doubled, a still larger proportion of the sugar decomposed is not fermented. With 1·2 grams of zinc chloride to 10 grams of yeast, no action takes place.

In a similar manner the addition of 0·5 gram of methylene-blue affects the fermentation. Only two-thirds of the sugar decomposed is fermented, although carbon dioxide and alcohol are produced in equal proportions. The fermentative energy is decreased.

The experiments indicate that the two end-products of fermentation are not formed simultaneously. Alcohol is partly replaced by acetaldehyde. E. F. A.

Alcoholic Fermentation. V. Decomposition of Protein by Dry Yeast in Presence of Zinc Chloride. S. KOSTYTSCHEV and W. BRILLIANT (*Zeitsch. physiol. Chem.*, 1913, **85**, 507—516. Compare preceding abstract).—Generally speaking, external factors act in

an opposite manner towards zymase fermentation and protein decomposition by yeast.

In the absence of sugar, zinc chloride very slightly accelerates the auto-decomposition of dry yeast protein. In the presence of sugar the reverse is the case, the proteolysis being slightly retarded, no doubt owing to the presence of the sugar and the acetaldehyde formed from it. In concentrated sugar solutions the retardation is more marked.

The retardation of the zymase fermentation by zinc chloride is thus not due to acceleration of the antagonistic proteolysis, but to a direct action on the zymase. E. F. A.

Nitrogen Metabolism in Aspergillus niger. H. J. WATERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 1047—1057).—When grown in nutrient solution containing ammonium salts and dextrose or lævulose, the mould is found to give a high nitrogen : carbon ratio. This is attributed not to a simple adsorption of the nitrogen compound, but to its assimilation and immediate transformation into compounds insoluble in hot distilled water.

With increasing age the nitrogen : carbon ratio falls rapidly, and then remains practically constant.

An excretion of ammonia is observed, and this occurs irrespective of the nitrogen compound supplied; nitrate is reduced to ammonia, but not to free nitrogen. The addition of manganese salts increases the velocity of metabolism, whilst the substitution of rubidium for potassium in the nutrient solution is without effect. Where the amount of nitrogen is limited, there did not appear to be any assimilation of atmospheric nitrogen.

H. B. H.

Phosphorus Metabolism in Aspergillus niger. H. J. WATERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 1058—1063).—The ratio of phosphorus to assimilated carbon in old cultures was found to be constant. In the early stages of growth comparatively large quantities of phosphorus are taken up, but, in contradistinction to the same stage in nitrogen assimilation, this phosphorus does not appear to be transformed into organic compounds, such as lecithin or phytin, and can consequently be extracted with hot water. A retardation in spore-formation may be induced by the addition of excess quantities of phosphorus salts.

H. B. H.

Cleavage of Pyromykuric Acid by Mould Enzymes. ARTHUR W. DOX and RAY E NEIDIG (*Biochem. Bull.*, 1913, **2**, 407—408).—Various moulds cleave hippuric acid, and the products can be determined by Sörensen's formaldehyde method. If the synthesis of hippuric acid from benzoic acid in the body is due to an enzyme, the synthesis of corresponding derivatives from substituted benzoic acids may be attributed to the same cause, but there is no reason to suppose that a separate enzyme is necessary for each. This reasoning may be extended to analogous compounds, in which a

heterocyclic replaces the benzene nucleus. In the present experiments, in which pyromykuric acid was subjected to the influence of moulds, the cleavage produced was comparatively small, but this is no evidence that the enzyme is a specific one. W. D. H.

Importance of Oxygen in the Germination of Peas. VL. P. MALTSCHEVSKI (*Bull. Acad. Sci. St. Pétersbourg*, 1913, 639—664).—The results of experiments on the germination of peas under various conditions bring out the following points.

In the case of living seeds, the action of oxygen in causing germination cannot be replaced by that of methylene-blue. The initial influence of the air in stimulating resting seeds under anærobic conditions is of great importance, and changes the character of the anærobic development of carbon dioxide. The alcoholic fermentation produced by seeds under strictly anærobic conditions is accompanied by another process, which leads to the evolution of carbon dioxide from another source, but furnishes no alcohol. Such process is apparently peculiar to living seeds, and is lacking or, at any rate, greatly enfeebled with dead seeds. In the investigation of the anærobiosis of seeds, it is essential to deprive the latter of oxygen even in the first stages of steeping. For the initiation of the germination of peas, absorption of atmospheric oxygen is necessary, not merely for supplying the energy liberated by the oxidation of substances existing in the resting seeds, but also for the formation of new compounds. T. H. P.

Assimilation of Iron by Plants. WILHELM VAUBEL (*Chem. Zeit.*, 1913, **37**, 737).—Iron and ammonium nitrate interact with production of ferrous oxide, ferric hydroxide, and a small amount of a soluble compound, $Fe_2O_4(NO\cdot NH_4)_2$, or $Fe_2O_6(NO\cdot NH_4)_3$ (*ibid.*, 637; Kaufmann, A., 1901, ii, 554). It is suggested that iron is taken up by plants partly in this form. The compound only exists in solution, and decomposes when the solution is evaporated down. According to the concentration, the solution is colourless or dark grey; if yellow, ferric nitrate is present. N. H. J. M.

The Oxidative Formation of Nitrous Acid in Extracts of Plants. ALEXIS BACH (*Biochem. Zeitsch.*. 1913. **52**, 418—422).—The author confirms the observation of Mazé, that nitrous acid is formed in plant extracts when exposed to the action of air. The nitrous acid thus produced is spontaneously destroyed. Nitrous acid is formed only in traces, if the extract is first heated. Reasons are given for assuming that nitrous acid is formed from the amino-acids present and not from nitrates, and against the assumption that the formation of iodine from potassium iodide is not due to the presence of nitrous acid, but is due directly to the existence of an oxydase in the tissues. S. B. S.

Relationship of Bases and Mineral Acids in Plant Tissues. GUSTAVE ANDRÉ (*Compt. rend.*, 1913, **156**, 1914—1916).—In connexion with Warington's observation (A., 1900, ii, 569), that crops

usually show a deficiency of bases on the assumption that all the nitrogen enters the plant in the form of nitrates, the author points out that this is the case for barley (A., 1912, ii, 675, 803) and for linseed (A., 1913, i, 688), but not for spurrey (*loc. cit.*). In the last case the bases are in excess. T. A. H.

Detection of Urea in Plants. ROBERT FOSSE (*Compt. rend.*, 1913, **156**, 1938—1941. Compare A., 1912, ii, 1203; 1913, i, 432). —Some objection might be taken to the work already done on this subject (*loc. cit.*) owing to the fact that the plant preparations in which urea was detected had been concentrated by heat in presence of acetic acid. The author has therefore repeated and extended the work by operating on plant preparations obtained by expression or maceration in the cold. From such products the xanthhydrol derivative of urea is readily precipitated. Urea has thus been detected in the following plants: *Aspergillus niger*, *Penicillium glaucum*, carrot, potato, spinach, endive, chicory, turnip, green haricot, peas, purslane, lettuce, pumpkin, maize grain, and in the embryos of wheat, rye, sunflower, beet, field-bean, lucerne, lentil, lathyrus, grain, pumpkin, horse-bean, dwarf-bean, *Trifolium incarnatum*, and common haricot. Examples of the three methods used in preparing the extracts are given. T. A. H.

The Detection of Formaldehyde in Plants. HEINRICH FINCKE (*Biochem. Zeitsch.*, 1913, **52**, 214—225).—For these researches, the Grosse-Bohle reagent for the detection of formaldehyde was employed. This consists of a rosaniline salt in the presence of sulphites and free hydrochloric acid, and is to be distinguished from the ordinary magenta-sulphite solution for detection of aldehydes, by the presence of free mineral acid. It was found by the author to be capable of detecting formaldehyde in the dilution 1 in 500,000, giving with the aldehyde a violet colour. In numerous experiments on plants, no indication of the presence of formaldehyde was obtained with the use of this reagent; furthermore, formaldehyde could not be detected by the reagent after addition to certain living plants. The author draws the conclusion that his investigations throw no light on the correctness or otherwise of Bayer's assimilation hypothesis. S. B. S.

The Reduction Ferments. IV. Vegetable Perhydrases. ALEXIS BACH (*Biochem. Zeitsch.*, 1913, **52**, 412—417).—It has been shown by the author that animal tissues contain a perhydrase which can reduce nitrates to nitrites in the presence of aldehydes. The existence of a similar vegetable ferment is now demonstrated, which can be obtained from potatoes by extraction with water and filtration of the extract. If this extract is kept under antiseptic conditions (in the presence of sodium fluoride) and in the absence of air, a co-ferment is gradually produced, which can replace the aldehyde in the above-described perhydrase reaction. The co-ferment which activates the animal perhydrase, and which is obtained by extraction of animal tissues by hot water, will not

activate the vegetable perhydrase, which also differs from the animal perhydrase in that it will not reduce methylene-blue. It has not yet been found possible to replace the co-ferment in the vegetable perhydrase reaction with amino-acids or keto-acids, and its exact nature is still undetermined. S. B. S.

Arsenic and Manganese in Young and Old Leaves. F. JADIN and A. ASTRUC (*Compt. rend.*, 1913, **156** 2023—2024. Compare A., 1912, ii, 478, 976).—The observation of Pichard (A., 1899, ii, 40) that manganese appears to become concentrated in those parts of a tree which are in vegetative activity, appears to depend for its correctness on the method of analysis.

According to their age, the different organs contain variable proportions of water and of mineral matter. The experimental results indicate that the amounts of arsenic and manganese in the old leaves of various trees examined are decidedly greater than in the young leaves, if the percentage is calculated on the weight of the fresh leaves. The difference becomes less marked if the percentage of the elements is referred to the dried organs, whilst if the percentages are calculated on the ash the case is actually reversed. D. F. T.

Variation of Carbohydrates in Leaves During Development. E. MICHEL-DURAND (*Compt. rend.*, 1913, **156**, 1926—1929. Compare Combes, A., 1909, ii, 426).—The author has determined the dry weight, reducing and non-reducing sugars, glucosides, dextrin, starch, non-nitrogenous extractive matter, amyloids, and cellulose in the leaves of *Fagus sylvatica*, *Ampelopsis hederacea*, and *Betula alba*, at various stages of development during the year. The results for *Betula alba* leaves are quoted in full in the original. The following conclusions are drawn from the whole of the results. There is a general diminution in carbohydrates towards the end of the season. After attaining a maximum dry weight in August to September, the leaves lose weight until and after they fall. The leaves of *Fagus* and *Betula* contain the maximum amount of reducing sugars when yellow; those of *Ampelopsis* when red; these are corresponding states, and after these stages the amount diminishes rapidly. Starch, when it exists, reaches a maximum while the leaves are green, and then diminishes gradually; yellow leaves contain only traces, but in *Fagus* it persists in the dead leaves until these are dry. Amyloids are at a maximum in *Betula* leaves when these are yellow, but in *Ampelopsis* leaves while they are still green. Cellulose diminishes steadily in *Ampelopsis* leaves, but increases steadily in *Betula* leaves. Rain and dew carry off some soluble carbohydrates from dead leaves. The diminution of carbohydrates in leaves as the season's growth proceeds is due partly to migration of these substances into the stem, partly to respiration, and partly to the effect of atmospheric water. The formation of soluble sugars towards the end of the season is favoured by low temperatures. T. A. H.

Organic Chemistry.

Formation of Methane by Catalysis, Starting with Carbon Monoxide and Water Vapour. LÉO VIGNON (*Compt. rend.*, 1913, **157**, 131—134. Compare A., 1911, i, 101; ii, 391).—An examination of the effect of the metals iron, nickel and copper, and the oxides of aluminium, magnesium and silicon as catalysts, at temperatures varying from 250° to 1250°, in the formation of methane from carbon monoxide and water vapour. They are all effective, but to a variable degree, nickel being the most active at 600°. The mechanism of the action is different for the various catalysts. In all probability iron and the oxides of aluminium and silicon act through the intermediate formation of a carbide, which is decomposed by the water vapour as fast as it is formed. W. G.

Pyrogenetic Decomposition of the Butadiene Hydrocarbons. HERMANN STAUDINGER, R. ENDLE, and J. HEROLD (*Ber.*, 1913, **46**, 2466—2477).—Isoprene when passed through a tube heated at 750° is converted to the extent of 45—55% into a tar, which in appearance and composition closely resembles coal tar, and contains benzene, toluene, naphthalene, α-methylnaphthalene, anthracene, chrysene, etc. The rest of the isoprene is converted into butadiene and into hydrogen, methane, ethylene, or into retort carbon.

At 400° under similar treatment isoprene is partly unattacked, and partly polymerised to unsaturated hydrocarbons—terpenes. Very little gas is formed, but there is some amylene and β-methyl-Δ^{β}-butylene produced.

At 600—700° a mixture of unsaturated hydrocarbons results, which no longer contains terpenes, but resembles crude petroleum. At temperatures above 700°, aromatic compounds are formed; at 750° they are almost entirely, and at 800° they are, the only products.

At 700°, but in a vacuum of 20—25 mm., almost half the isoprene remains unchanged. Unsaturated compounds are formed, but no tar.

When isoprene or butadiene is prepared by pyrogenetic reactions it is advisable to work in a vacuum and to cool rapidly if a high yield is desired.

Isoprene is primarily condensed to hydroaromatic compounds. These polymerise further, or condense with isoprene to form substances which decompose into aromatic compounds, the side-chains being eliminated. The formation of the tar from acetylene and ethylene derivatives, which might have been formed primarily by the pyrogenetic decomposition of isoprene, is improbable, since these compounds are not formed at the lower temperatures, or on heating in a vacuum.

Butadiene may originate from the hydroaromatic substances or from amylene.

β-Methyl-Δ^{β}-butylene at 750° gives rise to butadiene, but this is obtained in much larger quantity on decomposing amyl alcohol. The alcohol yields relatively little tar; β-methyl-Δ^{β}-butylene gives a considerable quantity. In this case also hydrogen is separated from carbon, and there is no scission of carbon linkings with the formation of methane.

Butadiene also takes part in the formation of the aromatic tar, but it polymerises more slowly than isoprene, and the amount of tar products formed is therefore less.

Dimethylbutadiene behaves just as isoprene does at high temperatures, forming tar and small quantities of butadiene at 800°.

It is considered that the polymerisation of butadiene hydrocarbons plays only a small part in the formation of tar from coal. The tar is mainly formed by the dehydrogenation or decomposition of hydroaromatic substances. E. F. A.

The Action of Sodium in Liquid Ammonia on the True Acetylenic Hydrocarbons of the Fatty Series, and a Method of Formation of Ethylenic Hydrocarbons. PAUL LEBEAU and MARIUS PICON (*Compt. rend.*, 1913, **157**, 137—139).—Sodium in liquid ammonia reacts with the acetylenic hydrocarbons of the fatty series quantitatively, giving the sodium derivative of these hydrocarbons (2 mols.) and the corresponding ethylenic hydrocarbon (1 mol.) according to the equation :

$$3C_3H_4 + 2NaNH_3 = 2C_3H_3Na + 2NH_3 + C_3H_6.$$

The products of the reaction are pure, and no secondary reactions were noticed. W. G.

Ethylenic Isomerism of *s*-Dibromoethylene. H. VAN DE WALLE (*Bull. Soc. chim. Belg.*, 1913, **27**, 209—217).—Crude *s*-dibromoethylene is best obtained in quantity by the action of zinc on an alcoholic solution of tetrabromoethane. It boils at 108—112°, and the two isomerides cannot be separated by fractional distillation on account of the spontaneous reversion of the different fractions to the equilibrium mixture. Attempts to separate them by fractional solidification and also by fractional precipitation by water of a solution of the crude bromo-derivative in acetic acid were unsuccessful. Their isolation can be effected, however, by taking advantage of the fact that each isomeride forms a binary mixture with alcohol. By repeated fractionation of a solution of the crude substance in absolute ethyl alcohol with careful exclusion of moisture, two binary mixtures can be isolated. The first of these has b. p. 75·6—75·9°/760 mm., and contains 64% of s-*dibromoethylene*, m. p. $-6·5°$. The second has b. p. 77·7—78°/760 mm., and contains 32·5% of s-*dibromoethylene*, m. p. $-53°$. The pure compound, m. p. $-6·5°$, has b. p. 108°, $D_4^{17·5}$ 2·2667, $n_{H\alpha}^{17·5}$ 1·54563, $n_D^{17·5}$ 1·55054, $n_G^{17·5}$ 1·57381, whilst the other isomeride has b. p. 112·5°, $D_4^{17·5}$ 2·2846, $n_{H\alpha}^{17·5}$ 1·53837, $n_{H\alpha}^{18·5}$ 1·53791, $n_D^{17·5}$ 1·54312, $n_D^{18·5}$ 1·54256, $n_G^{18·5}$ 1·55406. Slight errors are probably involved in the determination of the density owing to rapid isomerisation which occurs with such facility that an equilibrium mixture is formed in the course of a few hours. On exposure to air and moisture, the dibromo-compounds are readily decomposed with evolution of hydrogen bromide.

The equilibrium mixture of the two isomerides has $D_4^{17·5}$ 2·2788, $n_{H\alpha}^{17·5}$ 1·54092, $n_D^{17·5}$ 1·54560, and thus contains about 33·5% of the modification, m. p. $-6·5°$.

The compounds are readily decomposed by alcoholic potassium

hydroxide according to the equation:

$$C_2H_2Br_2 + KOH = C_2HBr + KBr + H_2O,$$

the isomeride, m. p. $-53°$, being by far the more readily decomposable. H. W.

An Application of Young's Method for the Preparation of Absolute Alcohol. GEORGES CHAVANNE (*Bull. Soc. chim. Belg.*, 1913, **27**, 205—209).—The author criticises Young's method of dehydrating aqueous alcohol by means of benzene, and has examined the effect of substituting *s*-dichloroethylene for the latter substance. The general course of the process is similar in each case. *s*-Dichloroethylene, b. p. 48·35°, yields with aqueous alcohol a ternary mixture, b. p. 44·4°, which has the composition, *s*-dichloroethylene 94·5%, alcohol 4·4%, water 1·1%. The binary mixture of *s*-dichloroethylene and alcohol has b. p. 46·5° and contains 94·0% of the former, whilst the binary mixture of *s*-dichloroethylene and water, containing 98·1% of the former, has b. p. 45·3°. With the isomeric *s*-dichloroethylene, b. p. 60·25°, the ternary mixture has the composition, *s*-dichloroethylene 90·5%, alcohol 6·65%, water 2·85%, and b. p. 53·8°. The binary mixture of *s*-dichloroethylene and alcohol, containing 90·2% of the former, has b. p. 57·7°, whilst the corresponding mixture of *s*-dichloroethylene and water contains 96·65% of the former and has b. p. 55·3°. The following are the main conclusions:

(i) The loss of alcohol due to the formation of a ternary mixture is rather greater than when benzene is used if the isomeride, b. p. 48·35°, is employed, rather less in the case of the isomeride, b. p. 60·25°. The use of a mixture of equal weights of the two isomerides, corresponding approximately with commercial *s*-dichloroethylene, leads to a slightly greater loss of alcohol than is the case with benzene, whilst the employment of the equilibrium mixture gives results practically identical with those obtained with the aid of benzene.

(ii) In practice, a portion of the alcohol would also be removed in the form of a binary mixture. Such loss, however, would be less serious than that encountered when benzene is used, since the binary mixtures of alcohol and *s*-dichloroethylene are poorer in alcohol than the corresponding mixtures of alcohol and benzene.

(iii) The use of the dichloro-derivatives has the advantage that the b. p. of alcohol is 20·6° higher than that of the least volatile binary mixture. In this respect, the dichloro-derivatives are superior to benzene or *n*-hexane.

The author is led to the conclusion that the above method is not suited to the commercial preparation of absolute alcohol, since the losses are much greater than those involved by the use of lime.

H. W.

Composition of Certain Formates. CHARLES H. HAMPSHIRE and W. R. PRATT (*Pharm. J.*, 1913, **91**, 138—142).—An examination of commercial specimens of the principal formates and an investigation of the methods of preparation gave the following results: Sodium formate sometimes consists of the anhydrous salt and sometimes of crystals of the dihydrate. Ferric formate has the formula,

$$Fe_3(OH)_2(HCO_2)_7,4H_2O,$$

assigned to it by Belloni (A., 1909, i, 283), and not $Fe_2(HCO_2)_6,H_2O$,

as stated in the B. P. Codex. Magnesium formate has the formula $Mg(HCO_2)_2,2H_2O$, and calcium formate the formula $Ca(HCO_2)_2$. Quinine formate is not anhydrous, but has the composition

$$C_{20}H_{24}O_2N_2,HCO_2H,H_2O.$$

When freshly prepared, strychnine formate contains $2H_2O$, but it effloresces quickly. W. P. S.

Esters of Palmitic Acid. MARJORY STEPHENSON (*Biochem. J.*, 1913, 7, 429—435).—Palmityl chloride, a colourless oil, b. p. 198—200°/15 mm., condenses with glycol in presence of pyridine with chloroform as a solvent to *ethylene dipalmitate*, $(C_{15}H_{31}\cdot CO_2)_2C_2H_4$, which crystallises in rosettes of fine needles, m. p. 65° (corr.).

Glyceryl tripalmitate (tripalmitin), prepared in a similar manner, crystallises in colourless, fine needles, m. p. 62° (corr.).

Mannityl hexapalmitate crystallises in rosettes of fine needles, m. p. 64·5° (corr.).

Dextrose pentapalmitate,

$$C_{15}H_{31}\cdot CO_2\cdot CH_2\cdot[CH\cdot O\cdot CO\cdot C_{15}H_{31}]_4\cdot CHO,$$

has m. p. 62°. E. F. A.

The Action of Complex-forming Acids or their Salts on Platinum Ammonia Compounds. II. Reactions with Ethylthiolacetic Acid. LUDWIG RAMBERG (*Ber.*, 1913, 46, 2353—2362. Compare this vol., ii, 607).—An intermediate product of the action of ethylthiolacetic acid on *cis*-dinitratodiammineplatinum is *nitratodiammineplatinum ethylthiolacetate*, $Pt(NH_3)_2(NO_3)(CO_2\cdot CH_2\cdot SEt)$, which crystallises in large, colourless prisms, m. p. 188—189°. When distilled with dilute sodium hydroxide only one half of the ammonia is liberated. When, however, ethylthiolacetic acid is added to dissolve the compound and then, after an interval, it is distilled with sodium hydroxide, the whole of the ammonia is set free. When the above nitratodiammineplatinum ethylthiolacetate is boiled with concentrated acetic acid one molecule of ammonia is liberated, and *nitratomonammineplatinum ethylthiolacetate*, $CH_2{<}{}^{CO\cdot O}_{SEt}{>}P{<}{}^{NO_3}_{NH_3}$, is obtained. This crystallises in large, flat, colourless prisms, grouped in rosettes, m. p. 193—194° (decomp.).

On shaking *cis*-dinitritodiammineplatinum with an aqueous solution of ethylthiolacetic acid in a closed tube only a little dissolves, and some nitrous fumes are liberated on opening the tube. If, however, sodium ethylthiolacetate is substituted for the free acid and the mixture is boiled in an open vessel, the main product is *sodium dinitrito-(bisethylthiolacetato)-platinoate*, $(CO_2Na\cdot CH_2\cdot SEt)_2Pt(NO_2)_2,2H_2O$, which is also obtained on adding sodium nitrite to α-platinoethylthiolacetate; it forms small, colourless crystals.

trans-Dichlorodiammineplatinum reacts with ethylthiolacetate to form a colourless, complex substance of the composition

$$Pt_2(NH_3)_4Cl_3(CO_2\cdot CH_2\cdot SEt)(CO_2H\cdot CH_2\cdot SEt),$$

which evolves ammonia only slowly when distilled with sodium hydroxide, and decomposes on boiling with acetic acid into *trans*-dichloro-

diammineplatinum, *trans*-diammineplatinum bisethylthiolacetate, and ethylthiolacetic acid. Hence the formula given should probably be doubled.

Ethylthiolacetic acid combines with *trans*-dinitratodiammineplatinum to the compound $Pt(NH_3)_2(NO_3)_2 2CO_2H\cdot CH_2\cdot SEt,H_2O$; this crystallises in colourless rosettes of prismatic crystals, m. p. 115—116°.

Ethylthiolacetic acid and *trans*-sulphatodiammineplatinum combine to form the *additive product*, $Pt(NH_3)_2SO_4,2CO_2H\cdot CH_2\cdot SEt$, which crystallises in colourless tablets or prisms. It reacts with potassium platinochloride, K_2PtCl_4, forming platinoethylthiolacetate, which reacts with hydrogen chloride, forming *monochloro-(bisethylthiolacetato)-platinoic acid*, $(CO_2H\cdot CH_2\cdot SEt)PtCl(CO_2\cdot CH_2\cdot SEt)$, and *trans*-dichlorodiammineplatinum, $Pt(NH_3)_2Cl_2$. The former compound crystallises in greenish-yellow aggregates, m. p. 166—167°.

The above sulphate reacts with barium hydroxide, yielding colourless, microscopic needles of *trans*-diammineplatinum bisethylthiolacetate, which can also be obtained from the corresponding iodide on boiling with silver ethylthiolacetate. It has m. p. 200—203° (decomp.).

trans-Dinitritodiammineplatinum and sodium ethylthiolacetate react very slowly, yielding the same sodium dinitrito-(bisethylthiolacetato)-platinoate as was derived from the *cis*-derivative. E. F. A.

Lactonisation of α-Ketonic Esters. HENRI GAULT (*Compt rend.*, 1913, **157**, 135—137. Compare A., 1911, i, 709).—By a study of its compounds with hydrazine and ammonia the author has definitely established the constitution of the neutral substance, b. p. 176—177°/13 mm., obtained by saturating ethyl pyruvate with hydrogen chloride in the cold, as being the ethyl ether of the enolic form of ethyl α-keto-γ-valerolactone-γ-carboxylate,

$$CO_2Et\cdot CMe<\begin{matrix}O—CO\\ CH:C\cdot OEt\end{matrix}$$

(compare A., 1912, i, 237). It unites with hydrazine (1 mol.) to form the *lactone hydrazide*, $NH_2\cdot NH\cdot CO\cdot CMe<\begin{matrix}O—CO\\ CH:C\cdot OEt\end{matrix}$, m. p. 146°, and a small quantity of a crystalline *compound*, m. p. 230° (decomp.), is obtained at the same time. With excess of hydrazine it gives the *hydrazinolactone hydrazide*, $NH_2\cdot NH\cdot CO\cdot CMe<\begin{matrix}O—C(OH)\cdot NH\cdot NH_2\\ CH:C\cdot OEt\end{matrix}$, m. p. 180° (decomp.).

Ammonia reacts similarly in the cold, giving an *amide*, m. p. 190°, and a second *compound*, m. p. 245° (decomp.).

The compound, m. p. 230°, obtained in the action with hydrazine (1 mol.) and the compound, m. p. 245°, obtained in the action with ammonia are shown to be derivatives of ethyl α-chloro-γ-keto-α-methylglutarate, formed during the aldolisation of the pyruvic ester.

W. G.

Catalytic Preparation of Ketones Over Oxides of Iron. ALPHONSE MAILHE (*Compt. rend.*, 1913, **157**, 219—221).—Both ferrous and ferric oxides can replace cadmium oxide (compare this vol., i, 828) as catalysts in the preparation of simple or mixed ketones from their acids. The oxides are kept at a temperature of 430—490°. The acids employed may be aliphatic or aromatic, or mixtures of the two, and, as in the case of cadmium oxide, *iso*valeric and *iso*butyric acids give the worst yields. The yields are given for numerous ketones.

W. G.

The Mechanism of the Formation of Acrose. ERNST SCHMITZ (*Ber.*, 1913, **46**, 2327—2335).—At the time of their identification of α-acrose as *dl*-fructose, Fischer and Tafel suggested that the accompanying β-acrose present in smaller amount in the product from dibromopropaldehyde and from glycerose was a sugar probably allied to sorbose. From the occurrence of a ketose it is obvious that the process cannot be a simple aldol condensation of glyceraldehyde, but that at some stage of the change an aldehyde group must become transformed into a ketonic one; this probably occurs in the triose molecule, as the conditions of the condensation are not such as to cause a rearrangement in the hexose molecule; it has also been shown (Wohl and Neuberg, A., 1901, i, 12) that the trioses are easily interconvertible under these conditions, because whether aldehyde-free glycerose or pure glyceraldehyde is applied for the condensation, β-acrose is always produced.

By the condensation of pure glyceraldehyde, obtained conveniently by the hydrolysis of the corresponding acetal with $N/10$-sulphuric acid and subsequent treatment with baryta, under the influence of 0·1% excess of baryta at the ordinary temperature, a solution was obtained which yielded a crystalline mixture of two hexoses; this could be separated by recrystallisation from hot methyl alcohol; the less soluble constituent, needles, m. p. 129—130°, D^{16} 1·665, osazone m. p. 216—217°, was *dl*-fructose, whilst the more soluble, rhombic leaflets, m. p. 162—163°, D^{17} 1·634, osazone m. p. 169—170° (decomp.), was *dl*-sorbose, the identity being confirmed by comparison with an artificial mixture of the enantiomorphous forms. The *dl*-fructose, here obtained crystalline for the first time, of course represents α-acrose, whilst the *dl*-sorbose in spite of the somewhat higher m. p. doubtless represents the β-acrose which had previously not been obtained in a quite pure condition. The formation of a racemic sorbose would be expected on theoretical grounds from the condensation of dihydroxyacetone with *dl*-glyceraldehyde. D. F. T.

Cyanohydrins of Certain Monosaccharides. CYRILL KRAUZ and JAN KLOUD (*Eighth Inter. Cong. App. Chem.*, 1912, **25**, 397—401).—On the addition of hydrogen cyanide to a monosaccharide, two epimeric cyanohydrins are produced:

$$-CH(OH)\cdot CHO + HCN = CN\cdot CH(OH)\cdot CH(OH)-$$

(compare Votoček, A., 1911, i, 179). A study has now been made of

the products obtained by the action of hydrogen cyanide on certain monosaccharides.

When arabinose is treated with solution of hydrogen cyanide, a mixture of the amides of l-gluconic and l-mannonic acids is obtained; the former has m. p. 181°, not 160° (decomp.) as stated by Kiliani (A., 1887, 230). In the case of xylose and rhamnose, liquid products were obtained which could not be separated. Rhodeose yields α- and β-rhodeohexonamides (Krauz, A., 1910, i, 224). Fucose furnishes α-fucohexonamide and *β-fucohexonamide*, m. p. 176°. With galactose, α-galactoheptonamide, m. p. 201°, was obtained; the mother liquor when treated with phenylhydrazine gave the phenylhydrazide of this amide, m. p. 226°, together with another phenylhydrazide, m. p. 186°. Mannose yields a mixture of α- and β-mannoheptonamides, the former melting at 214—215°, and not at 182—183° (Fischer and Hirschberger, A., 1889, 482). E. G.

Hydrolysis of Cellulose. I. RICHARD WILLSTÄTTER and LÁSZLÓ ZECHMEISTER (*Ber.*, 1913, **46**, 2401—2412).—Whereas ordinary concentrated hydrochloric acid (37·6% of hydrogen chloride) decomposes and gelatinises cellulose after about a day's action, a more concentrated acid (40—41% of hydrogen chloride) dissolves cellulose completely within a few seconds. At first the cellulose can be precipitated again, but it is rapidly hydrolysed, and finally only dextrose remains in solution. It is possible to follow the course of the change both polarimetrically and gravimetrically, whereby 96% of the theoretical quantity of dextrose is obtained. The 1% solution of cellulose in the concentrated acid is at first optically inactive; it becomes active after about an hour, and increases until hydrolysis is complete in twenty-four to forty-eight hours at the ordinary temperature. The change in rotatory power gives indication of the intermediate formation of higher carbohydrates. An acid, D^{15} 1·212 (41·4% of hydrogen chloride), dissolves 15% of cellulose; the solution is at first colourless and clear; in time it becomes yellow, and later dark yellow as the dextrose is decomposed. On dilution of the solution during the first half-hour, unchanged cellulose is precipitated.

Cellulose dissolves similarly in 66% (D 1·78) hydrogen bromide, but not in concentrated hydriodic acid; hydrofluoric acid (70—75% of hydrogen fluoride) gelatinises, and quickly dissolves cellulose.

Pine-wood dissolves quickly in fuming hydrochloric acid, leaving 30% of its weight undissolved as lignin substance.

The rotatory power of dextrose ($[\alpha]_D$) increases from +54·5° in hydrochloric acid D 1·018 to +97·5° in an acid D 1·204, +106° in an acid D 1·212, and +164·6° in a 44·5% acid. E. F. A.

Certain Substances containing the Cetyl Radicle. ALBERT REYCHLER (*Bull. Soc. chim. Belg.*, 1913, **27**, 217—225).—Triethylcetylammonium iodide, $C_{16}H_{33}\cdot NEt_3I$, is obtained when a mixture of triethylamine and cetyl iodide is heated for two hours at 130°. It dissolves in water, yielding soapy solutions, which develop an abundant

lather when shaken. These solutions only give an opalescence with silver nitrate, and thus appear to be colloidal, this observation being confirmed by a study of their b. p.'s and electrical conductivities. The solid iodide has m. p. 179—181° without decomposition (contrast Krafft and Moye, A., 1889, 689).

An attempt has been made to prepare triethylcetylammonium hydroxide by the action of freshly prepared silver oxide on a boiling alcoholic solution of the corresponding iodide. Under these conditions, however, the base, if formed, is decomposed into diethylcetylamine.

Aqueous solutions of diethylcetylamine hydrochloride behave similarly to those of the above iodide. Determinations of the conductivity at different temperatures show that a period of rapid crystallisation occurs in the region of 0°. The values obtained for the molecular conductivity are greater than those observed for triethylcetylammonium iodide at similar dilutions.

Triethylcetylammonium cetylsulphonate, $C_{16}H_{33}·SO_3·NEt_3·C_{16}H_{33}$, is readily prepared by heating a boiling alcoholic solution of *silver cetylsulphonate* with triethylcetylammonium iodide. It is molten at 172—179° without showing any distinct m. p. It yields soapy solutions in hot water, which, on cooling, separate into a clear liquid and a jelly-like mass. It is soluble in alcohol and in ethyl acetate. From the latter it separates in crystals, m. p. about 53°, which contain solvent of crystallisation. Determinations of the conductivity of aqueous solutions lead to the conclusion that the substance is probably present in the form of multi-molecular aggregates.

In chemical constitution and in the behaviour of their aqueous solutions or pseudo-solutions, these substances are somewhat analogous to soaps. This is confirmed by the fact that solutions of triethylcetylammonium iodide or, better, of diethylcetylamine hydrochloride in water yield excellent results in the cleansing of samples of wool.

H. W.

The Homologue of Muscarine in the C_3 Series V. BRABANT (*Zeitsch. physiol. Chem.*, 1913, **86**, 206—214).—To prepare β-homomuscarine acraldehyde is converted into ethyl αγ-dichloropropyl ether, $CH_2Cl·CH_2·CHCl·OEt$, and this into the ethylacetal of β-chloropropaldehyde, $CH_2Cl·CH_2·CH(OEt)_2$. When this is heated with trimethylamine in a sealed tube on the water-bath, the *hydrochloride* of *β-homomuscarineacetal*, $NMe_3Cl·CH_2·CH_2·CH(OEt)_2$, is obtained.

This is hydrolysed by concentrated hydrochloric acid to *β-homomuscarine hydrochloride*, $NMe_3Cl·CH_2·CH_2·CHO$, which shows all the typical reactions of both aldehyde and amino-groups.

β-Homomuscarineacetal hydrochloride forms stellate aggregates of small needles which are very hygroscopic; the *platinichloride* forms large, prismatic-rhombic, orange-red crystals which blacken at 160°, m. p. 190—195° (decomp.); the *aurichloride* separates in broad, lustrous, straw-yellow needles, m. p. 93—95° (decomp.).

β-Homomuscarine hydrochloride forms hygroscopic crystals; the free base could not be isolated. The *platinichloride* separates in microscopic, orange-yellow rods, decomp. 156—160°. The *auri-*

chloride is straw-yellow, m. p. 150—155° (decomp.). The *semicarbazone* crystallises in small, colourless, regular octahedra, m. p. 247·5° (corr.).

E. F. A.

Compounds of Hydrated Salts with Organic Bases (Dithionates, Sulphates, Thiosulphates). FILIPPO CALZOLARI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 787—792. Compare A., 1912, i, 812).—The dithionate, $MgS_2O_6,8H_2O,2C_8H_{10}O_2N_4$, prepared from magnesium dithionate and a large excess of caffeine, forms colourless, prismatic crystals. The *manganese* derivative, $MnS_2O_6,8H_2O,2C_8H_{10}O_2N_4$, crystallises in colourless needles. The *ferrous* salt,

$$FeS_2O_6,8H_2O,2C_8H_{10}O_2N_4,$$

forms prismatic crystals. The *cobalt* salt, $CoS_2O_6,8H_2O,2C_8H_{10}O_2N_4$, crystallises in pale rose-coloured needles. The *nickel* salt,

$$NiS_2O_6,8H_2O,2C_8H_{10}O_2N_4,$$

forms green crystals isomorphous with those of the cobalt compound.

The compound of magnesium dithionate with hexamethylenetetramine, $MgS_2O_6,6H_2O,2C_6H_{12}N_4$, forms large crystals. The *manganese* compound, $MnS_2O_6,6H_2O,2C_6H_{12}N_4$, is a white, crystalline powder. The *ferrous* salt, $FeS_2O_6,6H_2O,2C_6H_{12}N_4$, is a greenish-white, crystalline powder. The *cobalt* salt, $CoS_2O_6,6H_2O,2C_6H_{12}N_4$, forms rose-red, regular crystals. The *nickel* salt, $NiS_2O_6,6H_2O,2C_6H_{12}N_4$, forms green crystals similar to those of the cobalt compound.

The *compound* of magnesium sulphate and hexamethylenetetramine, $MgSO_4,9H_2O,C_6H_{12}N_4$, forms colourless crystals. The *manganese* compound, $MnSO_4,9H_2O,C_6H_{12}N_4$, forms colourless crystals, and mixed crystals of this compound with that of nickel were also obtained. The *ferrous* compound, $FeSO_4,9H_2O,C_6H_{12}N_4$, must be prepared in the absence of air. The *cobalt* compound, $CoSO_4,9H_2O,C_6H_{12}N_4$, forms rose-red crystals, and mixed crystals of it with the magnesium compound can be obtained. The *nickel* compound, $NiSO_4,9H_2O,C_6H_{12}N_4$, forms large, emerald-green crystals isomorphous with those of the cobalt salt.

The compound of magnesium thiosulphate with hexamethylenetetramine, $MgS_2O_3,8H_2O,C_6H_{12}N_4$, forms colourless, rhombohedral crystals. The *manganese* compound, $MnS_2O_3,8H_2O,C_6H_{12}N_4$, forms very pale rose-coloured crystals. The *ferrous* compound,

$$FeS_2O_3,8H_2O,C_6H_{12}N_4,$$

must be prepared out of contact with the air; it forms greenish-white crystals. The *cobalt* salt, $CoS_2O_3,8H_2O,C_6H_{12}N_4$, forms rose-coloured crystals. The *nickel* compound, $NiS_2O_3,8H_2O,C_6H_{12}N_4$, forms emerald-green crystals.

R. V. S.

Condensation of Amino-acids with Formaldehyde. GINO GALEOTTI (*Biochem. Zeitsch.*, 1913, **53**, 474—492).—On heating amino-acids with formaldehyde, products are obtained which differ both from the original acids and fresh mixtures of the reacting products. Reddish-yellow solutions are obtained, which do not deposit crystals, but yield an amorphous residue on evaporating off the water. The solutions are acid, and only the tyrosine derivative is precipitated on the addition of dilute acids. The glycine, alanine, aspartic acid

and tyrosine derivatives are insoluble in alcohol or acetone, but the leucine and phenylalanine derivatives are soluble. All are insoluble in ether. The aqueous solutions give voluminous precipitates with phosphotungstic, picric and tannic acids, and with the salts of heavy metals. They do not reduce copper salts in alkaline solution, give the diazo-reaction with a yellowish-red or cherry-red colour, and give precipitates on saturation with ammonium sulphate. They dissolve copper hydroxide, yielding malachite-green solutions which give a precipitate on addition of alcohol. They no longer contain the amino-group, as no nitrogen is evolved in the van Slyke reaction, which can be employed for tracing the course of the reaction of the aldehyde on the acids. The glycine derivative was studied in some detail. It has a molecular weight of 288, corresponding with the formula $C_{12}H_{21}O_5N_3$, and m. p. 164°. Attention is called to the similarity in the behaviour of the compounds obtained to the polypeptides, and it is suggested that formaldehyde may play some part in forming complex derivatives from amino-acids in living organisms, analogous to the supposed formation of carbohydrates by condensation with this substance. S. B. S.

Synthesis of the Anhydrides of α-Aminoacyl Glucosamines. CHARLES WEIZMANN and ARTHUR HOPWOOD (*Proc. Roy. Soc.*, 1913, *A*, **88**, 455—461. Compare P., 1912, **28**, 261).—α-Bromoacyl haloids are condensed with glucosamine hydrochloride in the presence of sodium hydroxide (compare P., 1912, **28**, 261), and cold aqueous ammonia is allowed to act on the α-bromoacylglucosamines formed. Anhydrides of the expected α-aminoacylglucosamines are obtained.

Alanylglucosamine anhydride separates in colourless, prismatic needles, which turn brown at 245—250°, and melt at 269—272° to a black liquid. It reduces Fehling's solution on prolonged boiling, but does not react with either phenylhydrazine or semicarbazide.

Leucylglucosamine anhydride forms similar colourless, prismatic needles, which sinters at 205°, m. p. 213—215° (decomp.).

α-Aminolaurylglucosamine anhydride was obtained in colourless crystals. E. F. A.

Esters of Imino- and Oximino-carbonic Acid. JOSEPH HOUBEN and ERICH SCHMIDT (*Ber.*, 1913, **46**, 2447—2460).—Sandmeyer (A., 1886, 611) claimed to have reduced esters of chloroiminocarbonic acid, and obtained ethyl iminocarbonate, $HN:C(OEt)_2$, which was dried over potassium hydroxide. It is shown that under these conditions urethane is formed, and that it was present in Sandmeyer's product.

When the reduction product is carefully dried over ignited sodium sulphate and fractionated in a vacuum, pure iminocarbonic esters are obtainable. Even the pure esters change on prolonged keeping into crystalline cyanuric acid derivatives.

The hydrochloride of the imino-ester is to be regarded as a chloro-imino-ether, $NH_2\cdot CCl(OR)_2$. In presence of water the chlorine is exchanged for hydroxyl, $NH_2\cdot C(OR)_2\cdot OH,HCl$, following which the hydrogen chloride conditions elimination of ammonium chloride and the formation of alkyl carbonate, $CO(OR)_2$.

Similarly, with hydroxylamine the compound

$NH_2 \cdot C(OR)_2 \cdot NH \cdot OH,HCl$

formed decomposes into the oximinocarbonic ester, $C(OR)_2 \colon N \cdot OH$. Working in ethereal solution it was possible to prepare *diethyl* or *dimethyl oximinocarbonate* in this manner, and the method has been extended to the preparation of the true hydroximic esters of the aliphatic series, $OEt \cdot CR \colon N \cdot OH$.

The oximinocarbonic esters, which crystallise well, are obtained by a similar process from the chloroiminocarbonic esters.

Ethyl chloroiminocarbonate has m. p. 39°, agreeing with Sandmeyer's statement; during its preparation a product of unknown constitution crystallising in needles, m. p. 148—149°, is formed.

Methyl chloroiminocarbonate has m. p. 20°, b. p. 63—64°/13 mm., without decomposition.

Ethyl iminocarbonate is a transparent liquid of a strongly basic odour, D^{22} 0·9637.

Ethyl iodoiminocarbonate, $NI \colon C(OEt)_2$, forms yellow crystals and crusts. When shaken with mercury in ethereal or alcoholic solution, *aziethyl carbonate*, $C(OEt)_2 \colon N \cdot N \colon C(OEt)_2$, is formed.

Ethyl carbanilinoiminocarbonate, $C_6H_5 \cdot NH \cdot CO \cdot N \colon C(OEt)_2$, forms crystals sintering at 100°, m. p. 101°.

Ethyl thiocarbanilinoiminocarbonate has m. p. 117—118°.

E. F. A.

The Organic Acid Amides and their Metallic Derivatives as Acids and Salts of the Ammonia System of Acids, Bases, and Salts. EDWARD C. FRANKLIN (*Eighth Inter. Cong. App. Chem.*, 1912, **6**, 119—130. Compare A., 1912, ii, 451).—A recapitulation of the author's classification of amides and their derivatives into "ammono-acids," "ammono-bases," "ammono-salts," "ammono-esters," "mixed ammono-acids," and "acid anammonides." The ammono-acids vary in strength from acetamide, benzamide, and carbamide, which only form salts in liquid ammonia solution and have only a feeble conductivity in that solvent, to such compounds as phthalimide and "saccharin" which are not excelled in strength by the strongest carboxylic acids.

J. C. W.

Compounds of Ferricarbamide. GIUSEPPE A. BARBIERI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 867—870).—These compounds exhibit complete chemical and crystallographic similarity to the salts of chromicarbamide already known. They are all greenish-blue in the solid state and in concentrated solution, but dilute solutions are yellow and are precipitated by ammonia even in the cold. Compounds analogous to the hydrate and carbonate of chromicarbamide cannot be prepared.

The *perchlorate*, $[Fe(CON_2H_4)_6](ClO_4)_3$, is obtained by adding a concentrated solution of carbamide to a solution of ferric perchlorate containing excess of perchloric acid, or from a perchlorate and another ferricarbamide compound. It forms mixed crystals with the corresponding *chromicarbamide perchlorate*, $[Cr(CON_2H_4)_6](ClO_4)_3$, which is a green, crystalline powder.

Ferricarbamide nitrate, $[Fe(CON_2H_4)_6](NO_3)_3$, the *permanganate*, $[Fe(CON_2H_4)_6](MnO_4)_3$, the *dichromate*, $[Fe(CON_2H_4)_6](Cr_2O_7)_3$, the *chloride*, $[Fe(CON_2H_4)_6]Cl_3,3H_2O$, the *bromide*,

$$[Fe(CON_2H_4)_6]Br_3,3H_2O,$$

and the *nitrate periodide*, $[Fe(CON_2H_4)_6](NO_3)_2I,I_2$, are similarly prepared. On treating the bromide with bromine an unstable perbromide is obtained. R. V. S.

Preparation of Melamine and Ammeline from Dicyanodiamide; Triaminomelamine and Diaminoammeline. ROBERT STOLLÉ and K. KRAUCH (*Ber.*, 1913, **46**, 2337—2339).—When powdered dicyanodiamide is treated with concentrated ammonia solution in a sealed tube at 120° for three hours, a crystalline deposit is obtained consisting of melamine in 35% yield and of ammeline in 20% yield, which can be separated by the sparing solubility of the latter in water; a small quantity of carbamide and guanidine can be found in the liquid from which the crystalline mass has separated. It is suggested that possibly the dicyanodiamide is acted on concurrently by the ammonia and by water, with the production of guanidine and cyanamide and of guanidine and cyanic acid respectively; unchanged dicyanodiamide then reacts with the cyanamide yielding melamine, and with the cyanic acid yielding ammeline.

Triaminomelamine (cyanuric hydrazide; von Meyer and Näbe, A., 1911, i, 122; Finger, A., 1907, i, 298), microscopic needles, m. p. 287°, was obtained by heating melamine with a quinquemolecular proportion of hydrazine hydrate for five hours under pressure at 150°; it quickly reduces warm ammoniacal silver nitrate, and when shaken in hydrochloric acid solution with benzaldehyde yields a *tribenzylidene* derivative.

When ammeline is heated with an equal quantity of hydrazine hydrate for five hours under pressure at 130°, diaminoammeline, prisms, m. p. above 340°, is obtained; this in aqueous solution reacts with benzaldehyde, producing a *dibenzylidene* derivative, m. p. 315°. D. F. T.

Condensation of Melamine with Dextrose. LEOPOLD RADLBERGER (*Chem. Zentr.*, 1913, i, 2110; from *Österr-ung Zeitsch. Zuckerind.*, 1913, **42**, 236—239).—Melamine and dextrose were condensed by heating in 30% alcoholic solution on the water-bath. The product consisted of 2 mols. melamine to 1 mol. dextrose, namely, $[C_3N_3(NH_2)_2\cdot NH]_2CH\cdot[CH\cdot OH]_4\cdot CH_2\cdot OH$. It has m. p. 281°, forming colourless, lustrous crystals which do not reduce Fehling's solution. E. F. A.

Synthesis of Mercury Fulminate from Propyl Alcohol. A. L. KIBLER (*Eighth Inter. Cong. App Chem.*, 1912, **25**, 239—243). —Experiments are described in which propyl alcohol, *iso*butyl alcohol, amyl alcohol, acetone, and propaldehyde were substituted for ethyl alcohol in the usual process for the preparation of mercury fulminate. A small quantity of mercury fulminate was obtained from the propyl alcohol, but not from any of the other substances. In the experi-

ments with propyl alcohol, an intermediate compound was isolated, which forms large, white, lustrous plates, and decomposes either spontaneously or when treated with water, leaving traces of a grey powder, probably composed of mercury. E. G.

Azides of Carbamic Acid from Ketens. VII. E. OLIVERI-MANDALÀ and E. CALDERARO (*Gazzetta*, 1913, **43**, i, 538—543. Compare this vol., i, 716).—Azoimide reacts with ketens giving azides of carbamic acid. The stages in the reaction are probably indicated by the scheme: $CR_2{:}CO \longrightarrow CHR_2{\cdot}CO{\cdot}N_3 \longrightarrow [CHR_2{\cdot}CO{\cdot}N] \longrightarrow CHR_2{\cdot}N{:}CO$, and from this carbimide the azide, $CHR_2{\cdot}NH{\cdot}CO{\cdot}N_3$, is produced by the addition of a further molecule of azoimide.

Keten reacts with an ethereal solution of azoimide at the temperature of a mixture of ice and salt, yielding *methylcarbamazide*, $N_3{\cdot}CO{\cdot}NHMe$, which forms lustrous laminæ or tablets, m. p. 46—47°. The formation of the azide shows that keten has reacted as though it had the ketonic formula of Staudinger, and not the hydroxylic formula of Wilsmore. With aniline, the azide yields *s*-phenylmethylcarbamide and aniline azoimide. Alcoholic ammonia reacts with the azide, yielding methylcarbamide and ammonium azoimide. Boiling water decomposes the azide, carbon dioxide, azoimide and methylamine being formed; by keeping an aqueous solution of the azide in a desiccator, *methylammonium azoimide*, CH_6N_4, can be obtained; it is a deliquescent substance, which is completely fused at 115°.

Diphenylketen and azoimide yield *diphenylmethylcarbamazide*,

$$N_3{\cdot}CO{\cdot}NH{\cdot}CHPh_2,$$

which crystallises in colourless, silky needles, m. p. 121—123°. When heated for four hours at 100—110° in a sealed tube with alcoholic ammonia, the azoimide yields *as*-diphenylmethylcarbamide. When heated with aniline in a sealed tube for two hours at 90°, the azide is converted into *diphenylmethylphenylcarbamide*,

$$NHPh{\cdot}CO{\cdot}NH{\cdot}CHPh_2,$$

which forms silky crystals, m. p. 208—209°. This substance dissolves in concentrated sulphuric acid, giving an orange-red coloration.

R. V. S.

Action of Magnesium Methyl Iodide on Silicon Hexachloride. GEOFFREY MARTIN (*Ber.*, 1913, **46**, 2442—2447. Compare P., 1913, **29**, 190).—The yellow substance formed by the action of magnesium methyl iodide on silicon hexachloride has the composition $Si_6H_9O_{13}Me$. When heated, hydrogen and methane are evolved, and a silicon compound is obtained practically without carbon, but which still contains coupled silicon groups, since on dissolution in potassium hydroxide hydrogen is evolved. On the addition of excess of acid, silicic acid is precipitated. E. F. A.

Researches on the Direct Introduction of Substituents into the Benzene Nucleus During the Years 1910, 1911, and 1912. ARNOLD F. HOLLEMAN (*Chem. Weekblad*, 1913, **10**, 604—620). —A summary of papers on this subject published since the issue of

the author's work, "Die direkte Einführung von Substituenten in den Benzolkern," in the year 1910. A. J. W.

A Simple Method of Preparing Hexamethylbenzene. HANS RECKLEBEN and JOHANNES SCHEIBER [with K. SCHNABEL] (*Ber.*, 1913, **46**, 2363—2365).—When the vapour from a molecular mixture of acetone and methyl alcohol is passed over aluminium oxide, heated at about 400°, clean crystals of hexamethylbenzene are obtained in about 10% of the theoretical quantity. The oily residue represents a complicated mixture. Replacement of aluminium oxide by other oxides led to unfavourable results.

On bromination of hexamethylbenzene, a mixture of bromides, m. p. 231—269°, and containing from 64% to 80% of bromine, is obtained. E. F. A.

Nitro-derivatives of High-boiling Mineral Oils. KONSTANTIN CHARITSCHKOFF (*Chem. Zeit.*, 1913, **37**, 869).—When Caucasian lubricating oils are warmed with fuming nitric acid, they form syrupy, very viscous nitro-derivatives, which are soluble in most organic solvents with the exception of light petroleum. They are weak acids, dissolve in alkalis, and form insoluble salts with the alkaline earths and heavy metals which are similar to the salts of polynaphthenic acids (A., 1910, i, 110). Moreover, their composition and properties agree with those of the nitro-derivatives of polynaphthenic acids.
J. C. W.

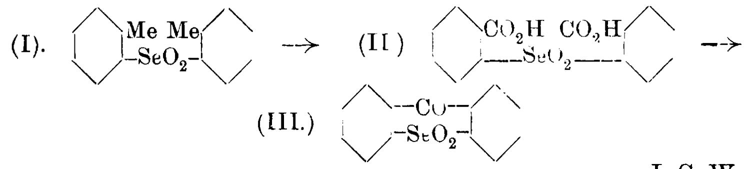
The Reaction Between Selenic Acid and Toluene. HOWARD WATERS DOUGHTY and FRANK ROSE ELDER (*Eighth Inter. Cong. App. Chem.*, 1912, **6**, 93—101).—Toluene and concentrated selenic acid were left together for some months during which time carbon dioxide was evolved. The lower, dark red, viscous layer was then poured into water and separated into an acid solution and a small amount of a red oil with a solid admixture.

The acid solution was exactly neutralised with barium hydroxide, filtered from barium selenate, evaporated to dryness, and extracted during several days with chloroform, which removed traces of the above red oil. The residue gave a mixture of *o*- and *p*-tolueneselenonic acids which could not be separated, but on reduction of a concentrated solution with hydrogen chloride, p(?)-*tolueneseleninic acid*, $C_6H_4Me\cdot SeO_2H,H_2O$, was precipitated in long, silky, white needles, m. p. 160°, whilst the mother liquor yielded o(?)-*tolueneseleninic acid*, with $\frac{1}{2}H_2O$, in nodules of short, white needles, m. p. 99—101°.

The red oil was washed with ether in which the solid substance is insoluble, and then distilled. It had b. p. 201—202°/18—20 mm., and solidified to a light yellow, crystalline mass, m. p. 69·5—70·5°, which was identified with *p*-ditolyl selenide (Zeiser, A., 1895, i, 512). On oxidation with hot permanganate, it yielded *diphenylselenone*-4 : 4′-*dicarboxylic acid*, $SeO_2(C_6H_4\cdot CO_2H)_2$, as a heavy, white solid, m. p. 283°, which is sparingly soluble in hot alcohol, and insoluble in all other common solvents.

The crystalline substance, insoluble in ether or water, was recrystal-

lised from alcohol in colourless, stout, hexagonal prisms, m. p. 183°. It was not affected by boiling alkalis or permanganate, but yielded salicylic acid on fusion with potassium hydroxide. It is, therefore, *benzophenoneselenone* (III), and its formation is explained by assuming that *o*-ditolyl selenide (I) is formed as an intermediate product, and is then oxidised to diphenylselenone-2 : 2′-dicarboxylic acid (II), which condenses with loss of carbon dioxide and water.



J. C. W.

Action of Sodium in Liquid Ammonia on Phenylacetylene and Styrene. PAUL LEBEAU and MARIUS PICON (*Compt. rend.*, 1913, **157**, 223—224. Compare this vol., i, 950).—Sodium in liquid ammonia reacts with phenylacetylene, giving the corresponding sodium derivative (2 mols.) and ethylbenzene (1 mol.), with the formation of sodamide. Unlike the true acetylenes of the fatty series, the hydrogenation does not stop at the ethylenic hydrocarbon, but the fully saturated hydrocarbon is produced:

$$3CPh\colon CH + 4NH_3Na = 2CPh\colon CNa + C_6H_5\cdot Et + 2NaNH_2 + 2NH_3.$$

Styrene itself reacts slowly with sodium in liquid ammonia, the products being ethylbenzene and sodamide. W. G.

A Yellow Hydrocarbon of the Fluorene Series. RUDOLF PUMMERER and GUSTAV DORFMÜLLER (*Ber.*, 1913, **46**, 2386—2389).—When fluorene is heated with lead dioxide and sodium ethoxide in pyridine solution, small quantities of a yellow hydrocarbon are formed, owing to the formation of acetaldehyde, and coupling of this with two molecules of fluorene. The final product is *dehydroethylidenebisfluorene* (I), but *ethylidenebisfluorene* (II) is formed first, and may also be obtained by reducing the dehydro-compound with zinc dust and acetic acid. It is very readily oxidised by lead dioxide and even by atmospheric oxygen. The double bond only very slowly absorbs bromine, and does not react with permanganate in pyridine solution.

$$\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}{>}C\colon CMe\cdot CH{<}\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}$$
(I.)

$$\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}{>}CH\cdot CHMe\cdot CH{<}\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}$$
(II.)

Dehydroethylidenebisfluorene crystallises in oblique-ended, yellow prisms; it darkens at 280°, but has not melted at 350°. In small quantities it apparently distils unchanged.

Ethylidenebisfluorene is colourless, m. p. 262—263°, to a yellowish-brown liquid. E. F. A.

Orthohalogenated *p*-Nitroanilines and their Derivatives. WILHELM KÖRNER and ANGELO CONTARDI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 823—836).—2-Chloro-4-nitroaniline forms pale yellow

needles, m. p. 104·5°. Its acetyl derivative crystallises in straw-coloured prisms, m. p. 139°.

3-*Chloro*-4-*bromo*-1-*nitrobenzene* (obtained from the perbromide of the diazonium compound of the preceding substance) forms colourless needles or prisms, m. p. 62°.

3-*Chloro*-4-*iodo*-1-*nitrobenzene* (similarly prepared) crystallises in almost colourless needles, m. p. 103°.

2-Bromo-4-nitroaniline crystallises in pale yellow needles, m. p. 104·5°. Its monoacetyl derivative forms flat prisms, m. p. 114°; the *diacetyl* derivative in stout prisms, m. p. 132°.

From the amino-derivative by diazotisation, 4-chloro-3-bromo-1-nitrobenzene can be obtained; it crystallises in almost colourless prisms, m. p. 61°, and is identical with the compound obtained from 6-chloro-3-nitroaniline. The corresponding 3-bromo-4-iodo-1-nitrobenzene crystallises in needles or prisms, m. p. 106°. 2-Iodo-4-nitroaniline, m. p. 109°, occurs in yellowish-red prisms and also in golden-yellow laminæ; the former is the more stable form. The substance yields a *monoacetyl* and a *diacetyl* derivative.

2-Iodo-4-nitroaniline can be diazotised, and by the subsequent introduction of chlorine, 4-chloro-3-iodo-1-nitrobenzene can be prepared; it crystallises in colourless needles, m. p. 78°, and is identical with the compound obtained from 6-chloro-3-nitroaniline in a similar way.

2 : 6-Dichloro-4-nitroaniline crystallises in lemon-yellow needles, m. p. 195°. It is best diazotised in nitric acid (D 1·38) at 0°. It yields a monoacetyl derivative (almost colourless, flat needles, m. p. 215°) and a diacetyl derivative, m. p. 142·5°, which crystallises in prisms of the monoclinic system

[E. Artini: $a:b:c = 1{\cdot}1361:1:0{\cdot}8753$; $\beta = 70{\cdot}4°$, D 1·565].

When an alcoholic solution of the preceding amino-compound containing a little concentrated sulphuric acid is treated with ethyl nitrite, 3 : 5-dichloro-1-nitrobenzene is produced; it crystallises in colourless plates, m. p. 65·4°. On reduction with tin and hydrochloric acid it yields the corresponding dichloroaniline, which forms needles or prisms, m. p. 51·5°. From this substance, 1 : 3 : 5-trichlorobenzene is obtainable; it crystallises in colourless needles, m. p. 63·5°, and is identical with that obtained from 2 : 4 : 6-trichloroaniline, m. p. 77·5°. 3 : 5-Dichloro-1-bromobenzene crystallises in colourless needles, m. p. 75·8°. 3 : 5-*Dichloro*-1-*iodobenzene* has m. p. 54°; it is identical with that obtained from 2 : 4-dichloro-6-iodoaniline, m. p. 84°.

3 : 4 : 5-Trichloro-1-nitrobenzene (from 2 : 6-dichloro-4-nitroaniline) forms pale yellow prisms, m. p. 72·5°. On reduction and elimination of the amino-groups it yields 1 : 2 : 3-trichlorobenzene, m. p. 50·8°, identical with that obtained from 2 : 6-dichloroaniline (Körner and Contardi, A., 1909, i, 220).

3 : 5-Dichloro-4-bromo-1-nitrobenzene (from the dichloronitro-derivative) crystallises in pale yellow prisms, m. p. 88°.

3 : 5-*Dichloro*-4-*iodo*-1-*nitrobenzene* forms yellow prisms, m. p. 154·8°. On reduction with ferrous sulphate and ammonia, and subsequent elimination of the amino-group, it yields 1 : 3-*dichloro*-2-*iodobenzene*, which crystallises in thin, colourless plates, m. p. 68°. The same

substance can be prepared from the 2 : 6-dichloroaniline already mentioned.

2 : 6-Dibromo-4-nitroaniline (by the action of bromine on *p*-nitroaniline) crystallises in golden-yellow laminæ, m. p. 202·5°. Its monoacetyl derivative forms almost colourless needles, m. p. 232°. The diacetyl derivative, m. p. 136°, crystallises in the pinaconic class of the triclinic system [$a : b : c = 1·0901 : 1 : 0·8325$, α 88°43′4″, β 70°49′34″, γ 93°25′39″, D 1·939].

3 : 5-Dibromo-1-nitrobenzene is obtained by diazotising (in alcoholic solution containing sulphuric acid) either 2 : 6-dibromo-4-nitroaniline or 4 : 6-dibromo-2-nitroaniline; it crystallises in thin, almost colourless laminæ, m. p. 104·5°. From it *s*-chlorodibromobenzene (m. p. 119°) and s-*dibromoiodobenzene* (m. p. 124·8°) can be readily prepared. These substances can also be obtained from the following corresponding halogenated anilines: 4-chloro-2 : 6-dibromoaniline (m. p. 102°); 2 : 6-*dibromo*-4-*iodoaniline* (colourless needles, m. p. 147°); 2 : 4-*dibromo*-6-*iodoaniline* (colourless needles, m. p. 123·5°).

3 : 4 : 5-Tribromo-1-nitrobenzene (from the perbromide of the diazo-compound of the dibromonitroaniline already mentioned) crystallises in yellow prisms, m. p. 111·9°. On diazotisation and elimination of the amino-group it yields 1 : 2 : 3-tribromobenzene, m. p. 87·8°.

4-*Chloro*-3 : 5-*dibromo*-1-*nitrobenzene* (obtained in an analogous manner to the nitrotribromo-derivative) crystallises in yellow, tabular prisms, m. p. 92·7°. On reduction and elimination of the amino-group it yields 1-chloro-2 : 6-dibromobenzene, which forms colourless plates, m. p. 71°, and is identical with the product obtained from the corresponding dibromoaniline.

3 : 5-*Dibromo*-4-*iodo*-1-*nitrobenzene* crystallises in prisms, m. p. 135·5°. It is not possible to reduce this compound without altering it. The corresponding 1 : 3-dibromo-2-iodobenzene (colourless, tabular prisms, m. p. 72°) is prepared from *o*-dibromoaniline.

2 : 6-Di-iodo-4-nitroaniline (from iodine chloride and an acetic acid solution of *p*-nitroaniline) forms golden-yellow scales or flat needles, m. p. 245°. Its *monoacetyl* derivative forms slightly yellow needles, m. p. 249°; the *diacetyl* derivative forms stout prisms, m. p. 171°, of the pinacoidal class of the triclinic system [$a : b : c = 0·9682 : 0 : 0·7260$, α 83°6′43″, β 76°8′29″, γ 99°42′44″, D 2·290].

3 : 5-Di-iodo-1-nitrobenzene (from the di-iodonitroaniline above described by diazotisation in alcoholic solution in presence of sulphuric acid) forms slightly yellow prisms, m. p. 104·5°. When reduced with ferrous sulphate and ammonia it gives 3 : 5-di-iodoaniline (colourless needles, m. p. 110°).

5-*Chloro*-1 : 3-*di-iodobenzene* is obtained from 4-chloro-2 : 6-di-iodoaniline, and forms lustrous, colourless needles, m. p. 101°.

5-*Bromo*-1 : 3-*di-iodobenzene* (similarly obtained) crystallises in long needles, m. p. 140°

1 : 3 : 5-Tri-iodobenzene (from 2 : 4 : 6-tri-iodoaniline, m. p. 185·6°, or from *s*-di-iodoaniline, m. p. 110°) forms opaque, colourless needles, m. p. 184·2°.

4-*Chloro*-3 : 5-*di-iodo*-1-*nitrobenzene* (prepared by the action of cuprous chloride on the nitrate of the diazo-compound from 4 : 6-di-iodo-2-nitro-

aniline) crystallises in almost colourless needles, m. p. 110°. Reduction of this compound is best effected with an alcoholic solution of ammonium sulphide; a small quantity of a sulphur *compound* is formed at the same time. 2-*Chloro*-1 : 3-*di-iodobenzene* is obtained by decomposing the diazo-salt of this amino-compound with absolute alcohol; it forms thin, rhombic plates, m. p. 82°.

4-*Bromo*-3 : 5-*di-iodo*-1-*nitrobenzene* (from the nitrate of the diazo-compound of the di-iodonitroaniline and cuprous bromide) forms almost colourless needles, m. p. 125·4°, and crystallises from benzene with $1C_6H_6$ in prisms.

3 : 4 : 5-Tri-iodo-1-nitrobenzene (from di-iodonitroaniline by way of the diazo-compound) crystallises in shining yellow prisms. It is reduced (with difficulty) to the corresponding aniline by ferrous sulphate and ammonia, and when this is treated with an alcoholic solution of ethyl nitrite, 1 : 2 : 3-tri-iodobenzene (m. p. 116°) is obtained, identical with that from 2 : 6-di-iodoaniline (m. p. 122°; Körner and Bellasio, A., 1908, i, 778).

2-Chloro-6-bromo-4-nitroaniline is obtained by treating 2-chloro-4-nitroaniline with the calculated quantity of bromine; it forms yellow needles, m. p. 177·4°. The monoacetyl derivative crystallises in pale straw-coloured needles, m. p. 224°, and the diacetyl derivative, tabular prisms, m. p. 139° [prismatic class of the monoclinic system, $a:b:c = 1·1127:1:0·8509$, β 70·36°, D 1·749].

3-Chloro-5-bromo-1-nitrobenzene (from 2-chloro-6-bromo-4-nitroaniline by means of ethyl nitrite) crystallises in thin plates, m. p. 81·2°. On reduction with tin and hydrochloric acid it yields 3-*chloro*-5-*bromoaniline* (colourless needles or prisms), from which 1-*chloro*-5-*bromo*-3-*iodobenzene* can be prepared by way of the diazo-compound; it forms lustrous needles, m. p. 85·8°, and can also be obtained from 4-*chloro*-2-*bromo*-6-*iodoaniline,* which crystallises in needles, m. p. 110·5°.

3 : 4-*Dichloro*-5-*bromo*-1-*nitrobenzene* (from the corresponding chlorobromonitroaniline already described) forms yellow prisms, m. p. 82·4°.

5-*Chloro*-3 : 4-*dibromo*-1-*nitrobenzene* (similarly prepared) crystallises in yellow prisms, m. p. 99·5°. The corresponding 3-chloro-1 : 2-dibromobenzene (prepared by replacing $-NH_2$ by $-Br$ in 2-chloro-3-bromoaniline) forms rhombic plates, m. p. 72·6°.

3-*Chloro*-5-*bromo*-4-*iodo*-1-*nitrobenzene* (prepared in a similar way to its analogues above described) crystallises in lustrous needles, m. p. 159°.

2-Chloro-6-iodo-4-nitroaniline (from 2-chloro-4-nitroaniline and iodine chloride) forms pale yellow needles, m. p. 195°. Its *monoacetyl* derivative forms needles or prisms, m. p. 207°, and the *diacetyl* derivative, m. p. 113°, prisms of the monoclinic system [$a:b:c = 1·038:1:0·799$, $\beta = 71·44°$, D 1·913].

By elimination of the amino-group the preceding aniline yields 3-*chloro*-5-*iodo*-1-*nitrobenzene*, which forms bundles of prisms, m. p. 70·4°.

3 : 4-*Dichloro*-5-*iodo*-1-*nitrobenzene* (from the above-described aniline) crystallises in pale yellow prisms, m. p. 59°. It is not possible to obtain the corresponding aniline by reduction. Ammonia and ferrous sulphate reduce it very slowly, tin and hydrochloric acid yield

3-*chloro*-5-*iodoaniline* (colourless plates, m. p. 69·8°), whilst ammonium sulphide in alcoholic solution gives 3 : 4-dichloroaniline.

3-*Chloro*-4-*bromo*-5-*iodo*-1-*nitrobenzene* (prepared like the analogous compound above described) crystallises in almost colourless needles, m. p. 95°.

5-*Chloro*-3 : 4-*di-iodo*-1-*nitrobenzene* (from 2-chloro-6-iodo-4-nitroaniline) forms almost colourless needles, m. p. 146·5°.

2-*Bromo*-6-*iodo*-4-*nitroaniline* (from 2-bromo-4-nitroaniline and iodine chloride) crystallises in pale yellow needles, m. p. 221°. The *monoacetyl* derivative forms yellow prisms, m. p. 226°, and the *diacetyl* derivative, m. p. 134°, stout prisms of the pinacoidal class of the triclinic system [$a:b:c = 0·9470:1:0·7288$, α 83°59′54″, β 77°30′18″, γ 99°6′14″, D 2·112].

3-*Bromo*-5-*iodo*-1-*nitrobenzene* (from the preceding aniline) forms thin, flat needles, m. p. 97·5°.

4-*Chloro*-3-*bromo*-5-*iodo*-1-*nitrobenzene* (from the above-described bromoiodonitroaniline) crystallises in yellow prisms, or in colourless needles, m. p. 84°. R. V. S.

Preparation of Benzylamine. MARTIN O. FORSTER and HILDA M. JUDD (*Eighth Inter. Cong. App. Chem.*, 1912, **6**, 118).—A cheap laboratory process for the preparation of benzylamine hydrochloride is described. Benzyl chloride is occasionally shaken during three days with sodium azoimide in spirit, the benzylazoimide is extracted with ether, and, without purification, reduced by means of zinc dust and 50% acetic acid. J. C. W.

Salts of Dibasic Organic Acids with *o*-, *m*-, and *p*-Toluidine, and with *m*-4-Xylidine. F. GRÜNWALD (*J. pr. Chem.*, 1913, [ii], **88**, 168—179).—The three toluidines and *m*-4-xylidine combine with malonic, succinic, malic, tartaric, and fumaric acids in aqueous solution to form acid salts. Attempts to prepare the normal salts were unsuccessful.

o-*Toluidine hydrogen malonate* crystallises in short prisms (decomp. 108°); the m-*toluidine* salt in colourless prisms (decomp. 93°). The corresponding *hydrogen succinates* also crystallise in prisms (decomp. 60° and 121° respectively).

o-*Toluidine hydrogen malate* forms leaflets (decomp. 120°); the isomeric m- and p-*toluidine* salts, colourless needles (decomp. 103° and 153°). o-*Toluidine hydrogen fumarate* crystallises in hexagonal leaflets (decomp. 150°); the m- and p-*toluidine* salts in colourless prisms (decomp. 165° and 175°).

Of the salts of *m*-4-xylidine, the *hydrogen malonate* forms thin needles (decomp. 93°), the *hydrogen succinate*, large prisms (decomp. 89°), the *hydrogen tartrate*, prisms (decomp. 170°), and the *hydrogen fumarate*, leaflets (decomp. 178°).

When heated with cupric oxide, an aqueous solution of *m*-toluidine hydrogen oxalate yields *cupric* m-*toluidine oxalate*, $Cu(C_9H_{10}O_4)_2$, which separates with $3H_2O$ in crystals resembling copper sulphate; the acid oxalates of *o*- and *p*-toluidine do not form similar copper salts.

Cupric o-*toluidine malonate*, $Cu(C_{10}H_{12}O_4)_2,5H_2O$, forms bluish-green

crystals, which become anhydrous and green at 100°. *Cupric* m-*toluidine malonate* separates with $3H_2O$ in steel-blue crystals; the anhydrous salt is green. *Cupric* p-*toluidine malonate* crystallises with $1H_2O$. *Cupric* m-4-*xylidine malonate*, $Cu(C_{11}H_{14}O_4)_2,3H_2O$, forms blue leaflets.

The acid toluidine succinates do not yield normal cupric salts.

When boiled with nickel hydroxide in aqueous solution, *o*-toluidine hydrogen malonate yields a *nickel* salt, which forms green crystals containing $6H_2O$; *nickel* m-*toluidine malonate*, $Ni(C_{10}H_{12}O_4)_2$, crystallises with $4H_2O$ in reddish-violet leaflets; *nickel* p-*toluidine malonate* forms green, rhombic leaflets containing $2H_2O$.

Nickel m-4-*xylidine malonate* separates in dove-grey crystals containing $4H_2O$. F. B.

Interactions with Succinylglycyl Chloride and Hippuryl Chloride. JOHANNES SCHEIBER and HANS RECKLEBEN (*Ber.*, 1913, **46**, 2412—2420).—*Succinylglycine*, $C_2H_4{<}{CO \atop CO}{>}N\cdot CH_2\cdot CO_2H$, is prepared by heating molecular proportions of succinic anhydride and glycine at 170—180°; the colourless crystals have m. p. 113°.

With phosphorus pentachloride, colourless needles, m. p. 76°, of *succinylglycyl chloride* are obtained.

The chloride reacts with aniline, forming *succinylglycylanilide*, which crystallises in colourless needles, m. p. 151°.

With benzene and aluminium chloride, *succinyliminoacetophenone*, $C_2H_4{:}(CO)_2{:}N\cdot CH_2\cdot COPh$, is formed; it separates in colourless needles, m. p. 143—144°, and yields a colourless *phenylhydrazone*, m. p. 201°.

Condensation of succinylglycyl chloride with ethyl sodiomalonate in boiling ether gives *ethyl di*(*succinylglycyl*)*malonate*,

$$C[CO\cdot CH_2\cdot N{:}(CO)_2{:}C_2H_4]_2(CO_2Et)_2;$$

it separates in colourless platelets, m. p. 107°, and gives no coloration with ferric chloride.

Phenylhydrazine converts it into *ethyl* 1-*phenyl*-3-*succinylimidomethyl*-5-*pyrazolone*-4-*carboxylate*,

$$C_2H_4{:}(CO)_2{:}N\cdot CH_2\cdot C{<}{CH(CO_2Et) \atop N\text{——}NPh}{>}CO.$$

This crystallises in matted needles, m. p. 157°, giving a bluish-red coloration with ferric chloride.

Succinylglycylphenylhydrazide,

$$C_2H_4{:}(CO)_2{:}N\cdot CH_2\cdot CO\cdot NH\cdot NHPh,$$

forms colourless needles, m. p. 213°.

A second product of the condensation is *ethyl succinylglycylmalonate*, $C_2H_4{:}(CO)_2{:}N\cdot CH_2\cdot CO\cdot CH(CO_2Et)_2$, which forms colourless needles, m. p. 55°.

Succinylglycyl chloride and ethyl sodioacetoacetate condense to *ethyl succinylglycylacetoacetate*, of which the colourless needles have m. p. 102°.

Condensation with sodium acetylacetone leads to two products. *Succinylglycylacetylacetone*, $C_2H_4{:}(CO)_2{:}N\cdot CH_2\cdot CO\cdot CH(COMe)_2$, forms

needles, m. p. 122°. *Di(succinylglycyl)acetylacetone* also yields needles, m. p. 150°.

Ethyl cyanosuccinylglycylacetate,

$$C_2H_4{:}(CO)_2{\cdot}N{\cdot}CH_2{\cdot}CO{\cdot}CH(CN){\cdot}CO_2Et,$$

forms colourless needles, m. p. 73°.

Hippuryl chloride and ethyl sodiomalonate condense to a derivative of 2 : 5-*diketo*-1 : 4-*dibenzoylpiperazine* and *ethyl hippurylmalonate*, $C_6H_5{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO{\cdot}CH(CO_2Et)_2$. The latter has m. p. 85°, and shows a positive ferric chloride reaction. With phenylhydrazine, *ethyl* 1-*phenyl*-3-*benzamidomethyl*-5-*pyrazolone*-4-*carboxylate*,

$$NHBz{\cdot}CH_2{\cdot}C{<}{\begin{matrix}CH(CO_2Et)\\N\text{——}NPh\end{matrix}}{>}CO,$$

is obtained, m. p. 122—123°. It forms a well characterised, crystalline *sodium* salt. The above derivative of 2 : 5-diketo-1 : 4-dibenzoylpiperazine has m. p. 116°; it dissolves in sodium carbonate, and on precipitation with acid, a substance, m. p. 137°, is obtained containing $\frac{1}{2}H_2O$ less, and likewise giving a bluish-violet ferric chloride reaction; on crystallising the compound m. p. 137° from ethyl alcohol, the substance of m. p. 116° is obtained. The latter is regarded as a condensation of two molecules of the piperazine with a molecule of water.

O-*Hippurylacetylacetone*, $NHBz{\cdot}CH_2{\cdot}CO{\cdot}O{\cdot}CMe{:}CH{\cdot}COMe$, crystallises in platelets, m. p. 109°.

Ethyl cyanohippurylacetate, $NHBz{\cdot}CH_2{\cdot}CO{\cdot}CH(CN){\cdot}CO_2Et$, forms colourless needles, m. p. 139°. The additive product with phenylhydrazine has m. p. 107°.

E. F. A.

Cholesterol. XVII. α-Cholestanol. ADOLF WINDAUS and C. UIBRIG (*Ber.*, 1913, **46**, 2487—2491).—α-Cholestanol yields on oxidation a ketonic acid, $C_{32}H_{56}O_3$. This is not in agreement with the usual formula $C_{27}H_{48}O$ for cholestanol, and it is proved that the analytical data, particularly of cholestyl chloride and bromide, agree with the formula $C_{32}H_{56}O$ or $C_{32}H_{58}O$. Apparently on treatment of cholesterol with sodium and amyl alcohol, condensation and ring closure to a saturated compound takes place. Accordingly, cholestanol is not a dihydrocholesterol, but an *iso*amyl derivative of cholesterol,

$$C_{25}H_{44}{<}{\begin{matrix}CH{\cdot}OH\\|\\CH{\cdot}C_5H_{11}\end{matrix}}.$$

Cholestyl bromide crystallises in hexagonal platelets, m. p. 118°.

Ketocholestanolcarboxylic acid, $C_{25}H_{44}{<}{\begin{matrix}CO_2H\\CO{\cdot}C_5H_{11}\end{matrix}}$, separates in long, slender needles which sinter at 110°, m. p. 125°. The *semicarbazone* crystallises in long needles, m. p. 207°.

E. F. A.

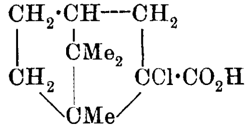
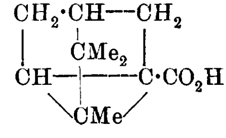
Isomeric Naphthenic Acids. FRANK W. BUSHONG and I. W. HUMPHREY (*Eighth Inter. Cong. App. Chem.*, 1912, **6**, 57—67).—A quantity of commercial naphthenic acid from Baku, which contained about 50% of water and 5% of illuminating oils, was fractionally esterified. Several portions of 2 litres were heated with 200 c.c. of alcohol and 400 c.c. of sulphuric acid until the temperature rose to 140°, when a further 200 c.c. of alcohol was slowly run in. The distillate

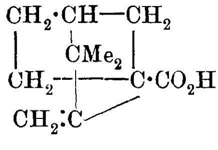
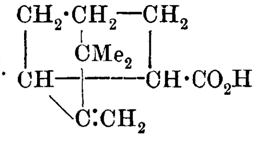
was saponified, the hydrocarbons were removed by steam distillation, and, finally, the naphthenic acids were liberated and converted into methyl esters. These were fractionated and the constants of twenty-six fractions are given. The fraction 165—170° contained methyl hexanaphthenecarboxylate; fraction 189—192°, methyl heptanaphthenecarboxylate; fraction 210—212°, methyl octanaphthenecarboxylate, and fraction 220—224°, methyl nonanaphthenecarboxylate. The densities of the fractions rise continuously with the exception of fraction 200—204°, which agrees with the formula $C_8H_{15}\cdot CO_2Me$, and thus contains a methyl *iso*octanaphthenecarboxylate.

The residual, partly esterified naphthenic acids were then distilled in a current of natural gas from a copper still, when 40% passed over below 285° and 10% between 285—295°. The lower-boiling ethyl esters were redistilled and the fractions boiling below 236° were saponified, freed from hydrocarbons, and the naphthenic acids were finally separated into eighteen fractions. By means of diagrams it is shown that the optical-rotation curve for the acids is parallel to the curve for the methyl esters. The cause of the activity of petroleum is thus due to the naphthenic acids and not to impurities. The maximum lævorotation is exhibited by the hexanaphthenecarboxylic acid and its ester. J. C. W.

The Condensation of Aromatic Aldehydes with Pyruvic Acid. EVA LUBRZYNSKA and IDA SMEDLEY (*Biochem. J.*, 1913, **7**, 375—379).—A full account of work of which an abstract has already appeared (P., 1913, **29**, 174). W. D. H.

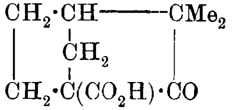
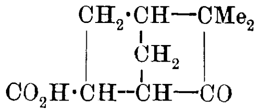
Camphenecarboxylic Acids and the Constitution of Camphene. JOSEF HOUBEN and ERNST WILLFROTH (*Ber.*, 1913, **46**, 2283—2299).—If Wagner's views with respect to the formation of camphene by the loss of hydrogen chloride from bornyl chloride are correct, the intermediate compound (II), formed by a similar removal of hydrogen chloride from α-chloro*allo*camphanecarboxylic acid (I), should give rise to two isomeric camphanecarboxylic acids (III and IV):

I. 
II. 

III. 
IV. 

The authors find that two isomeric unsaturated acids of this composition are formed when the methyl ester of α-chloro*allo*camphanecarboxylic acid is heated with methyl-alcoholic potassium hydroxide, although only one of them could be isolated in a state of purity.

On oxidation, the camphanecarboxylic acids should be transformed into α- and β-camphenilonecarboxylic acids (V and VI).

V.  VI. 

Oxidation of the acids formed by the removal of hydrogen chloride from chloro*allo*camphanecarboxylic acid resulted in the formation of two isomeric ketonic acids having the composition of the camphenilonecarboxylic acids. The investigation of these acids is not yet complete; both are very stable and can be distilled without decomposition, whereas α-camphenilonecarboxylic acid, being a β-ketonic acid, should be readily transformed by loss of carbon dioxide into camphenilone. In addition to the above ketonic acids, considerable quantities of hydropinenecarboxylic (*allo*camphanecarboxylic) acid were found amongst the oxidation products. It is probable that this acid was originally present in the mixture of unsaturated acids submitted to oxidation, and was formed by the reducing action of the methyl-alcoholic potassium hydroxide on the methyl ester of α-chloro*allo*-camphanecarboxylic acid.

Hydropinenecarboxylic acid, prepared from pinene hydrochloride by Houber's method (A., 1906, i, 21), has m. p. 78°, $[\alpha]_D^{21}$ $-18{\cdot}26°$ in alcohol, and is converted by phosphorus pentachloride or thionyl chloride into the *chloride*, $C_{10}H_7{\cdot}COCl$, which forms a colourless liquid, b. p. 110°/10 mm., and yields a *methyl* ester, b. p. 119°/18 mm., and *phenyl* ester, b. p. 187°/14 mm.

When heated for one hour with phosphorus pentachloride, hydropinenecarboxyl chloride yields *α-chloro*allo*camphanecarboxyl* (*chlorohydropinenecarboxyl*) *chloride*, $C_{10}H_{16}Cl{\cdot}COCl$, which sublimes with partial decomposition into hydrogen chloride and an unsaturated chloride. The chloro-chloride is obtained as a white, camphor-like mass, m. p. 118—119°, by evaporation of its ethereal solution after shaking with aqueous sodium carbonate. It probably consists of a mixture of two stereoisomerides related to one another as the *endo*- and *exo*-modifications of bornyl chloride. This view is supported by the behaviour of the *methyl* ester, which is obtained by boiling the chloro-chloride with methyl alcohol for fifteen hours, and apparently consists of two stereoisomerides of different stability, one of the isomerides readily losing hydrogen chloride on distillation, whilst the other is stable. The stable (presumably *exo*-) chloro-ester can be isolated from the mixture by repeated distillation under diminished pressure and has b. p. 131°/13 mm.

*α-Chloro*allo*camphanecarboxylamide*, prepared from the chloro-chloride and ammonia in ethereal solution, has m. p. 122°, and when boiled with water loses hydrogen chloride, yielding an unsaturated *amide*, $C_{10}H_{15}{\cdot}CO{\cdot}NH_2$, which crystallises in lustrous leaflets, m. p. 210°, and when kept in contact with fuming hydrochloric acid overnight, is transformed into the original chloro-amide.

When boiled with methyl-alcoholic potassium hydroxide, methyl α-chloro*allo*camphanecarboxylate yields an oil which consists of a

mixture of hydropinenecarboxylic acid and two isomeric *camphenecarboxylic acids.* One of the latter acids has been isolated, and crystallises in needles, m. p. 105°, b. p. 149—151°/11 mm.

From the product of oxidation of the above acid mixture with potassium permanganate in alkaline solution, two isomeric *ketonic* (*camphenilonecarboxylic?*) *acids*, $C_{10}H_{14}O_3$, of m. p. 106° and 131°, together with a hydropinenecarboxylic acid of m. p. 71°, were isolated. The last-mentioned acid gave the same copper, lead, ferrous, ferric, mercuric and silver salts, and the same *anhydride* (microscopic, regular octahedra, m. p. 210°, b. p. 228°/16 mm.) as the original hydropinenecarboxylic acid of m. p. 78°, but differed from it in the magnitude and sign of its rotation ($[\alpha]_D^{21}$ 11·29° in alcohol).

The ketonic acid of m. p. 106° forms a *semicarbazone* (decomp. 203°), and when boiled with acetic anhydride yields an *anhydride*, $C_{20}H_{26}O_5$, crystallising in leaflets, m. p. 114°. F. B.

Ethyl *p*-Bromobenzoylacetate. WILLIAM J. HALE and LAMBERT THORP (*Eighth Inter. Cong. App. Chem.*, 1912, **6**, 132—137).—The preparation of dehydro-*p*-bromobenzoylacetic acid by the method employed by Perkin in the case of the unsubstituted acid (A., 1885, 277) is described.

p-Bromotoluene was oxidised by boiling permanganate to *p*-bromobenzoic acid; this was converted into the chloride, which was then condensed with ethyl sodioacetoacetate, and, finally, the sodium compound of ethyl *p*-bromobenzoylacetoacetate was gently warmed with aqueous ammonia. The resulting *ethyl* p-*bromobenzoylacetate*, $C_6H_4Br\cdot CO\cdot CH_2\cdot CO_2Et$, was obtained as a heavy oil, which, in extremely small quantities, gives a deep red colour with ferric chloride. It could not be distilled, and, when boiled in an open tube, it gave a quantitative yield of *dehydro*-p-*bromobenzoylacetic acid*, $C_6H_4Br\cdot CO\cdot CH<\begin{matrix}CO\text{—}O\\CO\cdot CH\end{matrix}>C\cdot C_6H_4Br$, in the form of small, yellow needles from glacial acetic acid, m. p. 261°. p-*Bromobenzoylacetic acid*, $C_9H_7O_3Br$, was obtained by hydrolysing the ester with cold 3% potassium hydroxide in the form of needle-like plates which decompose at 106—107° into *p*-bromoacetophenone, and give a violet colour with ferric chloride. J. C. W.

Spirans. III. Attempts to Prepare Optically Active Spirans and Asymmetric Rearrangement. HERMANN LEUCHS and JOHANNES WUTKE (*Ber.*, 1913, **46**, 2420—2435. Compare Leuchs and Gieseler, A., 1912, i, 714).—In the preparation of bis-1-hydrindone-2:2-spiran from dibenzylmalonyl chloride, when aluminium chloride serves to eliminate hydrogen chloride, two by-products are obtained. The one, $C_{16}H_{13}Cl$, 1-chloro-2-benzylindene, m. p. 65°, amounts to 19% of the theoretical. The other is a yellow oil identified by means of its phenylhydrazone as 2-benzylhydrindone. Although only 10% have been separated, it amounts to 50% of the theoretical quantity.

When ferric chloride is substituted for aluminium chloride, a much better yield of the bishydrindonespiran is obtained. Its properties

are in accord with the formula $C_6H_4<\begin{smallmatrix}CH_2\\CO-\end{smallmatrix}>C<\begin{smallmatrix}CH_2\\CO-\end{smallmatrix}>C_6H_4$. It forms a diphenylhydrazone and a mono-oxime, and also reacts with two molecules of hydroxylamine, forming a dioxime dihydrate from which the excess of hydroxylamine oxidises away two atoms of hydrogen.

The mono-oxime (m. p. 215°) is converted by phosphorus pentachloride in ethereal suspension into an amide, either 1-hydrindone-dihydrocarbostyril-2 : 3-spiran or *iso*carbostyrilspiran. The mono-oxime shows no tendency to form an *iso*oxazole.

The 2-position of the carbonyl group in the spiran makes it possible to convert it into an acid, $C_{17}H_{14}O_3$,

$$CO_2H\cdot C_6H_4\cdot CH_2\cdot CH<\begin{smallmatrix}CH_2\\CO-\end{smallmatrix}>C_6H_4,$$

which when heated regenerates the spiran.

Semicarbazide acetate in cold alcoholic solution converts the spiran into an insoluble mixed hydrazide of the carbamic acid and the acid $C_{17}H_{14}O_3$, namely, $C_6H_4<\begin{smallmatrix}\text{————————}CH_2\cdot CH\cdot CH_2\\CON_2H_2\cdot CO\cdot NH_2\ \ CO-C_6H_4\end{smallmatrix}$, from which the free acid is recovered.

Hydroxylamine yields an oximic acid,

$$CO_2H\cdot C_6H_4\cdot CH_2\cdot CH<\begin{smallmatrix}CH_2\text{———}\\C(N\cdot OH)\end{smallmatrix}>C_6H_4,$$

which can be easily reduced with sodium amalgam. Two hydrogen atoms are taken up, and a new asymmetric carbon atom formed, the hydroxy-acid having the formula

$$CO_2H\cdot C_6H_4\cdot CH_2\cdot CH<\begin{smallmatrix}\text{—}CH_2\text{—}\\CH(OH)\end{smallmatrix}>C_6H_4,$$

and being a mixture of two racemic forms. It does not tend to form an anhydride. The keto-acid is converted into the corresponding acid chloride by means of phosphorus pentachloride; this as low as 60° loses hydrogen chloride, and forms bishydrindonespiran.

Ammonia acts on the spiran to form two compounds—the one, $C_{17}H_{15}O_2N$, representing the amide of the ketonic acid, and the other, $C_{17}H_{13}ON$, being the corresponding nitrile,

$$CN\cdot C_6H_4\cdot CH_2\cdot CH<\begin{smallmatrix}CH_2\\CO-\end{smallmatrix}>C_6H_4.$$

This constitution is confirmed by the fact that the action of ammonia on the keto-chloride gives rise to the same amide.

The amide is not hydrolysed by cold concentrated hydrochloric acid, but converted into an anhydride, which is hydrolysed by heating with 70% sulphuric acid at 170° to a spiran-anhydride.

Crystallisation of the brucine salt of the ketonic acid yields a theoretical yield of the optically active *dextro*-salt, both the crystals and the mother liquor being dextrorotatory. It is assumed that the *laevo*-acid salt is enolised and the enol re-converted into the ketonic *d*-salt, since the equilibrium is determined entirely in this direction owing to the crystallisation of the *d*-salt as fast as it is formed.

The transformation is an instance of asymmetric rearrangement

rather than of autoracemisation, since the optically inactive enol gives rise exclusively to an optically active acid.

The *d*-ketonic acid slowly but completely loses its activity on keeping in chloroform solution, and still more quickly in neutral or alkaline aqueous solution, owing to conversion into the enol.

An optically active bishydrindonespiran could not be obtained by eliminating hydrogen chloride from the active keto-chloride.

Bishydrindonespirandioxime dihydrate forms colourless, slender needles, m. p. 175° (decomp.).

The Beckmann rearrangement product, $C_{17}H_{13}O_2N$, of the mono-oxime separates in long, colourless needles, m. p. 255° (decomp.); it gives no ferric chloride reaction.

The mixed *hydrazide* from the spiran and carbamic acid, $C_{18}H_{17}O_3N$, crystallises in short needles, m. p. 245° (decomp.).

The *oxime* of 1-hydrindone-2-benzyl-*o*-carboxylic acid forms dome-like prisms, m. p. 188° (decomp.).

The *amide*, prepared from the keto-chloride by the action of ammonia, has m. p. 138—140°, crystallising in massive, four-sided platelets.

The *brucine* salt of the *dextro*-ketonic acid forms transparent, massive crystals, m. p. 180—183°. The acid derived from it has $[\alpha]_D^{20}$ +64° in chloroform. The pure active acid could not be obtained —a product evaporated at 20° had m. p. 128—141°, $[\alpha]_D^{20}$ +56°. In benzene the pure acid had $[\alpha]_D^{22}$ +79°; it racemises here more quickly than in chloroform. E. F. A.

Spirans. IV. Stereochemical Treatment of the Keto-Enol Question. HERMANN LEUCHS (*Ber.*, 1913, **46**, 2435—2442. Compare Lapworth, T., 1904, **85**, 30; K. H. Meyer, A., 1911, i, 350, 940).—1-Hydrindone-2-benzyl-*o*-carboxylic acid when treated with bromine in chloroform solution readily forms a brominated ketonic acid, $CO_2H\cdot C_6H_4\cdot CH_2\cdot CBr<\substack{CH_2\\CO}>C_6H_4$. Proof of this structure is afforded by the fact that on heating with ammonium hydroxide, the bromine is displaced and a lactone formed, namely, *dihydro*iso*coumarin-1-hydrindone-3 : 2-spiran*, $C_6H_4<\substack{CH_2\\CO\cdot O}>C<\substack{CH_2\\CO}>C_6H_4$.

If in the process of bromination the first stage is the formation of an enol, $CO_2H\cdot C_6H_4\cdot CH_2\cdot C<\substack{-CH_2-\\C(OH)}>C_6H_4$, which contains no asymmetric carbon atom, then on bromination of the optically active 1-hydrindone-2-benzyl-*o*-carboxylic acid, an optically inactive product should result.

Actually an optically active ($[\alpha]_D$ +6·5°) product is obtained containing much inactive brominated keto-acid. Heating with sodium carbonate changes the sign of the rotation, and it was possible to isolate the pure 1-*dihydro*iso*coumarin*-1-*hydrindone*-3 : 2-*spiran*, which crystallises in lustrous needles, m. p. 175—176°, $[\alpha]_D^{20}$ −65·3°.

This is the first optically active substance in which the spiran carbon atom is the asymmetric centre.

Bromination of ketones does not in consequence necessarily involve the intermediate formation of enol; in this case about 5—10% of

the brominated product is optically active. It is considered that even in this instance the greater part of the bromination involves the intermediate formation of the enol, and that this will be still more the case with substances which are more easily enolised.

2-*Bromo-α-hydrindone-2-benzyl-o-carboxylic acid* forms colourless crystals pointed at one end, m. p. 154°; they are converted into the lactone on fusion.

*Dihydro*iso*coumarin-1-hydrindone-3 : 2-spiran* crystallises in needles or prisms, m. p. 153—154°. E. F. A.

Studies in Esterification. V. Esterification of Amides and Thioamides and the Formation of Dithio-esters. E. Emmet Reid (*Eighth Inter. Cong. App. Chem.*, 1912, **25**, 423—430. Compare A., 1909, ii, 650; 1910, i, 481; 1911, i, 199; ii, 477).—In earlier papers it has been shown with reference to esterification that benzamide is the analogue of benzoic acid, and that mercaptan is the analogue of alcohol. It is now shown that benzamide can be esterified by mercaptan, and thiobenzamide by alcohol or mercaptan.

Ethyl thiolbenzoate is readily decomposed into mercaptan and benzamide by the action of ammonia at 20°, whereas ethyl benzoate reacts but slowly with ammonia even at 200°. Benzamide is readily esterified in presence of hydrochloric acid, which not only catalyses the reaction, but also combines with the ammonia so that the action proceeds to completion, and it was therefore expected that hydrogen chloride would similarly accelerate the esterification of benzamide by mercaptan. On heating benzamide in a sealed tube at 100° with mercaptan, saturated with hydrogen chloride at −20°, ethyl thiolbenzoate and ammonium chloride were produced. Thiobenzamide unites with about 1·5 mols. of hydrogen chloride to form an amber-coloured liquid, whilst other thioamides combine with about 1 mol.

Ethyl dithiobenzoate can be prepared by treating thiobenzamide, saturated with dry hydrogen chloride at 0°, with rather more than the calculated amount of mercaptan, and leaving the mixture in a sealed tube for about five weeks; the ester has b. p. 180°/28 mm., D_{25}^{25} 1·1477, D_4^{25} 1·1439, apparent coefficient of expansion 0—25°, 0·000699, molecular volume, 159·28, viscosity at 25°, 0·03117, and fluidity at 25°, 32·09. These constants are compared with those of ethyl benzoate and ethyl thiolbenzoate. Ethyl dithiobenzoate is readily transformed into thionbenzamide by alcoholic ammonia at the ordinary temperature. The reaction: $Ph\cdot CS\cdot NH_2 + C_2H_5\cdot SH \rightleftarrows Ph\cdot CS\cdot SEt + NH_3$ is therefore reversible. E. G.

Action of Potassium Xanthate on Halogen-malonic Acids. Einar Biilmann and Erik Host Madsen (*Eighth Inter. Cong. App. Chem.*, 1912, **25**, 339—342).—It has been shown in earlier papers (A., 1905, i, 625; 1906, i, 625, 626) that by the action of potassium xanthate on the halogen derivatives of certain organic acids, xanthyl derivatives are produced which, on treatment with ammonia, are converted into thiol acids. The action of potassium xanthate on bromomalonic, bromo*iso*propylmalonic, bromoethylmalonic, and bromobenzylmalonic acids has now been studied. These acids yield xanthyl derivatives which are very unstable, and from which pure xanthylmalonic acids

cannot be obtained. On heating the acidified solutions, the corresponding monobasic acids are produced, and in this way xanthylacetic, α-xanthylbutyric, and β-phenyl-α-xanthylpropionic acids have been isolated.

If the solutions of potassium xanthate and alkali halogenmalonates are acidified immediately after they have been mixed, an entirely different reaction takes place and dixanthyl is produced, thus: $2OEt{\cdot}CS{\cdot}SK + R{\cdot}CBr(CO_2K)_2 + 3HCl = OEt{\cdot}CS_2{\cdot}CS_2{\cdot}OEt + R{\cdot}CH(CO_2H)_2 + KBr + 3KCl$.

β-Phenyl-α-xanthylpropionic acid, $CH_2Ph{\cdot}CH(CO_2H){\cdot}S{\cdot}CS{\cdot}OEt$, m. p. 89—90°, prepared by the action of potassium xanthate on sodium α-bromophenylpropionate, forms colourless crystals, and when treated with a mixture of aqueous ammonia and alcohol, is converted into *α-thiol-β-phenylpropionic acid*, $CH_2Ph{\cdot}CH(SH){\cdot}CO_2H$, b. p. 184—187°/11—12 mm., m. p. 46°, which forms colourless crystals. By the action of copper sulphate on the alkali salts of this thiol acid, the latter is oxidised to *α-disulphido-β-phenylpropionic acid*,

$$[CH_2Ph{\cdot}CH(CO_2H)]_2S_2,$$

and the cuprous salt of the thiol acid is precipitated. The disulphido-acid can be obtained as a crystalline solid by oxidising the thiol acid with iodine. E. G.

as-**Phthalyl Chloride.** JOHANNES SCHEIBER (*Ber.*, 1913, **46**, 2366—2370).—The author (A., 1912, i, 542, 559) has shown that the unsymmetrical formula, $C_6H_4{<}{}^{CCl_2}_{CO}{>}O$, proposed for phthalyl chloride is untenable on both chemical and physical grounds, and Ott (A., 1912, i, 828) has obtained the isomeric asymmetric form of phthalyl chloride. The behaviour of the new chloride towards compounds of the type of ethyl sodioacetoacetate and towards ammonia has been now studied as well as the ultra-violet absorption spectra.

Both chlorides behave similarly with ethyl acetoacetate, since in each case reaction involves the formation of a compound

$$COCl{\cdot}C_6H_4{\cdot}CO{\cdot}CHAc_2.$$

Hence the behaviour of such chlorides with sodium acetoacetate as also with ammonia gives no clue as to their structure.

Both chlorides give exclusively *o*-cyanobenzoic acid with ammonia, but the new asymmetric chloride reacts more slowly. There is thus a considerable difference in the stability of the complexes $C_6H_4{<}{}^{CCl_2}_{SO_2}{>}O$ and $C_6H_4{<}{}^{CCl_2}_{CO}{>}O$. The asymmetric chloride absorbs less strongly than phthalic acid or its esters in the ultra-violet. E. F. A.

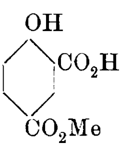
Methylcarbonato-derivatives of Phenolcarboxylic Acids and Their Use for Synthetical Operations. IX. EMIL FISCHER and MAX RAPAPORT (*Ber.*, 1913, **46**, 2389—2401).—In part already abstracted (this vol., i, 731).

[With H. STRAUSS.]—*Trimethylcarbonatophloroglucinolcarboxylic acid*, obtained on treating phloroglucinolcarboxylic acid with methyl chloroformate in presence of dimethylaniline, forms small, colourless prisms,

m. p. 122° (decomp.), and no longer shows a bluish-violet coloration with ferric chloride. It is converted into the corresponding chloride by phosphorus pentachloride. E. F. A.

Pyrimidines. LV. The Catalytic Action of Esters in the Claisen Condensation. TREAT B. JOHNSON and ARTHUR J. HILL (*Eighth Inter. Cong. App. Chem.*, 1912, **6**, 147—156 *).—Ethyl phenoxyacetate undergoes a Claisen condensation in ethereal solution in presence of sodium to form the sodium compound of ethyl $\alpha\gamma$-diphenoxyacetoacetate, $OPh\cdot CH_2\cdot CO\cdot CH(OPh)\cdot CO_2Et$. The same substance was produced in presence of ethyl acetate, and no evidence of the formation of the condensation product of the two esters, namely, ethyl γ-phenoxyacetoacetate, could be obtained. As has since been described (A., 1912, i, 912), the crude sodium salt condenses with thiocarbamide to form 2-thio-5-phenoxy-4-phenoxymethyltetrahydro-6-pyrimidone, and the yield of this insoluble product has been taken as an indication of the extent of the above Claisen condensation under different conditions. It is found that ethyl acetate acts as a catalyst, the addition of 0·5 mol. more than doubling the yield. J. C. W.

Some Derivatives of 4-Hydroxy*iso*phthalic Acid. FRANCIS D. DODGE (*Eighth Inter. Cong. App. Chem.*, 1912, **6**, 81—85).—During the steam-distillation of large quantities of methyl salicylate, the author has sometimes obtained, towards the end of the operation, crystals of dimethyl 4-hydroxy*iso*phthalate (Jacobsen, A., 1878, 583). Its presence is ascribed to irregularities in the manufacture of salicylic acid, since 4-hydroxy*iso*phthalic acid may be prepared by the action of carbon dioxide on sodium salicylate at 370° (Ost, A., 1876, 521).



Partial esterification of the acid and also partial hydrolysis of the dimethyl ester lead to the same *mono*-ester, which crystallises in transparent plates with $1H_2O$ from diluted alcohol, has m. p. 187° when anhydrous, and gives a reddish-purple coloration with ferric chloride. From the fact that it yields methyl anisate on heating, and according to V. Meyer's ester law, it is the para-ester (annexed formula). J. C. W.

Carminic Acid. OTTO DIMROTH (*Annalen*, 1913, **399**, 1—35).—Investigations of the three "insect" dyes, carminic acid, kermesic acid, and laccaic acid, have been carried out concurrently in the expectation, which has been justified, that the results would mutually confirm one another. The structure of kermesic acid, which is the simplest of the three, has been determined (Dimroth and Scheurer, this vol., i, 980). The present paper, however, deals mainly with carminic acid. The remarkable and unexpected result has been established that this acid and kermesic acid are derivatives of an anthraquinone.

[With G. WEURINGH and L. HOLCH.]—Carminic acid, isolated from cochineal by Schunck and Marchlewski's process (it is advantageous, however, to decompose the lead lake by sulphuric acid and methyl, not

* and *J. Amer. Chem. Soc.*, 1913, **35**, 1023—1034.

ethyl, alcohol), is oxidised by hydrogen peroxide and aqueous sodium hydroxide in the presence of a little cobalt sulphate as catalyst, whereby carminoquinone is formed as a labile intermediate product, the final product, after acidification with 80% acetic acid, being a sparingly soluble *sodium hydrogen* salt, $C_{26}H_{13}O_{16}Na_3,5H_2O$, yellow crystals. By trituration with dilute hydrochloric acid at 0° and crystallisation of the product from cold ethyl acetate, this salt yields 2 : 6-*dihydroxy*-8-*methyl*-α-*naphthaquinone*-3 : 5-*dicarboxylic acid*,

$$CO_2H\cdot C_6HMe(OH)<\begin{matrix}CO\cdot C\cdot OH\\ \quad\ \ \| \\ CO\cdot C\cdot CO_2H\end{matrix},$$

a pale yellow, extremely hygroscopic, crystalline powder, which forms a *sodium* salt, $C_{13}H_5O_8Na_3,4H_2O$, orange needles, and yields carminazarin by oxidation with potassium permanganate and sulphuric acid. The orientation of the substituents in the dicarboxylic acid is determined by its oxidation to carminazarin and by the colour reactions of the acid, which are identical with those of 2 : 6-dihydroxy-α-naphthaquinone (compare Dimroth and Kerkovius, following abstract). By gentle warming with water, the acid loses carbon dioxide and yields 2 : 6-*dihydroxy*-8-*methyl*-α-*naphthaquinone*-5-*carboxylic acid*, $C_{12}H_8O_6$, brownish-yellow needles (*potassium* salt, $C_{12}H_7O_6K$, citron-yellow needles; *dipotassium* derivative, $C_{12}H_6O_6K_2$, orange-red crystals), which develops a red coloration with alkalis, brownish-yellow with concentrated sulphuric acid, and brownish-red with alcoholic ferric chloride. The monocarboxylic acid, which is obtained more conveniently by heating the sodium hydrogen derivative of the dicarboxylic acid with *N*-hydrochloric acid on the water-bath, reacts with bromine in glacial acetic acid at 40° to form 7-*bromo*-2 : 6-*dihydroxy*-8-*methyl*-α-*naphthaquinone*-5-*carboxylic acid*, $C_{12}H_7O_6Br$, m. p. 240—244°, yellow needles. The brominated acid forms α-bromocarmin by treatment with hydrobromic acid, and Will and Leymann's β-bromocarmin by treatment with bromine in cold methyl alcohol; the latter is thus definitely proved to be 3 : 5 : 7-tribromo-2 : 6-dihydroxy-8-methyl-α-naphthaquinone.

The constitution, 2 : 3 : 6-trihydroxy-8-methyl-α-naphthaquinone-5-carboxylic acid, previously ascribed by the author to carminazarin, is supported by the fact that its oxidation product, carminazarinquinone, reacts with alcoholic *o*-phenylenediamine to form a *diphenazine*, $C_{24}H_{14}O_3N_4$, yellow needles, the *acetyl* derivative, $C_{26}H_{16}O_4N_4$, of which still forms a sparingly soluble *sodium* salt.

[With B. Kerkovius.]—The largest, well characterised fission product of carminic acid is coccinin, obtained by Hlasiwetz and Grabowski in 1867 by fusing the acid with potassium hydroxide. Prepared at 170—200° by a modification of these authors' process, coccinin, $C_{17}H_{14}O_6$, has been obtained as a crystalline substance which forms a *tetra-acetyl* derivative, $C_{25}H_{22}O_{10}$, m. p. 242—244°, faintly yellow crystals. By oxidation in 6% sodium hydroxide with air or oxygen until the colour of the solution has changed from yellow through green to a pure violet, and then acidifying with hydrochloric acid, coccinin

yields *coccinone*, $C_{17}H_{12}O_7$, dark brown, metallic crystals, which begins to decompose at 250°, and forms a *triacetyl* derivative, $C_{23}H_{18}O_{10}$, m. p. 210°, orange-red crystals, and three *barium* salts, one of which crystallises in glistening leaflets, and has a composition,

$$2C_{17}H_{10}O_7Ba,(C_{17}H_{11}O_7)_2Ba,$$

analogous to that of the sodium hydrogen salt of 2 : 6-dihydroxy-8-methyl-α-naphthaquinone-3 : 5-dicarboxylic acid. In concentrated sulphuric acid, coccinone develops a violet colour which changes to blue on the addition of boric acid—a reaction similar to those exhibited by most hydroxyanthraquinones.

Coccinone is reduced to coccinin by zinc dust and ammonia, and is oxidised by hydrogen peroxide and aqueous sodium hydroxide below 20°, yielding cochenillic acid and a second, unexamined acid. The author is of opinion that coccinin and coccinone are derivatives of anthranol and of anthraquinone respectively. The formation of cochenillic acid determines the orientation of a hydroxyl, methyl, and carboxyl group in coccinone which, therefore, receives the constitution

$$C_6HMe(OH)_2\!<\!\begin{array}{l}CO\cdot C\cdot CMe{=\!=}CH\\ CO\cdot C\cdot C(CO_2H){:}C\cdot OH\end{array},$$ whilst coccinin is regarded as

$$C_6HMe(OH)_2\!<\!\begin{array}{l}CH{-\!-}C\cdot CMe{=\!=}CH\\ C(OH)\cdot C\cdot C(CO_2H){:}C\cdot OH\end{array}$$ or

$$C_6HMe(OH)_2\!<\!\begin{array}{l}C(OH)\cdot C\cdot CMe{=\!=}CH\\ CH{-\!-}C\cdot C(CO_2H){:}C\cdot OH\end{array}.$$

By heating with water at 200° or with dilute sulphuric acid at 170°, coccinone loses carbon dioxide and yields *decarboxycoccinone*, $C_6HMe(OH)_2\!<\!\begin{array}{l}CO\cdot C\cdot CMe{:}CH\\ CO\cdot C\cdot CH{=}C\cdot OH\end{array}$, reddish-brown crystals, which forms a purplish-red solution in alkalis, and dissolves in concentrated sulphuric acid with a blue colour changing to violet after the addition of boric acid.

[With L. Holch.]—The question remains to be discussed whether carminic acid is a derivative of anthraquinone, or whether the anthracene nucleus in coccinin is produced during the fusion of carminic acid with potassium hydroxide. By distillation with zinc dust in a current of hydrogen, carminic acid yields about 5% of a mixture of hydrocarbons which apparently contains anthracene and α-methylanthracene, since in the mixture, after oxidation, anthraquinone has been certainly identified, whilst a substance, m. p. 165°, has also been obtained which has the very characteristic crystalline form of α-methylanthraquinone.

When boiled with dilute sulphuric acid, carminic acid yields about 10% of a *trihydroxymethylanthraquinonecarboxylic acid*, $C_{16}H_{10}O_7$, m. p. above 305° which crystallises in needles, and is converted by water at 230—240° into a *trihydroxymethylanthraquinone*, $C_{15}H_{10}O_5$, brick-red needles. C. S.

2 : 6- and 2 : 7-Dihydroxy-α-naphthaquinones. Otto Dimroth and Berthold Kerkovius (*Annalen*, 1913, **399**, 36—43).—By treatment with acetic anhydride containing a few drops of concentrated sulphuric acid, 6-hydroxy-β-naphthaquinone yields 1 : 3 : 4 : 6-*tetra-*

acetoxynaphthalene, $C_{18}H_{16}O_8$, m. p. 181—182°, colourless leaflets. By hydrolysis with methyl-alcoholic potassium hydroxide, the passage of oxygen through the resulting solution, and acidification, 2 : 6-*dihydroxy-α-naphthaquinone*, $C_{10}H_6O_4$, yellow crystals, is obtained. It forms a *diacetyl* derivative, yellow leaflets, and dissolves in sodium carbonate and sodium hydroxide with a blood-red colour, and in concentrated sulphuric acid with a brownish-yellow colour. By bromination in glacial acetic acid, 2 : 6-dihydroxy-α-naphthaquinone forms a *dibromo-*derivative, $C_{10}H_4O_4Br_2$, m. p. 283—286°, yellowish-brown crystals, which is converted by bromine in methyl alcohol into 3 : 5 : 7-*tribromo-*2 : 6-*dihydroxy-α-naphthaquinone*, $C_{10}H_3O_4Br_3$, m. p. 242°, yellow crystals; the latter dissolves in sodium carbonate or hydroxide, or in concentrated sulphuric acid, with a reddish-brown colour.

By reactions similar to the preceding, 7-hydroxy-β-naphthaquinone has been converted into 1 : 2 : 4 : 7-*tetra-acetoxynaphthalene*, m. p. 140—141°, colourless crystals, from which 2 : 7-*dihydroxy-α-naphthaquinone*, decomp. above 200°, orange-yellow needles, has been obtained. The latter dissolves in aqueous sodium hydroxide and in concentrated sulphuric acid with a crimson-red colour, and by bromination in glacial acetic acid yields 3 : 6 : 8-*tribromo-*2 : 7-*dihydroxy-α-naphthaquinone*, m. p. 228—229°, pale yellow prisms, the solution of which in sodium carbonate or hydroxide is much more blue than that of the preceding isomeride.

Mention has been made (Dimroth, preceding abstract) of the importance of the preceding colour reactions in connexion with the constitutions of β-bromocarmin and of 2 : 6-dihydroxy-8-methyl-α-naphthaquinone-5-carboxylic acid. C. S.

Kermes Dye. Otto Dimroth and Wilhelm Scheurer (*Annalen*, 1913, **399**, 43—61).—In addition to kermesic acid, kermes dye contains about 0·06% of a second acid, $C_{13}H_8O_6$, which is called *flavokermesic acid*. It crystallises in needles or prisms. In the optical properties of its solutions and as a dye, it shows very little resemblance to kermesic acid, and, therefore, has not been studied thoroughly. The separation of flavokermesic acid from kermesic acid is effected best by utilising the facts that the disodium salt of the latter is almost insoluble in hot 2*N*-sodium acetate, whilst sodium flavokermesate dissolves fairly easily. The presence of flavokermesic acid in kermesic acid is easily detected by the colour of the solution in concentrated sulphuric acid containing boric acid; the solution of the pure acid is a clear blue, that of the impure acid is dull, or a dirty bluish-violet.

When heated with water at 150°, kermesic acid loses carbon dioxide, and is converted into *decarboxykermesic acid*, $C_{17}H_{12}O_7$, red needles, which begins to sublime above 150°, carbonises without melting, is almost insoluble in sodium hydrogen carbonate, and dissolves in aqueous sodium hydroxide and in concentrated sulphuric acid containing boric acid, forming solutions which have the same colours as the corresponding solutions of kermesic acid. Kermesic acid yields α-bromocarmin by bromination in boiling 50% acetic acid. When brominated in boiling glacial acetic acid, however, it is converted into

bromococcin, $C_{16}H_9O_8Br$, m. p. 259—260° (decomp.), red needles, which forms a *potassium hydrogen* salt, $C_{16}H_8O_8BrK,C_{16}H_9O_8Br$, and a *tetra-acetyl* derivative, $C_{16}H_5O_8BrAc_4$, yellow crystals, and yields cochenillic acid by oxidation with warm alkaline hydrogen peroxide in the presence of a trace of a manganous salt. These results indicate that bromococcin must have the constitution

$$C_6Br(OH)_3<\begin{matrix}CO\cdot C\cdot CMe{=\!=\!=}CH \\ CO\cdot C\cdot C(CO_2H):C\cdot OH\end{matrix}.$$

The three homonuclear hydroxyl groups cannot be in the vicinal position because bromococcin resembles purpurin, not anthragallol, in its dyeing function.

When kermesic acid or bromococcin is brominated in methyl alcohol and the product is treated with concentrated hydrobromic acid, *tribromococcin*, $OH\cdot C_6MeBr_2<\begin{matrix}CO\\CO\end{matrix}>C_6Br(OH)_3$, m. p. 245—248° (decomp.), is obtained, which crystallises from acetic acid in long, red needles. It dissolves in concentrated sulphuric acid with a reddish-violet colour, which changes to deep blue by the addition of boric acid. It forms a *tetra-acetyl* derivative, $C_{15}H_3O_6Br_3Ac_4$, m. p. 223°, greenish-yellow needles, and is converted into nitrococcusic acid by fuming nitric acid. A *substance*, $C_{15}H_6O_5Br_4$, yellow needles, is obtained as a by-product in the preparation of tribromococcin.

Kermesic acid, $C_{18}H_{12}O_9$, and bromococcin, $C_{16}H_9O_8Br$, are nearly related substances. Hence from the constitution of the latter, it is very probable that kermesic acid, which does not exhibit the properties of an aldehyde, has the constitution

$$C_6Ac(OH)_3<\begin{matrix}CO\cdot C\cdot CMe{=\!=\!=}CH \\ CO\cdot C\cdot C(CO_2H):C\cdot OH\end{matrix}.$$

This deduction is supported, not only by the formation of tribromococcin by bromination, but also by the result of the distillation of kermesic acid with zinc dust. The mixture of hydrocarbons thus obtained contains α-methylanthracene (isolated as the styphnic acid compound, and identified in the form of α-methylanthraquinone) and, probably, anthracene.

[With A. E. SHERNDAL.]—The wax which is obtained in working up the kermes dye is *ceryl cerotate*, $C_{52}H_{104}O_2$, m. p. 81°, colourless leaflets, since it yields ceryl alcohol and cerotic acid by hydrolysis.

C. S.

Stick-lac Dye. OTTO DIMROTH and STEPHAN GOLDSCHMIDT (*Annalen*, 1913, **399**, 62—90).—Stick-lac or gum-lac contains, embedded in resin, wax, and other substances, a small quantity of a red dye similar to cochineal. The dye has been called laccaic acid. It is not, as supposed formerly, identical with carminic acid, but the two are closely related, giving solutions in alkalis of the same colour and exhibiting the same spectrum; the characteristic absorption bands shown by the two acids in concentrated sulphuric acid, however, are differently situated in the two spectra.

Laccaic acid is isolated as follows: Stick-lac is digested with water at 50°, the clear red solution when cold, is acidified with acetic acid,

decanted from the precipitated resin, evaporated to a small bulk, and acidified with hydrochloric acid; the crude laccaic acid thus obtained is crystallised from hot 85% formic acid, washed, dried at 60—70°, and finally crystallised from hot dilute hydrochloric acid. It has the formula $C_{20}H_{14}O_{10}$, not $C_{16}H_{12}O_8$ as stated in the literature, crystallises in dark red, microscopic rhombohedra, decomposes and yields a trace of a red sublimate when heated, and does not form crystalline salts except a *sodium hydrogen* salt, $C_{20}H_{12}O_{10}Na_2,C_{20}H_{13}O_{10}Na$. Its dyeing properties are similar to those of carminic acid. Laccaic acid neutralises five equivalents of barium hydroxide, and when treated with acetic anhydride and a few drops of concentrated sulphuric acid yields a *triacetyl* derivative, $C_{26}H_{20}O_{13},C_2H_4O_2$, m. p. 176°, reddening at about 160°, yellow, microscopic needles (from acetic acid).

By reduction with tin and hydrochloric acid or with zinc dust and boiling aqueous ammonia, laccaic acid is converted into a *substance*, $C_{20}H_{16}O_9$, brownish-yellow rhombohedra, which is oxidised by hydrochloric acid and cupric chloride to a *substance*, $C_{20}H_{14}O_9$, which differs from laccaic acid in its colour reactions; the substances $C_{20}H_{16}O_9$ and $C_{20}H_{14}O_9$ are probably related as quinol and quinone.

An alkaline solution of laccaic acid is readily oxidised by hydrogen peroxide in the presence of a trace of a cobalt, manganese, cerous, or ferrous salt. When one molecular proportion of hydrogen peroxide is used, the solution contains an unstable intermediate oxidation product, since by acidifying the solution and adding sulphurous acid, laccaic acid is recovered. The complete oxidation requires 2·5 to 3 molecular proportions of hydrogen peroxide, manganous chloride being the best catalyst. The oxidation product thus obtained is *calaic acid*, $C_{18}H_{14}O_{11}$, which crystallises from ether in small, yellow prisms containing ether of crystallisation and from water in needles containing $2\frac{1}{2}H_2O$. Calaic acid contains three carboxyl groups and one carbonyl group, does not possess dyeing properties, and forms a crystalline *barium* salt (by means of which it is best purified) and a *silver* salt, $C_{18}H_{12}O_{11}Ag_2$.

By bromination in glacial acetic acid, calaic acid yields two products. One of these is an *a-ketonic acid*, $C_{12}H_{10}O_6Br_2$, m. p. 208—209°, brownish-yellow crystals, which forms a *phenylhydrazone* and *semicarbazone*, develops a dirty reddish-violet coloration with ferric chloride, and by treatment with methyl-alcoholic hydrogen bromide yields an additive *compound* of the *methyl* ester, $C_{13}H_{12}O_6Br_2,HBr$, m. p. 133—134° (decomp.), colourless needles. When heated with concentrated sulphuric acid at 80—90°, the ketonic acid loses carbon monoxide and yields an *acid*, $C_{11}H_{10}O_5Br_2$, m. p. 245—246° (decomp.), which is monobasic and develops an intense violet coloration with ferric chloride.

The second and more important product of the bromination of calaic acid is *β-bromolaccain*, $C_{12}H_5O_8Br$, which is separated from the other product by means of its solubility in cold acetone. β-Bromolaccain has m. p. 234—235° (decomp.), separates from aqueous solution in stout crystals containing $2H_2O$, and forms a *potassium* salt,

$$C_{12}HO_8BrK_4,H_2O,$$

hexagonal plates. It develops a deep red coloration with ferric

chloride, dyes wool reddish-yellow in an acid-bath, and by treatment with acetic anhydride and concentrated sulphuric acid forms *diacetyl-β-bromolaccain anhydride*, $C_{16}H_7O_9Br$; the last reaction proves that β-bromolaccain contains two carbonyl groups in the ortho-position and two hydroxyl groups.

Since β-bromolaccain presents in its behaviour a close analogy to β-bromocarmin and resembles 2 : 6-dihydroxy-α-naphthaquinone in its colour reactions (Dimroth and Kerkovius, preceding abstract), there can be little doubt that its constitution is

$$\begin{array}{l} CO_2H\cdot C\colon C(CO_2H)\cdot C\cdot CO\cdot C\cdot OH \\ \quad OH\cdot C{=\!=\!=\!=}CH\cdot C\cdot CO\cdot CBr \end{array}.$$

This is supported by the following evidence. Just as β-bromocarmin yields the indone derivative, α-bromocarmin, so β-bromolaccain in boiling aqueous solution yields with bromine, *α-bromolaccain*,

$$CBr_2\begin{array}{l} \diagup CO\cdot C\cdot C(CO_2H)\colon CBr \\ \diagdown CO\cdot C\cdot CBr{=\!=\!=\!=}C\cdot OH \end{array},$$

colourless needles, which decomposes when heated and yields bromoform and 2 : *6-dibromophenol*-3 : 4 : *5-tricarboxylic acid*, m. p. 257—258°, by treatment with sodium hypobromite; the tricarboxylic acid develops only a faint coloration with ferric chloride (therefore, the hydroxyl group is not in the ortho-position to a carboxyl group) and as a phthalic acid derivative yields a yellow dye by fusion with resorcinol and zinc chloride.

The constitution of β-bromolaccain is also supported by the fact that oxidation by hydrogen peroxide in glacial acetic acid on the water-bath produces *hydroxytricarboxyphenylglyoxylic acid*,

$$OH\cdot C_6H(CO_2H)_3\cdot CO\cdot CO_2H,$$

m. p. 229·5—230° (decomp.), flattened plates, which develops a brownish-red coloration with ferric chloride and is converted into a *phenoltetracarboxylic acid*, m. p. 212—214° (decomp.), quadratic crystals, by concentrated sulphuric acid at 130—140°.

A by-product of the oxidation of β-bromolaccain is a *substance*, $C_{12}H_6O_9Br_2$, m. p. 188—190° (decomp.), which readily loses bromine and probably has the constitution

$$CBr_2\begin{array}{l} \diagup C(OH)(CO_2H)\cdot C\cdot C(CO_2H)\colon C\cdot CO_2H \\ \diagdown CO{-\!-\!-\!-\!-\!-\!-\!-}C\cdot CH{=\!=\!=\!=}C\cdot OH \end{array}.$$

C. S.

[Angeli-Rimini Reaction of the Aldehydes.] ANGELO ANGELI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 851—854).—A reply to Balbiano (this vol., i, 733). R. V. S.

The New Decomposition of the Oximes. ANGELO ANGELI and LUIGI ALESSANDRI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 735—744. Compare Angeli, A., 1912, i, 269).—Benzophenoneoxime decomposes rapidly at about 180°, yielding benzophenone, nitrogen and ammonia. The decomposition occurs at a lower temperature (140°) in presence of copper oxide, whilst with cuprous chloride it begins a little above 100°. It was not possible to isolate a copper salt, but the *silver* salt was prepared. It is stable when dry, but if kept in a moist state in

the absence of air it evolves pure nitrogen, and benzophenone is formed at the same time.

The *silver* salt of piperonaldehydeoxime behaves similarly.

Fluorenoneoxime also decomposes at its m. p. (194°); the gas evolved contains nitric oxide as well as nitrogen, even when the decomposition is effected in the absence of air.

The mixture of stereoisomeric oximes prepared from phenyl *p*-tolyl ketone (m. p. about 120°) decomposes above 200° in a like manner, nitric oxide being also formed.

In the case of deoxybenzoinoxime and acetophenoneoxime decomposition is slight when the pure substance is heated, but becomes considerable in presence of cuprous chloride or of cupric oxide.

Benzophenoneoxime, phenyl *p*-tolyl ketoneoxime, and acetophenoneoxime are apt to decompose spontaneously on keeping. R. V. S.

Phototropy. FERDINANDO GRAZIANI and F. BOVINI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 793—797).—The authors have prepared a number of diphenylhydrazones and *p*-ditolylhydrazones, none of which is phototropic. In some cases in which the compounds had been previously prepared, the m. p.'s were found somewhat different from those given in the literature. Benzaldehydediphenylhydrazone has m. p. 125°.

Anisaldehydediphenylhydrazone, $NPh_2\cdot N:CH\cdot C_6H_4\cdot OMe$, forms colourless crystals, m. p. 76°.

Cuminaldehydediphenylhydrazone has m. p. 80—81°.

Salicylaldehydediphenylhydrazone has m. p. 139—140°.

Benzaldehyde-p-*ditolylhydrazone*, $N(C_7H_7)_2\cdot N:CHPh$, crystallises in small, yellow prisms, m. p. 99°.

Anisaldehyde-p-*ditolylhydrazone*, $N(C_7H_7)_2\cdot N:CH\cdot C_6H_4\cdot OMe$, forms large, flat needles, m. p. 128°.

Cuminaldehyde-p-*ditolylhydrazone*, $N(C_7H_7)_2\cdot N:CH\cdot C_6H_4\cdot CHMe_2$, crystallises in long, silky needles, m. p. 104°.

Cinnamaldehyde-p-*ditolylhydrazone*, $N(C_7H_7)_2\cdot N:CH\cdot CH:CHPh$, forms flat, deep yellow needles, m. p. 143°.

Salicylaldehyde-p-*ditolylhydrazone*, $N(C_7H_7)_2\cdot N:CH\cdot C_6H_4\cdot OH$, is a greenish-yellow, crystalline powder, m. p. 126°.

Piperonaldehyde-p-*ditolylhydrazone*, $N(C_7H_7)_2\cdot N:CH\cdot C_6H_3:O_2:CH_2$, forms colourless leaflets, m. p. 134°. R. V. S.

Tetra-alkylation of 1-Methyl*cyclo*hexanone. ALBIN HALLER (*Compt. rend.*, 1913, **157**, 179—185. Compare this vol., i, 629).—Whilst the alkylation of *cyclo*hexanone by means of sodamide proceeds but difficultly, methyl*cyclo*hexanone readily undergoes progressive alkylation. Thus 1-methyl*cyclo*hexan-6-one dissolved in ether, treated with sodamide, followed by the addition of methyl iodide, readily yields 1 : 5-dimethyl*cyclo*hexan-6-one, b. p. 170—171° (corr.), D_4^{18} 0·9146, n^{18} 1·4508 (compare Wallach, this vol., i, 482), together with a very small amount of the 1 : 1-isomeride. Further alkylation of the 1 : 5-compound yields 1 : 1 : 5-*trimethyl*cyclo*hexan-6-one*, b. p. 178—179°/755 mm. (corr.), D_4^{18} 0·9043, n_D^{18} 1·4493, yielding in its turn 1 : 1 : 5 : 5-tetramethyl*cyclo*hexan-6-one (*loc. cit.*). The corresponding alcohols are

obtained by reduction with sodium in absolute alcohol. 1 : 5-*Dimethyl*cyclo*hexan*-6-*ol*, a viscous liquid with an odour like eugenol, has b. p. 174·5—175·5°/748 mm. (corr.), D_4^{20} 0·9235, n_D^{20} 1·4628. 1 : 1 : 5-*Trimethyl*cyclo*hexan*-6-*ol* has a similar odour, b. p. 186—187°/753 mm. (corr.), D_4^{20} 0·9128, n_D^{20} 1·4600.

Ethyl derivatives have been similarly prepared from 1-methyl*cyclo*hexan-6-one, the first stage giving 1-*methyl*-5-*ethyl*cyclo*hexan*-6-*one*, b. p. 194—196°/745 mm. (corr.), D_4^{20} 0·9162, n_D^{20} 1·4555. This then yields 1-*methyl*-1 : 5-*diethyl*cyclo*hexan*-6-*one*, b. p. 222—224°/757 mm. (corr.), D_4^{20} 0·9054, n_D^{20} 1·4572, and finally 1-*methyl*-1 : 5 : 5-*triethyl*cyclo*hexan*-6-*one*, b. p. 249—252°/765 mm. (corr.), b. p. 123—126°/16 mm. (corr.), D_4^{20} 0·9132, n_D^{20} 1·4634.

The corresponding alcohols have been prepared by reduction.

1-*Methyl*-5-*ethyl*cyclo*hexan*-6-*ol*, b. p. 202—204°/761 mm. (corr.), D_4^{20} 0·9268, n_D^{20} 1·4689.

1-*Methyl*-1 : 5-*diethyl*cyclo*hexan*-6-*ol*, b. p. 232—235°/749 mm. (corr.), D_4^{20} 0·9206, n_D^{20} 1·473.

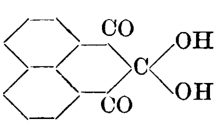
1-*Methyl*-1 : 5 : 5-*triethyl*cyclo*hexan*-6-*ol*, b. p. 258—260°/759 mm. (corr.), D_4^{20} 0·9255, n_D^{20} 1·4769.

The successive introduction of methyl groups into *cyclo*hexanone elevates the boiling point progressively, whilst causing a diminution in the density and the index of refraction, the same holding good for the corresponding alcohols.

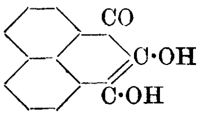
The introduction of ethyl groups into methyl*cyclo*hexan-6-one produces a steady rise in the boiling point, whilst the density diminishes for the first two stages and increases at the third, the refractive index showing steady rise throughout. The same remarks apply to the corresponding alcohols. W. G.

Interaction of Diketones and Acid Amides. L. H. FRIEDBURG (*Eighth Inter. Cong. App. Chem.*, 1912, **6**, 131).—When molecular quantities of pure benzil and benzamide are distilled, a quantitative yield of benzonitrile, together with benzaldehyde and benzoic acid, is obtained. J. C. W.

Oxidation of Hydroxy*peri*naphthindenone. III. GIORGIO ERRERA (*Gazzetta*, 1913, **43**, i, 583—594. Compare Errera and Cuffaro, A., 1912, i, 273).—The paper deals with some derivatives of hydroxy*peri*naphthindenone obtained from a substance mentioned in a former paper (A., 1911, i, 465) as having been prepared by the action of phenylhydrazine on hydroxy*peri*naphthindenone. The constitution of this substance is still being investigated. It dissolves in bromine water, yielding the *hydrate* of peri*naphthindantrione* (annexed formula) (compare Ruhemann, T., 1911, **99**, 1446), which forms golden-yellow, prismatic crystals. These begin to decompose at about 110°, yielding the anhydrous peri*naphthindantrione*, which forms red crystals, m. p. about 273° (decomp.). The hydrate dissolves in cold concentrated sodium carbonate, yielding a white, crystalline *substance* from which acids regenerate the triketone. The hydrate yields a *sodium bisulphite*



compound; hydroxylamine and phenylhydrazine do not give oxime or hydrazone, but reduce the substance. Both the hydrate and the anhydrous ketone readily yield an *alcoholate*, $C_{15}H_{12}O_4$, which crystallises in yellow, triclinic plates. The triketone reacts with *o*-phenylenediamine with production of the *phenazine*, $C_{19}H_{10}ON_2$, which crystallises in golden-yellow needles, m. p. 255—256°. The phenazine yields a *hydrazone*, $C_{25}H_{16}N_4$, crystallising in violet laminæ, m. p. about 299° (decomp.).



Reduction of the triketone (best with phenylhydrazine) leads to the formation of *dihydroxyperinaphthindenone* (annexed formula), which can also be prepared by boiling the substance from phenylhydrazine and hydroxy*peri*naphthindenone with alcohol and sulphuric acid for six hours. Dihydroxy*peri*naphthindenone crystallises in silky, red needles, m. p. 258—259° (sintering previously). The *potassium* salt,

$$C_{13}H_7O_3K,H_2O,$$

resembles permanganate in appearance. The salts of the substance are stable in the solid state, but are readily oxidised by air when in solution, yielding eventually naphthalic anhydride. Oxidation with bromine water regenerates the triketone. Conversely, the latter substance is partly reduced to dihydroxy*peri*naphthindenone when boiled with water. The author suggests that the blue coloration observed by Ruhemann (T., 1910, **97**, 2027) when triketohydrindene is treated with potassium hydroxide is probably due to the transitory appearance of hydroxydiketohydrindene in its tautomeric form.

On esterification with methyl sulphate, dihydroxy*peri*naphthindenone yields a *monomethyl ether*, $C_{14}H_{10}O_3,H_2O$, crystallising in golden-yellow leaflets or needles, which on heating melt and lose water below 100°, giving the anhydrous substance, m. p. 115—135°. The *dimethyl ether*, $C_{15}H_{12}O_3$, is obtained by the same method, and forms golden-yellow needles, m. p. 84—85°. The *dibenzoyl* derivative, $C_{27}H_{16}O_5$, crystallises in greenish-yellow prisms, m. p. 217—218°. R. V. S.

Improved Method for the Production of β-Aminoanthraquinone. M. L. CROSSLEY (*Eighth Inter. Cong. App. Chem.*, 1912, **25**, 351—352).—β-Aminoanthraquinone has been obtained by Bourcart and also by Perger by heating sodium anthraquinone-β-sulphonate with solution of ammonia (25%) in a sealed glass tube. This method has now been found unsuitable for the preparation of the compound, as it is dangerous and gives only a small yield. A modified method has therefore been devised in which the reagents are heated at 190° in an iron tube, and the yield increased from 14% to 45%. When the ammoniacal filtrate from the β-aminoanthraquinone is acidified with hydrochloric acid, a brown precipitate is obtained which shows strong tinctorial properties with animal fibres. E. G.

Syntheses in the Terpene Group. WILLIAM H. PERKIN, jun. (*Eighth Inter. Cong. App. Chem.*, 1912, **6**, 224—264).—A review of the chemistry of the known and possible menthenols and menthadienes with special reference to the syntheses accomplished by Perkin and his collaborators. J. C. W

Terpenes. Polymerisation of Pinene. GEORGE B. FRANKFORTER and F. W. POPPE (*Eighth Inter. Cong. App. Chem.*, 1912, **25**, 363—369).—By the action of iodine on pinene in presence of aluminium iodide, a pinene *hydriodide*, b. p. 107°/7 mm., D 1·447, and n_D 1·6245, is produced, together with a *di-iodide*, $C_{10}H_{16}I_2$, b. p. 119—125°/7 mm., D 1·69. Both the hydriodide and di-iodide are decomposed by light with formation of dipinene and colophonene.

Dipinene, $(C_{10}H_{16})_2$, b. p. 172°/7 mm., D_{20} 0·947, n_D^{23} 1·52517, is optically inactive, and has a viscosity 101 at 25° as compared with water. *Colophonene*, $(C_{10}H_{16})_4$, m. p. 102—103°, is a pale yellow, crystalline substance; it yields two *tetrachloro*-derivatives, $(C_{10}H_{15}Cl)_4$, one, m. p. 119—121°, obtained by treating it with potassium permanganate and hydrochloric acid, and the other, m. p. 99—102°, obtained by the action of sulphuryl chloride. Both dipinene and colophonene are remarkably stable. E. G.

Constituents of Essential Oils. Reductions in the Sesquiterpene Group. FRIEDRICH W. SEMMLER and FELIX RISSE (*Ber.*, 1913, **46**, 2303—2308).—Eudesmene, b. p. 122—124°/7 mm., D^{20} 0·91964, n_D 1·50874, $[\alpha]_D$ +54·6°, obtained by the action of alcoholic potassium hydroxide on eudesmene dihydrochloride (which is produced when eudesmol is treated with hydrogen chloride in acetic acid solution; compare Semmler and Tobias, this vol., i, 885), can be reduced in acetic acid by free hydrogen under the catalytic influence of platinum black, producing *tetrahydroeudesmene*, $C_{15}H_{28}$, b. p. 122—122·5°/7·5 mm., D^{20} 0·8893, n_D 1·48278, $[\alpha]_D$ +10·2°.

Similar reduction of purified eudesmol, needles, m. p. 84°, not only removed the ethylenic linkings, but also affected the hydroxyl group, for the product is a *hydrocarbon*, $C_{15}H_{28}$, b. p. 117°/5·5 mm., D^{20} 0·8896, n_D 1·48425, $[\alpha]_D$ +11·8°; this is strikingly different from the result of reduction in ethereal solution (*loc. cit.*), the product of which is dihydroeudesmol, $C_{15}H_{28}O$.

The action of ozone on eudesmene in acetic acid solution gave decided indications of the distinct natures of eudesmene and selinene; one of the products was a *substance*, b. p. 180—200°/7 mm., D^{20} 1·081, n_D 1·49429, $[\alpha]_D$ +13°, which yields a *semicarbazone*.

Catalytic reduction of guajol, m. p. 91°, in acetic acid solution by free hydrogen resulted in the simultaneous elimination of the ethylenic linkings and the hydroxyl group with the formation of *tetrahydroguajene*, $C_{15}H_{28}$, b. p. 118—119°/7 mm., D^{20} 0·8806, n_D 1·47840, $[\alpha]_D$ +10·6°.

Reduction of tricyclic α-santalol, b. p. 147—148°/4·5 mm., D^{20} 0·9745, n_D 1·50552, $[\alpha]_D$ +0·6°, in a similar manner yielded almost quantitatively a bicyclic *tetrahydrosantalene*, $C_{15}H_{28}$, b. p. 115—116°/9 mm., D^{20} 0·8655, n_D 1·46908, $[\alpha]_D$ +5·6°, not only the ethylenic linkings and the hydroxyl group, but also one of the rings having been eliminated. Reduction of bicyclic β-santalol, b. p. 158—158·5°/5 mm., D^{20} 0·97174, n_D 1·51357, $[\alpha]_D$ −41·8°, yielded a product, b. p. 119°/10 mm., D^{20} 0·8550, n_D 1·46612, $[\alpha]_D$ +2·8°, which is mainly a *tetrahydrosantalene*, $C_{15}H_{28}$, probably containing a small quantity of a hexahydrosantalene due to a little monocyclic santalol, $C_{15}H_{24}O$, in the starting

product; at the same time in the reduction a bicyclic saturated alcohol, $C_{15}H_{28}O$, was obtained, b. p. 155—160°/10 mm., D^{20} 0·9380, n_D 1·48471, $[\alpha]_D$ +4·4°. D. F. T.

The Essential Oil of Jamaica Ginger. FRANCIS D. DODGE (*Eighth Inter. Cong. App. Chem.*, 1912, **6**, 77—80).—The lowest-boiling fractions of oil of ginger contain an aldehyde, which may be removed as the bisulphite compound, and has now been identified with decaldehyde (compare von Soden, A., 1900, i, 605). The aldehyde has D^{15} 0·828, is optically inactive, is unstable towards alkalis, and changes spontaneously with the lapse of some years into an oil which smells like geraniol, and does not form a bisulphite compound or a semicarbazone. J. C. W.

Essential Oil of Witch Hazel. H. A. DICKINSON JOWETT and F. LEE PYMAN (*Pharm. J.*, 1913, **91**, 129—130).—This oil had D 0·9001, an optical rotation of +4·29° in a 100 mm. tube, was slightly soluble in 90% alcohol, and gave a small quantity of colourless precipitate when mixed with absolute alcohol. It was found to consist chiefly of a sesquiterpene having $D_{15·5}^{15·5}$ 0·8970, α_D +14·88°, and n_D 1·4916. A trace of a phenolic substance, a mixture of fatty acids in the free and combined state, and a mixture of solid saturated hydrocarbons were also isolated, whilst indications of the presence of other compounds, including oxygenated substances, were obtained. The oil contained 0·6% of acids (expressed as acetic acid) and 7·3% of esters (expressed as $C_{10}H_{17}·C_2H_3O_2$). W. P. S.

Chemistry of Wood. The Resins of the Douglas Fir. GEORGE B. FRANKFORTER and HAROLD H. BROWN (*Eighth Inter. Cong. App. Chem.*, 1912, **25**, 359).—The resin extracted from the wood of the Douglas fir yields a crystalline acid, $C_{17}H_{24}O_2$, m. p. 143·5—144·5°, which has been termed *betic acid*; its salts, and bromine and iodine compounds have been prepared. E. G.

Oxidation of Caoutchouc. FRANZ KIRCHHOF (*Kolloid. Zeitsch.*, 1913, **13**, 49—61).—The author has carried out experiments on the oxidation of raw and vulcanised caoutchouc by means of air at the ordinary temperature and at 100°. It is shown that on account of the unsaturated nature of the caoutchouc, an autoxidation occurs which gives rise to the formation of a relatively unstable peroxide, which then undergoes a secondary oxidation: (1) $C_{10}H_{16}+O_2 \longrightarrow C_{10}H_{16}O_2$; (2) $C_{10}H_{16}+C_{10}H_{16}O_2 \longrightarrow 2C_{10}H_{16}O$; (3) $C_{10}H_{16}O + O_2 \longrightarrow C_{10}H_{16}O_3$. This process is accompanied, in the case of raw caoutchouc, by a softening of the material, which is quite sticky at first and later becomes hard and has a glassy nature. The latter condition is due to the presence of the higher oxidation products. The oxidation of vulcanised caoutchouc is in the same way to be regarded as a primary formation of a peroxide which then decomposes, producing the same soft and sticky substance. Further oxidation produces the hard substances and free sulphuric acid. The action of the acid appears also to consist in an oxidation of the rubber, since the acid

is reduced to sulphur dioxide. In the oxidation at 100°, a separation of water occurs; this appears to be a result of the formation of sulphuric acid, since under the same conditions raw caoutchouc does not give rise to water.

It is further shown that the combined sulphur-content after oxidation and extraction with alkali is reduced to two-thirds of the amount originally contained in the product. This and other observations lead to the conclusion that vulcanisation consists in the addition of S_8 or of a thiozone molecule to the hydrocarbon residue. Since the thiozone molecule is unstable, it is likely that vulcanised caoutchouc is a thiozonide, which probably is transformed into other products in the ageing process, and since the formation of the thiozone occurs most readily at 135—160°, the part played by the vulcanisation catalysts is to be explained by a local raising of the temperature. In the oxidation of caoutchouc by air, a notable increase in weight occurs with the formation of products soluble respectively in acetone and alkali which have an acidic character. It is also indicated that the bromide and nitrosite methods for the analysis of rubber consist of oxidation processes which are probably responsible for the untrustworthy nature of the results of these processes. J. F. S.

Synthesis of Glucosides by means of Ferments. ÉMILE BOURQUELOT (*Bull. Soc. chim.*, 1913, [iv], **13**, i—xxviii).—A lecture delivered to the Chemical Society of France on May 9th, 1913.

J. F. S.

Synthetic β-Glucosides of Terpene Alcohols. III. JUHO HÄMÄLÄINEN (*Biochem. Zeitsch.*, 1913, **53**, 423—428. Compare this vol., i, 497, 639, 888).—By condensation of α-santenol and camphene hydrate with bromoacetyldextrose in the presence of silver carbonate, and the subsequent hydrolysis of the acetyl derivatives, the glucosides were obtained. *α-Santenoltetra-acetyl-*d*-glucoside*, $C_{23}H_{34}O_{10}$, m. p. 135·5—137° (corr.), yields on hydrolysis *α-santenol-*d*-glucoside*, $C_{15}H_{26}O_6$, m. p. 122·5—125·5° (corr.), $[\alpha]_D^{20}$ − 44·63°. It is readily hydrolysed by emulsin.

*Camphenehydratetetra-acetyl-*d*-glucoside*, $C_{24}H_{36}O_{11}$, m. p. 115—117° (corr.), yields on hydrolysis *camphenehydrate-*d*-glucoside*, $C_{15}H_{28}O_6$, m. p. 96·5—102·5° (corr.), $[\alpha]_D^{20}$ − 30·56°, which is slowly hydrolysed by emulsin. S. B. S.

Eutannin. WILHELM RICHTER (*Chem. Zentr.*, 1913, i, 1820—1821; from *Arb. Pharm. Inst. Univ. Berlin*, **9**, 85—112).—Eutannin has the composition $C_{28}H_{24}O_{19},H_2O$, $[\alpha]_D^{15}$ + 58·9°, and forms a crystalline *sodium* salt. It contains a carboxyl group and a lactone or anhydride grouping. When heated in a stream of hydrogen at 240°, a molecule of carbon dioxide is eliminated and pyrogallol sublimes. Some diphenylmethane is formed on distillation with zinc dust. *Eutannin hydrate*, $C_{28}H_{26}O_{20}$, contains two carboxyl groups owing to the opening of the lactone or anhydride ring; the *disodium* salt forms a colourless precipitate. Eutannin is hydrolysed by emulsin to gallic acid and a substance which reduces Fehling's solution on boiling. Gallic acid is similarly formed on hydrolysing with 10% sulphuric acid.

Acetyleutannin, $C_{28}H_{13}O_9(CO{\cdot}CH_3)_{11}$, formed on boiling with acetic anhydride, is a colourless powder composed of tiny, crystalline splinters which sinter at 180—185°, decomp. 215°.

Methyl chloro-formate acts on eutannin to form a compound
$$C_{28}H_{19}O_{14}(O{\cdot}CO_2Me)_5,$$
a colourless, amorphous powder, which sinters at 150—153°, decomp. 180°. Diazomethane acting on this introduces four further methyl groups, yielding a product $C_{28}H_{15}O_{10}(O{\cdot}CO_2Me)_5(OMe)_4,H_2O$. This is composed of small, crystalline splinters, which sinter at 125°, m. p. 137°, decomp. 179°.

Diazomethane acting on eutannin produces at first the *methyl* derivative, $C_{28}H_{20}O_{15}(OMe)_4$, an amorphous powder, which sinters at 145°, decomp. 210—215°. On continued treatment the fully methylated compound, $C_{28}H_{15}O_{10}(OMe)_9$, is obtained, forming minute, crystalline splinters, m. p. 154—155°. On hydrolysis with sodium hydroxide, trimethylgallic acid is obtained.

The tannin obtained on hydrolysis of eutannin with sodium hydroxide has the composition $C_{14}H_{16}O_{11}$. Six hydroxyl groups in it are replaced by $-O{\cdot}CO_2Me$ on treatment with methyl chloro-formate. The formula $[(OH)_3C_6H_2{\cdot}CO{\cdot}O]_2C_6H_2(CO_2H){\cdot}O{\cdot}C_6H_4O(CO)(OH)_4$ is proposed for eutannin. E. F. A.

Arsenites of Alkaloids. ALFRED C. MANGOLD (*Eighth Inter. Cong. App. Chem.*, 1912, **17**, 37—43).—Analyses of compounds of arsenious acid with various alkaloids showed that the acid does not form true salts with quinine, cinchonidine, cinchonine, quinidine, brucine, and strychnine; the compounds obtained under varying conditions of preparation were mixtures of arsenious acid with the alkaloids. Arsenic acid, however, forms well-crystallised, definite salts with these alkaloids. W. P. S.

Occurrence of Histidine-betaine in Fungi. ERNST WINTERSTEIN and CAMILLE REUTER (*Zeitsch. physiol. Chem.*, 1913, **86**, 234—237).—The base $C_9H_{15}O_2N_3$ obtained by Reuter (A., 1912, ii, 593) from fungi is shown to be histidine-betaine identical with that obtained by Barger and Ewins (this vol., i, 529) from ergothionin and the synthetic product made by Engeland and Kutscher (*ibid.*). The monopicrate, m. p. 201°, forms slender, soft needles. The dipicrate, $2H_2O$, loses this water at 105°, and forms flat, thin prisms, or long plates, m. p. 212—213°. The base has $[\alpha]_D$ +41·1°.

E. F. A.

Some Derivatives of 8-Hydroxyquinoline. HANS SCHÜLLER (*J. pr. Chem.*, 1913, [ii], **88**, 180—188).—8 : 8'-*Dihydroxy*-5 : 5'-*diquinolylmethane*, $CH_2(C_9H_5N{\cdot}OH)_2$, obtained in the form of its *sulphate* (stellar aggregates of yellow needles, m. p. 198—200°) by the addition of 40% aqueous formaldehyde to a well cooled solution of 8-hydroxyquinoline in sulphuric acid, is precipitated from its salts by aqueous ammonia as a white, amorphous precipitate (decomp. 247°), which separates from pyridine in hexagonal crystals and couples with diazotised *m*-toluidine and α-naphthylamine, yielding carmine-red and reddish-brown *azo-dyes*. The *hydrochloride*, B,2HCl, crystallises in

radiating clusters of lustrous, silky needles (decomp. 260°); the *zinci-chloride* forms yellowish-green, prismatic crystals; the *diacetyl* derivative has m. p. 160°, and decomposes slowly on exposure to air; the *dibenzoyl* derivative, prepared by the pyridine method, separates from alcohol in small crystals, and has an odour resembling that of ethyl benzoate.

7 : 7′-*Dinitroso*-8 : 8′-*dihydroxy*-5 : 5′-*diquinolylmethane* (or 7 : 7′-*di-oximino*-8 : 8′-*diketo*-5 : 5′-*di*-7 : 8-*dihydroquinolylmethane*),

$$CH_2[C_9H_4N(NO)\cdot OH]_2,$$

or $CH_2(C_9H_4ON\colon N\cdot OH)_2$, prepared by the addition of sodium nitrite to an aqueous solution of the sulphate or hydrochloride, is a yellow crystalline substance, which explodes at about 130°, and is precipitated from its solution in sodium carbonate by acetic acid in a red, gelatinous condition. With salts of iron, nickel, copper, and many other metals, it yields coloured precipitates, which are more or less soluble in mineral acids, but insoluble in dilute acetic acid. Unsuccessful attempts to condense 8-hydroxyquinoline with oxalic acid, formic acid, and carbon tetrachloride are also recorded. F. B.

The Desmotropy of *o*- and *p*-Quinonoid Salts in the Thiazine Group. RUDOLF PUMMERER and SEBASTIAN GASSNER (*Ber.*, 1913, **46**, 2310—2327).—In order to throw further light on the debated constitution of the thiazines, the authors have turned their attention to some of the simpler salts and have examined them chemically and optically; they find in certain cases an equilibrium between the ortho- and para-constitutions favoured by Kehrmann and Hantzsch respectively.

Their results with the phenazothionium salts differ in several respects from those of Kehrmann and Veselý (A., 1902, i, 186). The action of bromine on an alcoholic solution of thiodiphenylamine at even $-15°$ yielded a *dibromide*, $NHBr\lessdot\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}\gtrdot SBr$, prisms, which readily decomposes with liberation of hydrogen bromide; it is reconverted by sulphurous acid into thiodiphenylamine. The *dichloride* is still less stable, but the more stable *di-iodide*, blackish-brown crystals, can be obtained by double decomposition of the dibromide and potassium iodide and also by the action of iodine on thiodiphenylamine in chloroform solution. Treatment of an acetone solution of the di-iodide with sodium acetate causes the production of a salt derived probably from a bimolecular colourless *base*.

The ferrochloride described earlier, from its quantitative reduction with stannous chloride, appears to be a *meri*-quinonoid compound which readily accounts for the deposition of thiodiphenylamine when its solution in hydrochloric acid is diluted. *Phenazothionium perchlorate*, obtained by the action of perchloric acid on diphenylaminesulphoxide (Barnett and Smiles, T., 1910, **97**, 186), is a stable, crystalline substance, which, like the phenazothionium salts generally, shows in dilute hydrochloric acid an absorption band in the green portion of the spectrum; a green *diperchlorate* was also obtained. In addition to the green picrate obtained by Kehrmann and Veselý, the authors have isolated the unstable brown intermediate product, which proves to

be of the same composition, the green picrate being regarded as a polymeride of the brown; a very dilute solution of the green picrate in nitrobenzene turns brown, the change in colour being favoured by warming and dilution, whilst stronger solutions of both forms at first have the characteristic colour of the respective solids, but shortly assume an intermediate tone.

Phenazothione (for which the authors prefer the term thiazone), obtained by a slight modification of Kehrmann's method, judging from its absorption spectrum and its reaction with magnesium phenyl bromide, can hardly have the suggested phenol-betaine structure:

$$N{<}{\substack{C_6H_4{>}S\\ C_6H_3{-}O}}\ \text{(S–O linked)}.$$

This view is confirmed by the behaviour of its *hydrochloride*, which exists in two forms. On intimately mixing the base with hydrochloric acid a brown solution is obtained which changes to violet and subsequently deposits violet needles; the violet hydrochloride can be obtained directly by reaction in benzene-ether solution. The conversion of the brown form into the violet could be followed photometrically, and it was found that a unimolecular reaction occurs, yielding an equilibrium mixture, and that the velocity is independent of the concentration; from these facts the change must be an isomerisation, probably of the brown para-quinonoid salt, $N{<}{\substack{C_6H_3O(HCl)\\ C_6H_4}}{>}S$, into violet ortho-quinonoid, $N{<}{\substack{C_6H_3(OH)\\ C_6H_4}}{>}SCl$; reduction of the brown salt (which was only obtained in solution) was usually accompanied by more or less isomerisation to the violet salt, which is less easily reduced. Only one *hydriodide* was obtainable, and from its brown colour it is probably of the para-quinonoid structure. Similar phenomena are met with 3-*methoxythiodiphenylamine*, leaflets, m. p. 163°, which on oxidation by *p*-benzoquinone in acetic acid containing a little sulphuric acid gives a mixture of ortho- and para-quinonoid salts; addition of perchloric acid causes precipitation of the *o*-quinonoid violet *perchlorate*, which in the absence of any excess of acid gives a brown solution in water, but on addition of a few drops of acid the violet form is obtained. With 3-*benzoyloxythiodiphenylamine*, leaflets, m. p. 202—203°, obtained like the corresponding methoxy-compound by acting on a reduced solution of phenazothione, only ortho-quinonoid salt formation could be observed.

The acetylated amino-compounds, such as diacetylthionine (free *base*, needles, decomp. above 250°), are only ortho-quinonoid, whilst from similar colour considerations aminophenazothionium hydrochloride is of para-quinonoid constitution, but shows desmotropy analogous to that of phenazothione hydrochloride, and is transformed by concentrated acid into a brown ortho-quinonoid salt. Indications of such structural change could also be detected with thionine, but not with methylene-blue. D. F. T.

The Deepening of Colour by Auxochrome Groups and Colours of an Higher Order. FRITZ STRAUS and A. ZEIME (*Ber.*, 1913, **46**, 2267—2283).—From a study of the *meri*-quinonoid salts of

the *p*-phenylenediamine and benzidine series, Piccard (this vol., i, 895) has drawn the conclusion that Nietzki's rule, concerning the deepening of the colour from yellow to green by auxochrome groups, requires extension so as to include colours of a higher order. When the auxochromic effect has been gradually increased by substitution so that the colour has successively passed from yellow to red, blue and green, further increase in the auxochrome action is accompanied by a repetition of the colours in the same order; the colours of the second series are said to be of the second order.

The authors have arrived at the same conclusion from a consideration of the relationship of the yellow auramine to the blue and green dyes of the diaminodiphenyl and diaminotriphenyl series previously described by Straus and Bormann (A., 1910, i, 281). The latter dyes are derived from the reddish-blue salts of tetramethyldiaminobenzhydrol, $NMe_2{\cdot}C_6H_4{\cdot}CH{:}C_6H_4{:}NMe_2Cl$ (I), by replacement of the central methane hydrogen by chlorine, cyanogen, phenyl and other groups.

The yellow auramine and the orange-yellow salts of Michler's ketone differ from the above dyes in that the chromophoric groups are replaced by the auxochromic, hydroxyl and amino-groups, which thus cause a change in colour from blue to yellow; the yellow colour of the auramine is, therefore, considered to be of the second order.

This view is supported by the observation of Semper (A., 1911, i, 577), that the acetylated auramine base yields reddish-blue salts, $NMe_2{\cdot}C_6H_4{\cdot}C(NHAc){:}C_6H_4{:}NMe_2Cl$; the auxochromic effect of the amino-group almost completely disappears on acetylation, so that the yellow colour of the second order of the auramine passes back again into the blue colour of the first order shown by the parent substance (I).

The conception of colours of a higher order also throws light on the relationships existing between the dyes of the diamino- and triamino-triphenyl series. The dyes of the triamino-series are not so deep in colour as those of the diamino-series, although they are produced from the latter by the introduction of the auxochrome amino-group. Thus, the red magenta corresponds with Döbner's violet, and the reddish-violet tetramethylmagenta with malachite-green. On the other hand, if the effect of the third amino-group in the magenta series is caused to disappear by acetylation, or by the conversion of the nitrogen atom into the quinquevalent condition, the colour apparently deepens. These anomalies disappear if it is assumed that the colours of the triaminotriphenyl series are of the second order, and those of the malachite-green group of the first order.

The authors also point out that whilst nitrosobenzene in the unimolecular condition is bluish-green and *p*-nitrosodimethylaniline pure green, the colour of *p*-nitrosodiphenylamine is yellow, and that tetramethyldiaminothiobenzophenone is orange-red, whilst thiobenzophenone is blue; from this the conclusion is drawn that the colours of *p*-nitrosodiphenylamine and tetramethyldiaminothiobenzophenone are of the second order.

Attempts have been made to prepare dyes having colours of the second order by replacing the *p*-hydrogen atoms of the terminal phenyl groups in viridine, $C_6H_5{\cdot}NH{\cdot}C_6H_4{\cdot}CPh{:}C_6H_4{:}NHCl{\cdot}C_6H_5$, by chlorine,

bromine, methyl, methoxy- and ethoxy-groups. The attempts, however, were not successful, the various substituents producing very little change in the colour of the parent substance; even replacement of the terminal phenyl groups by the naphthyl or diphenylyl groups failed to produce the desired effect.

The substituted viridines were all prepared by fusing di-*p*-methoxytriphenylcarbinol with the necessary substituted aniline (3 to 4 mols.) and benzoic acid (3 mols.) at 120—160° and isolated in the form of their chlorides.

The corresponding imine bases,

$$X\cdot C_6H_4\cdot NH\cdot C_6H_4\cdot CPh\colon C_6H_4\colon N\cdot C_6H_4X,$$

crystallise with benzene in dark reddish-brown needles having a green glance, and appear to polymerise when kept. The carbinols were prepared by dissolving the picrates or chlorides in pyridine and allowing the solution, after dilution with benzene or ether, to flow slowly into dilute aqueous alkali; only in a few cases could the carbinols be obtained crystalline. Ethers of the carbinols were also prepared, and resemble the latter in being difficult to obtain in the crystalline condition.

The *chloride* of *di*-p-*methylviridine*, prepared from *p*-toluidine, separates from acetone in small, lustrous, bronze crystals of the composition $C_{33}H_{29}N_2Cl,C_3H_6O$ (decomp. 248—250°); it crystallises with alcohol in needles having a green metallic glance. The *picrate* forms dark green needles, m. p. 211°, with previous sintering at 205°; the *imine base* has m. p. 182°.

The *chloride* of *di*-p-*chloroviridine*, prepared from *p*-chloroaniline, forms lustrous, metallic green needles, m. p. about 285°, the *picrate*, prismatic crystals, having a golden-yellow or green metallic lustre, m. p. 243°, with previous sintering at 236°; the *imine base* crystallises in dark brown needles, m. p. 136°, when rapidly heated.

The *chloride* of *di*-o-*chloroviridine* has m. p. 191°; the *picrate* crystallises in leaflets of a coppery-red, metallic lustre, m. p. 148°; the *imine base* has m. p. 107°.

The *chloride* of *di*-p-*bromoviridine* forms a powder having a bronze lustre, m. p. indefinite (290—305°); the *picrate* crystallises from acetone in prismatic crystals of a golden-yellow, metallic glance, m. p. 253—257°; the *imine base* has m. p. 186—187°.

The *chloride* of *di*-p-*methoxyviridine* forms green, metallic, lustrous needles; the *picrate* forms green or golden-bronze, lustrous crystals, m. p. 205—208°; the *imine base*, m. p. 167°, crystallises with benzene (1 mol.).

The *chloride* of *di*-p-*ethoxyviridine* has m. p. 243—245°; the *picrate* separates from acetone in light green, metallic, lustrous crystals, which on drying pass into a lustrous coppery modification, m. p. 176°; the *imine base* crystallises with benzene (1 mol.), m. p. 97°.

The following derivatives of *di*-p-*nitroviridine* were prepared: the *chloride*; *picrate*, lustrous, bronze crystals; *imine base*, dark brown needles, m. p. 176—178°; the *carbinol*, which sinters and decomposes at 110—115°, and is completely fused at 140°; the *ethyl ether*, which is light yellow, becomes brown at 200°, and has m. p. 204°.

The *chloride* of *di*-p-*phenylviridine*, prepared from *p*-aminodiphenyl,

forms a dark green, metallic, lustrous powder, m. p. 300—305°; the *picrate*, dark red scales, m. p. 252°, with previous sintering at 247°; the *imine base* crystallises with benzene (1 mol.), and has m. p. 136°; the *carbinol*, a light pink powder, and *ethyl ether* were also prepared.

β-Naphthylaminofuchsone-β-naphthylimine,

$$C_{10}H_7 \cdot NH \cdot C_6H_4 \cdot CPh{:}C_6H_4{:}N \cdot C_{10}H_7,$$

prepared from β-naphthylamine, has m. p. 147°; the *chloride* crystallises from acetone in brown needles of a bronze lustre, m. p. 290—300° (decomp.); the *picrate* in cubical crystals, sintering at 215°, m. p. 224°; the *carbinol* and *leuco*-compound do not crystallise.

F. B.

Ring Closing Accompanied by the Elimination of a Nitro-group from the Benzene Nucleus. SIEGMUND REICH and GEORGES GAIGAILIAN (*Ber.*, 1913, **46**, 2380—2386).—When potassium hydroxide is added to 2 : 6-dinitrobenzaldehydephenylhydrazone, the red alcoholic solution becomes deep blue, but in a few minutes the colour lessens and changes to a pale yellow; pale yellow needles, m. p. 165°, crystallise out. The change is analogous to that observed by V. Meyer with the phenylhydrazone of methyl dinitrophenylglyoxylate (compare A., 1889, 516).

The blue colour is due to the formation of the potassium salt, $C_6H_3(NO_2)_2 \cdot CH{:}N \cdot NPhK$, from which potassium nitrite is eliminated, and 7-nitro-1-phenyl*iso*indazole is formed, $NO_2 \cdot C_6H_3 < \begin{smallmatrix} CH \\ NPh \end{smallmatrix} > N$.

Corresponding *iso*indazole derivatives are formed by the substituted phenylhydrazones, or by the naphthyl- or benzyl-hydrazones. The semicarbazone does not react in this manner.

When the imide hydrogen atom is replaced there is no reaction; thus neither the phenylmethyl- nor the phenylbenzyl-hydrazones shows the reaction.

The *iso*indazole derivatives crystallise well, and are stable compounds. The presence of the phenyl and nitro-groups reduces the basic properties, so that the hydrochlorides are not precipitated on passing hydrogen chloride into the ethereal solution of the base. They are especially resistant towards reducing agents.

7-*Nitro*-1-*phenyl*iso*indazole* crystallises in yellow needles, m. p. 165°.

2 : 6-*Dinitrobenzaldehyde*-p-*bromophenylhydrazone* forms red crystals, m. p. 176° (blackening). The corresponding 7-*nitro*-1-p-*bromophenyl*-iso*indazole* separates in yellow crystals, m. p. 183° (blackening).

2 : 6-*Dinitrobenzaldehyde*-p-*nitrophenylhydrazone* forms reddish-brown crystals, m. p. 207—208°. The isomeric o-*nitrophenylhydrazone* gives similar-coloured crystals, m. p. 220—221°.

7-*Nitro*-1-p-*nitrophenyl*iso*indazole* yields yellow, microscopic crystals, m. p. 261°.

7-*Nitro*-1-o-*nitrophenyl*iso*indazole* forms yellow needles, m. p. 162—163°.

2 : 6-*Dinitrobenzaldehyde*-α-*naphthylhydrazone* forms red crystals, m. p. 205—206°.

7-*Nitro*-1-α-*naphthyl*iso*indazole* gives yellow crystals, m. p. 113—114°.

The isomeric *β-naphthylhydrazone* crystallises in tiny red needles, m. p. 183—184°, whilst the 7-*nitro*-1-*β-naphthyl*iso*indazole* separates in yellow crystals, m. p. 152—153°.

2 : 6-*Dinitrobenzaldehydebenzylhydrazone* crystallises in citron-yellow needles, m. p. 86°.

7-*Nitro*-1-*benzyl*iso*indazole* forms tiny, pale yellow, lustrous needles, m. p. 97—98°.

2 : 6-*Dinitrobenzaldehydephenylmethylhydrazone* separates in reddish-yellow crystals, m. p. 127°.

2 : 6-*Dinitrobenzaldehydephenylbenzylhydrazone* crystallises in yellow needles, m. p. 110°.

2 : 6-*Dinitrobenzaldehydesemicarbazone* forms a yellow, crystalline powder, m. p. 207—208°.

2 : 6 : 2′ : 6′-*Tetranitrobenzylideneazine*,

$$C_6H_3(NO_2)_2\cdot CH\colon N\cdot N\colon CH\cdot C_6H_3(NO_2)_2,$$

prepared by the interaction of hydrazine hydrochloride with the aldehyde, forms pale yellow-coloured needles, m. p. 246—247°.

E. F. A.

Bisdiphenyleneacetylhydrazide Chloride and its Reaction Products. ROBERT STOLLÉ, H. MÜNZEL, and F. WOLF (*Ber.*, 1913, **46**, 2339—2352).—The elimination of halogen or of halogen hydracid at the 1 : 6-position occurs with bisdiphenyleneacetylhydrazide chloride just as with bisdiphenylacetylhydrazide chloride (Stolle and Laux, A., 1911, i, 508; Stollé and Schmidt, A., 1912, i, 980, 1035). Corresponding with the greater mobility of the α-hydrogen atom of diphenyleneacetic acid it is found that derivatives such as bisdiphenyleneacetylhydrazide chloride readily undergo oxidation to azo-compounds, whilst others can be further oxidised to tetrazine derivatives (compare Wislicenus and Russ, A., 1910, i, 840).

Diphenyleneacetylhydrazide, $CH(C_6H_4)_2\cdot CH\cdot CO\cdot NH\cdot NH_2$, needles, m. p. above 360° (decomp.), was obtained by heating ethyl diphenyleneacetate with a sesquimolecular proportion of hydrazine hydrate at 120° for three hours; its *hydrochloride*, lustrous scales, is precipitated from solution by concentrated hydrochloric acid; *benzylidene* derivative, needles which sinter near 250°; *acetone* condensation product, lustrous needles, m. p. near 200° if rapidly heated.

If diphenyleneacetylhydrazide is heated for two hours with ethyl diphenyleneacetate in molecular proportion at 250°, symmetrical *bisdiphenyleneacetylhydrazide*, $CH(C_6H_4)_2\cdot CO\cdot NH\cdot NH\cdot CO\cdot CH(C_6H_4)_2$, needles, m. p. 340°, from nitrobenzene, is obtained, and it can also be produced by the interaction of equimolecular proportions of diphenyleneacetyl chloride and hydrazine hydrate in cooled ethereal solution. When treated in suspension in benzene or carbon tetrachloride with phosphorus pentachloride at water-bath temperature, this symmetrical hydrazide is converted into *bisdiphenyleneacetylhydrazide chloride*, $CH(C_6H_4)_2\cdot CCl\colon N\cdot N\colon CCl\colon CH(C_6H_4)_2$, colourless crystals, which at its m. p. (approximately 192°) or in solution in boiling xylene or nitrobenzene assumes a deep red colour, due doubtless to elimination of hydrogen atoms at the 1 : 6-positions by oxidation with formation of the *azo*-compound, $C(C_6H_4)_2\colon CCl\cdot N\colon N\cdot CCl\colon C(C_6H_4)_2$. The hydrazide

chloride, when treated in benzene solution with an alcoholic solution of sodium ethoxide or with ammonia, or such bases as mercuric oxide and lead oxide, loses a molecule of hydrogen chloride, producing *bisdiphenylenesuccinonitrile*, a colourless, crystalline powder, m. p. 242°. If in the reaction with sodium ethoxide the solution of the latter is a concentrated one and the reaction mixture is heated, the nitrile undergoes further hydrolysis with scission of carbon dioxide, yielding bisdiphenylene-ethane. By boiling with acetic acid and zinc dust the nitrile undergoes successive reduction and hydrolysis to diphenylene-acetamide, m. p. 251°.

If an intimate mixture of bisdiphenyleneacetylhydrazide chloride and phosphorus pentachloride is heated for an hour at 180—200°, *bischlorodiphenyleneacetylhydrazide chloride*,

$$CCl(C_6H_4)_2\cdot CCl:N\cdot N:CCl\cdot CCl(C_6H_4)_2,$$

pale red crystals, m. p. 240°, with reddening, is obtained. When heated in high-boiling solvents, a deep red colour develops, due to elimination of chlorine and formation of *bischlorodiphenylenevinyldi-imide*,

$$C(C_6H_4)_2:CCl\cdot N:N\cdot CCl:C(C_6H_4)_2,$$

almost black, lustrous needles, m. p. 295°, which is best produced by the action of mercury on the bischlorodiphenyleneacetylhydrazide chloride in benzene solution; the di-imide can unite with chlorine regenerating its parent substance, and is further reduced in benzene solution by hydrazine hydrate, yielding 3 : 6-difluorenyldihydrotetrazine, $CH(C_6H_4)_2\cdot C{<}{\genfrac{}{}{0pt}{}{N\text{——}N}{NH\cdot NH}}{>}C\cdot CH(C_6H_4)_2$, m. p. 290°, and by acetic acid and zinc dust to iminomethylfluorene, m. p. 148—149° (compare Wislicenus and Russ, *loc. cit.*). The addition of bromine to bischlorodiphenylenevinyldi-imide, effected in benzene solution, yields *bisbromodiphenyleneacetylhydrazide chloride*,

$$CBr(C_6H_4)_2\cdot CCl:N\cdot N:CCl\cdot CBr(C_6H_4)_2,$$

colourless crystals, m. p. 245°, which like the corresponding chloro-compound readily passes into the red azo-compound at its m. p. or when heated in high-boiling solvents. On treatment of the di-imide compound in benzene solution with amyl nitrite and acetic acid, the colour disappears and *α-nitroso-α′-hydroxy-αα′-bisdiphenyleneacetylhydrazide chloride*, $OH\cdot C(C_6H_4)_2\cdot CCl:N\cdot N:CCl\cdot C(C_6H_4)_2\cdot NO$, colourless, microscopic needles, m. p. near 145°, with reddening, is formed.

When bisdiphenyleneacetylhydrazide chloride is heated for several days in benzene solution with phosphoryl chloride and phosphoric oxide, *bisfluorenyl*-1 : 3 : 4-*oxadiazole*,

$$CH(C_6H_4)_2\cdot C{<}{\genfrac{}{}{0pt}{}{N\cdot N}{-O-}}{>}C\cdot CH(C_6H_4)_2,$$

colourless needles, m. p. 223°, is obtained; this assumes a blue coloration at its m. p. or when heated in high-boiling solvents; by heating in benzene solution with phosphorus pentachloride for several hours it is converted into 2 : 5-*bischlorodiphenylenemethyl*-1 : 3 : 4-*oxadiazole*, $C(C_6H_4)_2Cl\cdot C{<}{\genfrac{}{}{0pt}{}{N\cdot N}{-O-}}{>}CCl(C_6H_4)_2$, colourless prisms, m. p. 227°, which can also be obtained by the action of thionyl chloride on *s*-diphenylene-acetylhydrazide. This product when heated in high-boiling solvents, or

preferably when shaken in benzene solution with mercury, loses chlorine with formation of blue 2 : 5-*bisdiphenylenemethylenedihydro*-1 : 3 : 4-*oxadiazole*, $C(C_6H_4)_2{:}C<\substack{N{:}N \\ -O-}>C{:}C(C_6H_4)_2$, m. p. above 360°, and when boiled in alcoholic solution for several days undergoes conversion into 2 : 5-*bisethoxydiphenylenemethyl*-1 : 3 : 4-*oxadiazole*,

$$OEt\cdot C(C_6H_4)_2\cdot C<\substack{N\cdot N \\ -O-}>C\cdot C(C_6H_4)_2\cdot OEt,$$

a colourless, crystalline powder, m. p. 290° (decomp.).

Bisdiphenyleneacetylhydrazide chloride, when heated under reflux for five hours with an equal quantity of hydrazine hydrate, condenses with the latter, producing 3 : 6-*difluorenyldihydrotetrazine*,

$$CH(C_6H_4)_2\cdot C<\substack{N\text{——}N \\ NH\cdot NH}>CH(C_6H_4)_2,$$

a colourless powder, m. p. 290°, together with 1-*amino*-2 : 5-*difluorenyl*-1 : 3 : 4-*triazole*, $CH(C_6H_4)_2\cdot C<\substack{N\text{——}N \\ N(NH_2)}>C\cdot CH(C_6H_4)_2$, microscopic tablets, m. p. 285°, which is also obtained by the action of hot alcoholic hydrogen chloride on the former product. The latter substance when treated in cold alcoholic solution with hydrogen chloride and sodium nitrite undergoes conversion into 2 : 5-*difluorenyl*-1 : 3 : 4-*triazole*, $CH(C_6H_4)_2\cdot C<\substack{N\cdot N \\ NH}>C\cdot CH(C_6H_4)_2$, needles, m. p. 217°. The interaction of bisdiphenylacetylhydrazide chloride and aniline at 150° gives rise to 1-*phenyl*-2 : 5-*difluorenyl*-1 : 3 : 4-*triazole*,

$$CH(C_6H_4)_2\cdot C<\substack{N\cdot N \\ NPh}>C\cdot CH(C_6H_4)_2,$$

a pale yellow, crystalline powder, m. p. 270°, the course of the reaction being strikingly different from that with ammonia (see above). The last product, in suspension in carbon tetrachloride and exposed to the rays from a quartz lamp, is converted by chlorine into 1-*dichlorophenyl*-2 : 5-*bisdiphenylenechloromethyl*-1 : 3 : 4-*triazole*,

$$CCl(C_6H_4)_2\cdot C<\substack{N\text{———}N \\ N(C_6H_3Cl_2)}>C\cdot Cl(C_6H_4)_2,$$

a colourless powder, m. p. above 360°, the solution of which in molten naphthalene becomes blue on shaking with mercury, probably due to the formation of unstable 1-*dichlorophenyl*-2 : 5-*bisdiphenylenemethylene*-2 : 5-*dihydro*-1 : 3 : 4-*triazole*, $C(C_6H_4)_2{:}C<\substack{N\text{===}N \\ N(C_6H_3Cl_2)}>C{:}C(C_6H_4)_2$.

When shaken in benzene suspension with amyl nitrite, 3 : 6-difluorenyldihydrotetrazine becomes oxidised to 3 : 6-*difluorenyltetrazine*, $CH(C_6H_4)_2\cdot C<\substack{N-N \\ N=N}>C\cdot CH(C_6H_4)_2$, red needles, m. p. 225° (decomp.), the reverse change being possible by reduction with zinc dust and acetic acid. 3 : 6-Difluorenyltetrazine when subjected to the action of chlorine in boiling carbon tetrachloride under the influence of rays from a quartz lamp gives 3 : 6-*bischlorodiphenylenemethyltetrazine*, $CCl(C_6H_4)_2\cdot C<\substack{N-N \\ N=N}>C(C_6H_4)_2Cl$, violet-black needles, m. p. 206° (decomp.), as a substitution product. Although already formed 3 : 6-

difluorenyltetrazine is not further oxidisable by amyl nitrite, if 3 : 6-difluorenyldihydrotetrazine is heated in benzene solution with amyl nitrite, the oxidation passes this stage, yielding 3 : 6-*bisdiphenylenemethylenedihydrotetrazine*, $C(C_6H_4)_2:C<\begin{smallmatrix}N=N\\N=N\end{smallmatrix}>C:C(C_6H_4)_2$, green prisms, m. p. 240° (decomp.), which is also obtainable by the action of mercury on a benzene solution of 3 : 6-bischlorodiphenylenemethyltetrazine or 3 : 6-bisbromodiphenylenemethyltetrazine, into which substances it can be reconverted by the action of the respective halogens. When heated alone to 240°, 3 : 6-bisdiphenylenemethylenedihydrotetrazine loses half its total nitrogen, and passes into bisdiphenylenesuccinonitrile; by the action of bromine in benzene solution it is quantitatively converted into 3 : 6-*bisbromodiphenylenemethyltetrazine*, $CBr(C_6H_4)_2\cdot C\ll\begin{smallmatrix}N-N\\N=N\end{smallmatrix}\gg C\cdot CBr(C_6H_4)_2$, a reddish-violet powder, decomp. near 260°, from which the bromine is removable by the action of mercury on its benzene solution. The action of sodium ethoxide on the bromine compound failed to yield any corresponding ethoxy-derivative, the only product being bisdiphenylene-ethane.

D. F. T.

Preparation and Reactions of 2 : 4-Dichlorophenylhydrazonopyruvyl Chloride. CARL BÜLOW and PETER NEBER (*Ber.*, 1913, **46**, 2370—2379. Compare Bülow and Neber, this vol., i, 207).—On hydrolysing ethyl anilinoacetoacetate to the free carboxylic acid and allowing chlorine to act on this in alcoholic solution, 2 : 4-*dichlorophenylhydrazonopyruvyl chloride* is obtained,

$$CH_3\cdot CO\cdot CCl:N\cdot NH\cdot C_6H_3Cl_2,$$

whereas carbon dioxide and hydrogen chloride are liberated. The chloride is very reactive; on treatment with ammonia or hydrazine, action can be controlled, so that only the chlorine and not the keto-group is replaced by the amino- or hydrazino-group with the formation of the basic compounds, (A) 2 : 4-*dichlorophenylhydrazonopyruvamide*, $CH_3\cdot CO\cdot C(NH_2):N\cdot NH\cdot C_6H_3Cl_2$, and (B) 2 : 4-*dichlorophenylhydrazonopyruvylhydrazide*, $CH_3\cdot CO\cdot C\lessgtr\begin{smallmatrix}NH\cdot NH_2\\N\cdot NH\cdot C_6H_3Cl_2\end{smallmatrix}$.

When phenylhydrazine acts on the aminohydrazone (A), the colourless basic osazone having the constitution

$$NHPh\cdot N:CMe\cdot C(NH_2):N\cdot NH\cdot C_6H_3Cl_2,$$

which is sensitive to light, is formed. The Bordeaux-red solution in concentrated sulphuric acid is turned blue both by oxidising agents and by atmospheric oxygen with the formation of osotetrazone.

The same osazone is obtainable from 2 : 4-dichlorophenylhydrazonopyruvyl chloride and phenylhydrazine, which condense to the *phenylhydrazone* of the chloride, $\begin{matrix}\alpha & ClC:N\cdot NH\cdot C_6H_3Cl_2\\ & |\\ \beta & CH_3\cdot C:N\cdot NHPh\end{matrix}$. This is converted by alcoholic acid into the corresponding α-amino-osazone,

The *hydrazone* of 2 : 4-dichlorophenylhydrazonopyruvamide,

$$NH_2\cdot C(:N\cdot NH\cdot C_6H_3Cl_2)\cdot CMe:N\cdot NH_2,$$

is typical of another class of compounds belonging to the basic osazonoid series; it no longer dissolves with a characteristic coloration in concentrated sulphuric acid, and cannot be oxidised to osotetrazone. The corresponding *hydrazide* behaves similarly.

2 : 4-*Dichlorophenylhydrazonopyruvyl chloride* crystallises in snow-white needles, m. p. 125°, dissolving in concentrated sulphuric acid with a pure yellow coloration. With pyridine on boiling or on prolonged contact in the cold it forms a *compound* crystallising in red needles, m. p. 168°. The corresponding *amide* crystallises in centimetre-long, faintly yellow needles, m. p. 193°, and dissolves in concentrated sulphuric acid with a faint yellow coloration.

The *phenylhydrazone* of 2 : 4-*dichlorophenylhydrazonopyruvamide* separates in bunches of snow-white needles, m. p. 149° (decomp.).

The *phenylhydrazone* of the corresponding *chloride* is deposited in large, straw-yellow needles from chloroform or fine matted needles from acetic acid, m. p. 208° (decomp.), giving a brownish-yellow solution in concentrated sulphuric acid.

The *hydrazone* of 2 : 4-*dichlorophenylhydrazonopyruvamide* crystallises in large, colourless needles becoming yellow on exposure; it sinters at 120°, m. p. 130°. The corresponding *acetylhydrazone* forms colourless crystals, m. p. 217°.

2 : 4-*Dichlorophenylhydrazonopyruvylhydrazide* forms pale yellow needles, m. p. 131°. It is remarkably electric. It dissolves in concentrated sulphuric acid with a yellowish-brown coloration which deepens on keeping. The corresponding *acetylhydrazide* crystallises in colourless needles which sinter at 150°, m. p. 199°; they become yellow on exposure. E. F. A.

Purines. XI. 2 : 8-Dioxy-6-methyl-9-ethylpurine. CARL O. JOHNS and EMIL J. BAUMANN (*J. Biol. Chem.*, 1913, **15**, 119—125).—The preparation of a derivative of 9-ethylpurine is described. 6-Chloro-2-ethylthiol-4-methylpyrimidine,

$$\mathrm{SEt{\cdot}C}\left\langle\begin{matrix}\mathrm{N{=}CCl}\\ \mathrm{N{\cdot}CMe}\end{matrix}\right\rangle\mathrm{CH},$$

was heated with aqueous ethylamine, and gave an excellent yield of 6-*ethylamino*-2-*ethylthiol*-4-*methylpyrimidine*,

$$\mathrm{SEt{\cdot}C}\left\langle\begin{matrix}\mathrm{N{:}C(NHEt)}\\ \mathrm{N{-\!-\!-}CMe}\end{matrix}\right\rangle\mathrm{CH},$$

colourless, pointed prisms, m. p. 70°. Boiling with hydrochloric acid converted this into 6-*ethylamino*-4-*methyl*-2 : 3-*dihydro*-2-*pyrimidone*, $\mathrm{CO}\left\langle\begin{matrix}\mathrm{N{:}C(NHEt)}\\ \mathrm{NH{-\!-\!-}CMe}\end{matrix}\right\rangle\mathrm{CH}$, acicular prisms, m. p. 245—250° (decomp.) (*hydrochloride*, colourless, diamond-shaped plates, m. p. 214—215°); this gave 5-*nitro*-6-*ethylamino*-4-*methyl*-2 : 3-*dihydro*-2-*pyrimidone*, colourless needles, decomp. 238°, charring at 260—265°, which was very readily reduced by means of freshly precipitated ferrous hydroxide to 5-*amino*-6-*ethylamino*-4-*methyl*-2 : 3-*dihydro*-2-*pyrimidone*, $\mathrm{CO}\left\langle\begin{matrix}\mathrm{N{:}C(NHEt)}\\ \mathrm{NH{-\!-\!-}CMe}\end{matrix}\right\rangle\mathrm{C{\cdot}NH_2}$, clusters of needles. Heating with carbamide converted this into the desired 2 : 8-*dioxy*-6-*methyl*-9-*ethylpurine*,

$CO<\begin{matrix}N:CMe \\ NH-C\end{matrix}>C\!-\!\!-NH$ with $C\!\!\!\searrow\!NEt\cdot CO$, which crystallises in sheaves of needles like tyrosine; it has a pearly lustre, and does not melt at 310°.

E. F. A.

Etherification of *o*-Hydroxyazo-compounds. III. G. CHARRIER and G. FERRERI (*Atti R. Accad. Sci. Torino*, 1913, **48**, 854—872. Compare A., 1912, i, 812; this vol., i, 535).—In the present paper are described nitrates of azo-2-naphthyl ethers. They are obtained by adding an ethereal solution of nitric acid to ethereal solutions of the ethers. They are more stable than the corresponding hydrochlorides (*loc. cit.*), and have a definite m. p., but on cooling after fusion an equimolecular mixture of the corresponding 1-nitro-2-naphthyl ether and the diazonium nitrate is found to have been formed. The constitution of these nitrates is probably that represented by the formula: $C_{10}H_6<\begin{matrix}N:NHAr(ONO_2) \\ OHR(ONO_2)\end{matrix}$.

The nitrate of 1-benzeneazo-2-naphthyl methyl ether, m. p. 67°, has already been described (*loc. cit.*), as has also the corresponding ethyl ether derivative, m. p. 80—81°.

1-o-*Tolueneazo-2-naphthyl methyl ether hydrochloride*, $C_{18}H_{16}ON_2,2HCl$, forms metallic green needles; the *nitrate*, $C_{18}H_{16}ON_2,2HNO_3$, forms large, green, acicular crystals, m. p. 71° (decomp.). The *nitrate* of the ethyl ether, $C_{19}H_{18}ON_2,2HNO_3$, crystallises in cantharides-green laminæ, m. p. 62—63° (decomp.).

The *nitrate* of 1-m-*tolueneazo-2-naphthyl methyl ether*, $C_{18}H_{16}ON_2,2HNO_3$, forms cantharides-green leaflets, m. p. 72° (decomp.). The *nitrate* of the ethyl ether, $C_{19}H_{18}ON_2,2HNO_3$, m. p. 84° (decomp.), crystallises similarly.

1-p-*Tolueneazo-2-naphthyl methyl ether hydrochloride*, $C_{18}H_{16}ON_2,2HCl$, crystallises in red needles having a golden lustre. The *hydrobromide*, $C_{18}H_{16}ON_2,2HBr$, forms metallic green needles. The *nitrate*, $C_{18}H_{16}ON_2,2HNO_3$, m. p. 77° (decomp.), forms dark red needles with a green metallic lustre. The *nitrate* of the ethyl ether, $C_{19}H_{18}ON_2,2HNO_3$, m. p. 94° (decomp.), crystallises in garnet-red leaflets, which have a golden lustre.

1-o-4-*Xyleneazo-2-naphthol*, $C_{18}H_{16}ON_2$, crystallises in cherry-red needles with a golden lustre, and has m. p. 146°; it dissolves in concentrated sulphuric acid, giving an intense red coloration. The *methyl ether*, $C_{19}H_{18}ON_2$, forms red, prismatic leaflets, m. p. 106°. The *hydrochloride* of the methyl ether, $C_{19}H_{18}ON_2,2HCl$, forms red needles having a golden lustre. The *hydrobromide*, $C_{19}H_{18}ON_2,2HBr$, crystallises in garnet-red needles. The *nitrate*, $C_{19}H_{18}ON_2,2HNO_3$, m. p. 87—88° (decomp.), crystallises in coffee-coloured scales, which have a golden lustre. The *ethyl ether*, $C_{20}H_{20}ON_2$, m. p. 94—95°, forms

red needles which have a golden lustre. The *hydrochloride* of the ethyl ether, $C_{20}H_{20}ON_2,2HCl$, crystallises in metallic, coffee-coloured needles. The *hydrobromide*, $C_{20}H_{20}ON_2,2HBr$, forms red needles.

1-m-4-*Xyleneazo-2-naphthyl methyl ether*, $C_{19}H_{18}ON_2$, m. p. 72—73°, crystallises in garnet-red, prismatic leaflets, which have a violet lustre. The *hydrochloride*, $C_{19}H_{18}ON_2,2HCl$, and the *hydrobromide*,

$$C_{19}H_{18}ON_2,2HBr,$$

crystallise in microscopic, red needles. The *nitrate*, $C_{19}H_{18}ON_2,2HNO_3$, forms cantharides-green needles, m. p. 83° (decomp.). 1-m-4-*Xyleneazo-2-naphthylamine*, $C_{18}H_{17}N_3$, crystallises in orange-red leaflets, m. p. 128°; it dissolves in concentrated sulphuric acid, giving a reddish-violet coloration. 1-m-4-*Xyleneazo-2-naphthyl ethyl ether*, $C_{20}H_{20}ON_2$ forms garnet-coloured needles, m. p. 47°. The *hydrochloride*,

$$C_{20}H_{20}ON_2,2HCl,$$

forms coffee-coloured needles, and the *hydrobromide*, $C_{20}H_{20}ON_2,2HBr$, crystallises in garnet-red needles. The *nitrate*, $C_{20}H_{20}ON_2,2HNO_3$, forms cantharides-green needles, m. p. 82°.

1-p-*Xyleneazo-2-naphthyl methyl ether*, $C_{19}H_{18}ON_2$, crystallises in garnet-red, prismatic tablets, m. p. 91—92°. The *hydrochloride*, $C_{19}H_{18}ON_2,2HCl$, forms garnet-red needles, and the *hydrobromide*, $C_{19}H_{18}ON_2,2HBr$, forms coffee-coloured needles. The *nitrate*,

$$C_{19}H_{18}ON_2,2HNO_3,$$

crystallises in cantharides-green laminæ, m. p. 75° (decomp.). The *ethyl ether*, $C_{20}H_{20}ON_2$, crystallises in aggregates of red laminæ, or in needles, m. p. 61—62°. The *hydrochloride*, $C_{20}H_{20}ON_2,2HCl$, forms copper-coloured needles, as does also the *hydrobromide*,

$$C_{20}H_{20}ON_2,2HBr.$$

The *nitrate*, $C_{20}H_{20}ON_2,2HNO_3$, forms dark red, prismatic laminæ, m. p. 71° (decomp.).

The *hydrochloride* of 1-α-naphthaleneazo-2-naphthyl methyl ether, $C_{21}H_{16}ON_2,2HCl$, crystallises in bluish-violet needles, and the hydrobromide, $C_{21}H_{16}ON_2,2HBr$, forms iridescent, greenish-brown needles.

R. V. S.

Formation of the Azo- and Bisazo-phenols. GIACOMO PONZIO (*Gazzetta*, 1913, **43**, i, 559—562).—Azo- and bisazo-phenols can be prepared very conveniently by keeping benzenediazonium acetate for a short time. If the solution prepared by diazotising 9·3 grams of aniline in the presence of 20 c.c. of hydrochloric acid (D 1·19) is treated with 25 grams of sodium acetate and diluted to a volume of 5 litres, *p*-benzeneazophenol is deposited after keeping for twenty-four hours at the ordinary temperature. The substance forms yellow leaflets, m. p. 154°, although in the literature the m. p. 148° is usually given. Both its acetate and its benzoate exhibit chromoisomerism, for they exist in red and in yellow forms. If phenol is added to the above solution an immediate precipitate of the azo-compound occurs, so that its spontaneous production when the solution is kept is due to interaction of the diazo-compound with phenol which is slowly formed from it.

If the above-mentioned solution is diluted to a volume of only

500 c.c., 2 : 4-bisbenzeneazophenol is rapidly deposited by it. In the same way, the corresponding bisazocresol, as well as the azocresol, can be obtained from *o*-toluidine. R. V. S.

Polyazoxy-compounds. II. ANGELO ANGELI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 844—850. Compare this vol., i, 658).—The present paper deals with bisazoxybenzene, previously described (*loc. cit.*). On reduction with aluminium amalgam it yields bisazobenzene (Mills, T., 1895, **67**, 929). By the action of concentrated sulphuric acid at 100°, bisazoxybenzene yields benzeneazobenzeneazophenol (*loc. cit.*), which is identical with that obtained by diazotising aminoazobenzene and treating the product with phenol. This derivative yields an *ethyl ether*, $C_{20}H_{18}ON_4$, which crystallises in red laminæ, melting to a turbid liquid at 138°, becoming then viscous and subsequently limpid again at about 210°. When bisazoxybenzene is treated with concentrated sulphuric acid for some hours at 0°, three substances are formed: (1) a substance, $C_{18}H_{14}O_2N_4$, which forms ruby-red crystals, m. p. 203°; (2) a substance, $C_{18}H_{14}O_2N_4$, which crystallises in shining, orange-yellow laminæ, m. p. 168°; and (3) a substance,

$$C_{18}H_{14}O_2N_4,$$

crystallising in deep orange-yellow laminæ, m. p. 148°. The first-mentioned compound (m. p. 203°) is soluble in alkalis and yields a *benzoyl* derivative, $C_{25}H_{18}O_3N_4$ (yellow crystals, m. p. 178°) and an *ethyl* derivative, $C_{20}H_{18}O_2N_4$ (orange-coloured prisms, m. p. 142°, forming a turbid liquid which becomes clear about 180°). The compound of m. p. 168° yields bisazobenzene on reduction, and gives a small quantity of a polybromo-derivative when heated with bromine; it is an isomeride of the bisazoxybenzene of m. p. 155°

$$[Ph\cdot N\colon NO\cdot C_6H_4\cdot NO\colon NPh,$$

termed the *β*-form], and is assigned the formula

$$Ph\cdot NO\colon N\cdot C_6H_4\cdot N\colon NOPh$$

(*α*-form). The compound of m. p. 148° is probably a third isomeride (*γ*-form), to which the constitution $Ph\cdot NO\colon N\cdot C_6H_4\cdot NO\colon NPh$ is ascribed. R. V. S.

Colloidal Chemical Studies on the Proteins. HUGO ROHONYI (*Biochem. Zeitsch.*, 1913, **53**, 179—209).—Solutions of proteoclastic ferments possess the property of precipitating proteins and albumoses from their solutions under certain conditions. The latter are as follows: (1) The solutions should contain at the most only traces of neutral salts, as the precipitates are soluble in salt solutions; (2) as the precipitates are soluble in acids and alkalis, precipitation only takes place within narrow limits of the hydrogen-ion concentration; (3) the reacting substances must be present in certain definite proportions, as the precipitates are often soluble in excess of either reagent. The reactions can take place even after activation of the ferment, and the precipitates are probably complexes of the protein and ferment. If acid is added to protein solutions, and the conductivity curve is plotted, the formation of precipitates causes no discontinuity in the curve. The combination of acids with proteins depends there-

fore on the absolute amount of protein present, and is independent of the surface of the latter. Paranuclein is not a product of hydrolysis, but a caseinogen-caseose complex. The paranuclein of Brailsford Robertson is a complex compound of caseose and a protein contained in Grübler's pepsin preparation. It is not formed when certain other preparations of pepsin are employed. Reasons are given for supposing that the so-called plasteins are complex albumose-enzyme compounds.

S. B. S.

The Precipitation of Egg-Albumin by Ammonium Sulphate. The Theory of the "Salting Out" of Proteins. HARRIETTE CHICK and CHARLES J. MARTIN (*Biochem. J.*, 1913, **7**, 380—398).—The precipitation of egg-albumin by ammonium sulphate is, as Spiro showed for sodium sulphate and caseinogen and gelatin, due to the separation of the system into a protein-rich phase and a watery phase, and is to a certain extent analogous to the salting out of alcohol. The first effect of concentrated salt is to withdraw water from the protein aggregates; a surface tension is in consequence developed at the interfaces, which causes the protein particles to aggregate, thus dividing the system into two distinct phases (precipitate and filtrate). The various factors which influence the precipitation are discussed at length; a dominating influence is the concentration of hydrogen ions.

W. D. H.

The Molecular Weight of Hæmin. HANS FISCHER and AMANDUS HAHN (*Ber.*, 1913, **46**, 2308—2309).—Ebullioscopic measurements in pyridine solution indicate for hæmin a molecular weight of 651, and therefore a molecular formula $C_{34}H_{32}O_4N_4FeCl$; the trustworthiness of the method is confirmed by numbers indicating the molecular weight 655 for the complex iron salt of mesoporphyrin,

$$C_{34}H_{36}O_4N_4FeCl.$$

The solution of free haematoporphyrin in pyridine appears to be colloidal, for the elevation in the b. p. of the solvent is so slight as to indicate a molecular weight over 3000 (compare Piloty and Dormann, A., 1912, i, 519).

D. F. T.

Hæmatin. III. Chemistry of the Formation of Hæmatoporphyrin. WILLIAM KÜSTER and PAUL DEIHLE (*Zeitsch. physiol. Chem.*, 1913, **86**, 51—76. Compare A., 1912, i, 670).—The age of hæmin preparations makes a considerable difference in their behaviour towards hydrogen bromide. Whereas freshly prepared hæmin yields almost exclusively hæmatoporphyrin and ferric iron, old hæmin preparations give both ferrous and ferric iron and much by-product. The changes in hæmin on keeping obviously take place at the centres which play a part in the formation of hæmatoporphyrin; these are considered to be the vinyl groups.

Hæmatoporphyrin is very readily esterified with methyl alcohol and hydrogen chloride. The product is a dimethyl derivative, insoluble in sodium carbonate, m. p. 142°, proving that the two carboxyl groups were present in hæmin, whereas the hydroxyl groups were formed

during the formation of hæmatoporphyrin. The ester is readily hydrolysed by sodium hydroxide.

A tetramethyl hæmatoporphyrin is obtained on prolonged heating with methyl alcohol and hydrogen chloride; the non-crystalline product has m. p. 81°.

A tetramethyl derivative is also obtained when the intermediate product formed by the action of hydrogen bromide in acetic acid on hæmin is warmed with anhydrous methyl alcohol. This substance, *methyl dimethoxydihydrohaematerindicarboxylate,* forms large crystals, m. p. 128°.

On hydrolysis the tetramethyl derivative forms *haematoporphyrin dimethyl ether*, a bright scarlet, amorphous powder, m. p. 105°, soluble in alkali; the *hydrochloride* is crystalline, forming needles; the *zinc* salt is bright red, and blackens at 100°. When esterified, it yields the original tetramethyl compound again.

A further argument against the assumption that hæmin contains, as supposed by Piloty, lactam junctions is afforded by the discovery of a dimethoxydihydrohæmin amongst the products of the action of methyl alcohol on the above intermediate product.

Hæmatoporphyrin forms a silver salt containing two atoms of metal; its dimethyl ether forms one with three atoms of metal; both compounds fix three molecules of ammonia. Hæmatoporphyrin forms a stable dihydrochloride, whereas the hydrochloride of the dimethyl ether is very unstable, and that of the dimethyl ester could not be prepared. This behaviour indicates betaine formation between the nitrogen and the methyl group of the ester, and to a less extent the methyl group of the dimethyl ether. Prolonged action of concentrated hydrochloric acid displaces one of the methyl groups, forming a monomethyl ether, which, however, has a stable monohydrochloride.

The *dimethyl* ester of *anhydrohaematoporphyrin* forms an intense scarlet, bulky powder, m. p. 140—141°. E. F. A.

Hæmatin. V. Methylation of Hæmin and the Addition of Bromine to Chlorodimethylhæmin and Bromodimethylhæmin. WILLIAM KÜSTER and ALFRED GREINER (*Zeitsch. physiol. Chem.*, 1913, **86**, 185—205).—Dimethylhæmin is the dimethyl ester of the dibasic acid hæmin. Reasons are discussed for attributing a different degree of acidity to the two carboxyl groups, particularly the behaviour of hæmin to methyl sulphate. In strongly alkaline solution there is no action, in weak alkali a monomethyl derivative is formed, whereas in acid solution dimethylhæmin is formed without difficulty; it is identical with the product produced by means of methyl alcohol and hydrogen chloride. The monomethyl derivatives from hæmatin and dehydrochlorohæmin did not crystallise.

When bromine in chloroform solution acts on dimethylhæmin, bromine is absorbed without the liberation of hydrogen bromide; more or less of the chlorine of the hæmin is replaced by bromine, so that a complex mixture results. In acetic acid solution, however, a chlorodimethylhæmin dibromide is obtained. Very little of a tetrabromo-product is formed. In a similar manner, bromodimethylhæmin dibromide is formed. It can be crystallised from acetic acid.

No methyl is eliminated by the action of aniline on dimethylhæmin. The dimethyl dehydrochlorohæmin so obtained is partly soluble in ether; the two portions differ in the amount of chlorine they contain. When converted into the corresponding bromodimethylhæmins, compounds which differ in their crystalline habit are obtained. Aniline reconverts both of these into dehydrobromo-products which are soluble and insoluble in ether respectively.

Bromine may be eliminated from hæmin dibromide by means of aqueous alkali, sodium methoxide, or by zinc and acetic acid. On oxidation one molecule of the dibromide yields two molecules of hæmatic acid. The conclusion is drawn that the addition of bromine takes place at the vinyl residues.

The complex $C_{32}H_{34}N_4$ is termed *haematerin*, and its dicarboxylic acid, $C_{34}H_{34}O_4N_4$, *haematerindicarboxylic acid*. Hæmin, bromohæmin, and hæmatin are thus complex chloro-, bromo- and hydroxy-ferric salts, of this acid. E. F. A.

Tetrachloromesoporphyrin. HANS FISCHER and HEINRICH RÖSE (*Ber.*, 1913, **46**, 2460—2466).—On the cautious addition of fuming hydrochloric acid and hydrogen peroxide to mesoporphyrin dissolved in glacial acetic acid, the hydrochloride of a dye crystallising in green needles is obtained. This is *tetrachloromesoporphyrin*, chlorine being substituted for hydrogen in the four methine groups uniting the pyrrole nuclei in pairs. On reduction of the tetrachloro-compound with sodium amalgam, porphyrinogen is obtained, whereas mesoporphyrin results on heating with sodium methoxide at 220—230°. The green compound is also formed when chlorine is passed into a solution of mesoporphyrin in acetic acid. Reduction with acetic acid and hydrogen iodide converts it into mesoporphyrin again and not into porphyrinogen. One of the chlorine atoms is much less firmly held than the others.
E. F. A.

Chondroitin-sulphuric Acid. PHŒBUS A. LEVENE and FREDERICK B. LA FORGE (*J. Biol. Chem.*, 1913, **15**, 69—79).—Chondrosine, the nucleus of chondroitin-sulphuric acid, when hydrolysed by means of sodium amalgam yields glycuronic acid, identified by the phenyl- and *p*-bromophenyl-hydrazine derivatives.

The glycuronic acid is not bound to the amino-group of the second component, since the nitrous acid process demonstrates the presence of an unsubstituted amino-group in chondrosine. Neither does the carbonyl group of glycuronic acid take part in the linking. On oxidation of chondrosine with nitric acid a product is obtained which on distillation with hydrochloric acid gives rise to a minimal quantity of furfuraldehyde, whilst chondrosine yields the quantity required by a complex composed of one molecule of glycuronic acid and one of a carbohydrate of about the same molecular weight. The oxidation product does not contain free saccharic acid until it has been hydrolysed with alkali. Hence chondrosine contains saccharic acid

in a conjugated form. In chondroitin-sulphuric acid both the carboxyl and the amino-groups are combined with other radicles.

E. F. A.

Identity of Rennet, Casease, and Trypsin from the Same Latex. Existence of Two Types of Vegetable Proteolytic Ferments. C. GERBER (*Compt. rend.*, 1913, **157**, 241—243. Compare A., 1907, i, 1100; 1908, i, 745; 1909, i, 74, 278; ii, 512, 824; 1910, ii, 64; 1911, ii, 647; 1912, ii, 801; this vol., i, 806).—Rennet, casease, and trypsin obtained from the same latex exhibit the same resistance to heat, and their diastatic actions are influenced in the same manner by certain electrolytes and by certain substances, such as lactalbumin and lactoglobulin, which accompany the substances on which they act. A study of these enzymes obtained from *Ficus carica* and *Broussonetia papyrifera* shows further that their diastatic actions obey the same laws of mass, time, and temperature, and their variations in intensity, seasonal for the same plant or individual for the same period, are strictly parallel. From these results the author maintains that rennet, casease, and trypsin from the same latex are but three different or successive aspects of the same diastase, coagulating the milk and carrying the hydrolysis of the casein and the fibrin to the formation of amino-acids. The characteristics distinguishing the three proteolytic actions of the latex are due to differences in the action of calcifying and decalcifying salts, acids, and bases on the coagulation and diastatic digestion of milk. The proteolytic ferments of the latex belong to two groups, the one having for type the proteolytic disastase of *Ficus carica* and the other that of *Broussonetia papyrifera*, the former being inactive towards milk, whilst the latter are active.

W. G.

Action of Hydrogen Chloride on a Diastase Preparation which had been Altered by Heating. IX. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1913, **86**, 322—339).—A diastase preparation of which the activity had been destroyed by heating was rendered slightly active again by treatment with dry hydrogen chloride and subsequently removing this in a vacuum. It is considered that the original active groups in the enzyme have not been restored by the acid, but that this has attacked other atomic groupings, which become active as enzymes when the hydrogen chloride is removed.

E. F. A.

Identity of the Hydrolytic and the Synthetic Activities of Emulsin. ÉMILE BOURQUELOT and MARC BRIDEL (*J. Pharm. Chim.* 1913, [vii], **8**, 15—19).—Emulsin hydrolyses the β-glucosides of the alcohols and causes the combination of dextrose with the alcohol to a β-glucoside. Both these reactions are incomplete, and there is a tendency to attain an equilibrium. The position of this equilibrium is independent of the quantity of emulsin added and of the temperature, but it varies with the strength of the alcohol and with the amount of

dextrose present. It is shown experimentally that in a solution containing 30·2% by weight of methyl alcohol, and equivalent quantities of dextrose or β-glucoside together with emulsin, the rates of hydrolysis and synthesis are the same, and the same point of equilibrium is reached from both directions. The probability of emulsin acting synthetically in plants is emphasised. E. F. A.

Reversibility of Enzyme Action: α-Glucosidase and α-Methylglucoside. ÉMILE BOURQUELOT and ÉMILE VERDON (*J. Pharm. Chim.*, 1913, [vii], **8**, 19—21).—Bottom yeast extract was allowed to act in solutions containing 20 grams per 100 c.c. of methyl alcohol and equivalent quantities of dextrose or α-methylglucoside. In about twenty-nine days both solutions had the same rotatory power, indicating that the same equilibrium is attained starting from either end. E. F. A.

The Rennin Coagulation of Milk from a Colloid Chemical Standpoint. JEROME ALEXANDER (*Eighth Inter. Cong. App. Chem.*, 1912, **6**, 12—14).—Silver nitrate gives a clear silver chloride sol in presence of fresh lactalbumin, but, after digestion with pepsin, lactalbumin does not exert the influence of a protective colloid. The action of acids or rennin on milk is thus to destroy the colloidal protection of the lactalbumin for the unstable, irreversible suspensoid, casein (compare A., 1910, i, 530). J. C. W.

New Function of the Catalyst termed "Peroxydase" and the Biochemical Transformation of Orcinol into Orcein. JULES WOLFF (*Eighth Inter. Cong. App. Chem.*, 1912, **26**, 417—419. Compare A., 1912, i, 928).—Experiments are described which show that dilute solutions of orcinol are slowly oxidised by ammonia with production of orcein. This action is greatly accelerated by peroxydase, the effect of which is to promote the formation of the colouring matter rather than to increase the amount of oxygen absorbed. E. G.

The Catalase of the Liver. LEONOR MICHAELIS and H. PECHSTEIN (*Biochem. Zeitsch*, 1913, **53**, 320—355).—The ferment solution employed was a highlydiluted extract of calves' liver, and hydrogen peroxide was used as the substrate. The course of the action was followed by determining the rate of destruction of the peroxide by titration with permanganate solution. It was found that for the catalase reaction, the ordinary equation $\Phi.t = f(x)$, where Φ is the quantity of the ferment, $t =$ time of action, and $f(x)$ a characteristic function of the ferment, does not hold, but must be replaced by the equation $\Phi^n.t = fx$, in which n is of the approximate value of 1·35, but varies slightly during the course of the reaction. The deviation from the ordinary law is due to the fact that the ferment is acted on by the hydrogen peroxide, as its action is weakened by previous treatment with this reagent. Oxygen itself does not act, and the same results are obtained when the reaction is carried out in a current of hydrogen

or in a corked flask. As determined by the wandering of the ferment in an electrical field, where the [H]˙ concentration was varied by different acetate mixtures, the isoelectric point of the ferment was found to be $4{\cdot}31.10^{-6}$. The rate of ferment action was determined in low salt concentrations (acetate mixtures) with varying hydrogen-ion concentrations. By the graphical methods already employed by Michaelis and his pupils, the amounts of ferment active in solutions of different hydrogen-ion concentrations were determined. The optimal condition of action is attained just after the hydrogen-ion concentration becomes less than the isoelectric point of the ferment. The conclusions drawn are, that catalase is an ampholyte with the acid dissociation constant $2{\cdot}88 \times 10^{-5}$, and that the catalytic action on hydrogen peroxide is due to the anions and electrically neutral particles. Neutral salts inhibit the action (hence all the experiments on the effect of the [H]˙ concentration were carried out with very dilute acetate mixtures). The inhibitory action is more marked in the neighbourhood of the isoelectric point than in more acid solutions. The conclusion is drawn that the anions of the salt exert the chief action, and affect chiefly the electrically neutral particles of the ferment. The order of the inhibitory action is $SO_4 > Cl >$ acetate $> NO_3$. S. B. S.

Constitution of the Mercuriated Products of Acetylene. WILHELM MANCHOT and JULIUS HAAS (*Annalen*, 1913, **399**, 123—154).—Phenylacetylene and an excess of aqueous mercuric chloride at 47—50° yield a *substance*, $C_{16}H_{11}O_2Cl_5Hg_5$ or $C_{16}H_{13}O_3Cl_5Hg_5$, in which the mercury is very firmly held. It does not react with aqueous sodium hydroxide or ammonia, but yields mercuric sulphide by treatment with ammonium sulphide. By treatment with dilute hydrochloric acid, it yields phenylacetylene and acetophenone. This decomposition indicates that the substance is an additive compound of an acetylene, not a mercuriated ketone, and consequently the constitution may be $Hg(C{:}CPh)_2,2HgCl_2,HgO,HgCl{\cdot}OH$, which is supported by the fact that the same substance is produced by the action of an excess of aqueous mercuric chloride on mercury phenylacetylide in the presence of a little hydrochloric acid at 50°.

A similar *substance*, $C_{16}H_{10}OBr_4Hg_4$, is produced by the interaction of phenylacetylene and aqueous mercuric bromide at 50°. It also does not react with sodium hydroxide or ammonia, yields mercuric sulphide by treatment with ammonium sulphide, and is decomposed by hydrochloric acid to form acetophenone and phenylacetylene. Probably, therefore, its constitution is $Hg(C{:}CPh)_2,2HgBr_2,HgO$. Both of these substances, suspended in chloroform in a freezing mixture, absorb a large amount of bromine; ultimately, however, hydrogen bromide is evolved.

Piperonylacetylene reacts with mercuric chloride and bromide to form substances which are analogous to the preceding, but which yield only acetopiperone by treatment with hydrochloric acid. This is due to the fact that the piperonylacetylene which is initially formed unites with water with extraordinary ease in the presence of hydrochloric acid.

Since the preceding substances are additive compounds of acetylenes,

it is probable that the substance obtained by the action of acetylene itself on aqueous mercuric chloride is an additive compound, not a mercuriated aldehyde, $C(HgCl)_3 \cdot CHO$, as suggested by Biltz and Mumm. The latter view is almost certainly incorrect, because the substance exhibits the reactions of mercurous and of mercuric salts. The substance, which is also obtained from mercury acetylide and aqueous mercuric chloride, yields only acetaldehyde by treatment with dilute hydrochloric acid, but is decomposed by ammonium sulphide to form acetylene and acetaldehyde. Probably, therefore, its constitution is $C_2Hg,HgCl_2,HgCl,H_2O$. A substance, exhibiting properties similar to those of the preceding substance is obtained from acetylene or mercury acetylide and an excess of aqueous mercuric bromide.

It is evident from the behaviour of the preceding mercury compounds that mercury can be retained very firmly in an organic compound without necessarily being attached to carbon in the place of hydrogen atoms. C. S.

Physiological Chemistry

A Calorimeter for Small Animals. FRANZ TANGL (*Biochem. Zeitsch.*, 1913, **53**, 21—35).—The calorimeter is constructed on the compensation principle. Two exactly similar cylinders of copper, each insulated in a Dewar flask, are connected with one another by constantan wires, so as to form thermoelectric couples, and a Broca galvanometer is placed in circuit between the two, so as to indicate any differences of temperature between them. The whole apparatus is immersed in a large thermostat. The animal is placed in one cylinder in a cage, and the other cylinder contains a similar cage without an animal. The heat produced by the animal in one cylinder is approximately compensated for by the passage of a known electric current through the other, which produces an experimentally measurable quantity of heat. The small differences of heat in the two cylinders can be measured by the deflexions produced when the galvanometer is thrown into the circuit. The galvanometer deflexions can be calibrated by passing two measured but slightly different currents through the two cylinders. The total heat produced by the animal is therefore calculated both from the compensation current and the galvanometer readings; the calorimeter can also serve as a respiration calorimeter, by the analysis and measurement of the air led in (which is first carefully warmed to the temperature of the thermostat by a long passage through pipes immersed in the water it contains), and the analysis of the expired air, in the usual manner adapted for such calorimeters. Illustrations in the text indicate the exact method of construction of the apparatus (compare A. V. and Miss Hill, this vol., i, 666). S. B. S.

The Response of the Respiratory Centre to Carbon Dioxide, Oxygen, and Hydrogen Ion Concentration. J. M. H. CAMPBELL, CLAUDE E. DOUGLAS, JOHN S. HALDANE, and F. G. HOBSON (*J. Physiol.*, 1913, **46**, 301—318).—A rise of 0·2% or 1·6 mm. in the pressure of carbon dioxide in the alveolar air doubles the pulmonary ventilation. A corresponding diminution causes apnœa. The alveolar oxygen pressure can be varied within wide limits without affecting the excitability of the respiratory centre to carbon dioxide. Summation of inhibitory vagus stimuli plays no part in causing apnœa in man. What the respiratory centre really responds to is the balance of hydrogen ion concentration in the blood. This balance is exquisitely regulated, probably for the most part by the kidneys. W. D. H.

Respiratory Mechanism in the Duck. J. B. ORR and ALEXANDER WATSON (*J. Physiol.*, 1913, **46**, 337—348).—In the duck, carbon dioxide in the inspired air acts inhibitingly on respiration. Lack of oxygen is stimulating to the respiratory rhythm. The vagus nerves probably play an essential part in the maintenance of respiratory movements. W. D. H.

The Influence of the Cerebrum on the Metabolism of Energy and of Matter. KARL HANNEMANN (*Biochem. Zeitsch.*, 1913, **53**, 80—99).—The experiments were carried out on frogs, the respiratory exchanges of which were measured in chambers made according to a method described in the text, from ordinary laboratory desiccators. These exchanges were measured in the cases of intact animals, and animals from which different parts of the brain had been extirpated. It was found that the extirpation of either the whole brain, or only the large hemispheres, or the optic lobe led to a considerable increase in the gaseous exchange, lasting for several days. Both the oxygen consumption and the carbon dioxide output were increased, especially the latter, which was not so much increased, however, when only the hemispheres were removed. The increase in the gaseous exchanges is accompanied by an increased heat production, which was measured in a Tangl calorimeter. S. B. S.

The Influence of Narcosis on the Gaseous Metabolism of the Brain. FRANZ G. ALEXANDER and STEPHAN CSERNA (*Biochem. Zeitsch.*, 1913, **53**, 100—115).—Dogs were used for the purpose of the experiments. They were tracheotomised under ether narcosis, hiradin was injected into the jugular vein and the femoral artery, and the sinus longitudinales was laid bare for the purpose of collecting blood samples. By means of blood-gas analyses, the gaseous metabolism could be determined when the animal had recovered from narcosis, and when it was under the influence of various anæsthetics. The rate of blood-flow was measured by Barcroft's method. It was found that the specific gaseous exchanges of the blood were considerable, the oxygen consumption of this organ being about 0·36 c.c. per gram per minute. During

narcosis the gaseous metabolism sinks considerably—from 60 to 90% according to depth of the narcosis. With ether, the carbon dioxide output diminishes less than the oxygen consumption; the reverse is the case in morphine narcosis. The action of various narcotics is different, and this fact must be taken into account in all theories dealing with the phenomenon. In narcosis with magnesium sulphate, the higher centres of the nervous system are the last to be paralysed. The actual narcosis is preceded by a stage of excitation, during which the gaseous metabolism of the brain is increased. S. B. S.

Blood-lipoids and Phagocytosis. B. STUBER (*Biochem. Zeitsch.*, 1913, **53**, 493—500).—The addition of cholesteryl esters of oleic and palmitic acids inhibits phagocytosis *in vitro*, and with the latter substance also *in vivo*, when the blood is withdrawn (from cats) half an hour after the injection. Owing to the rapidity with which clot formation takes place, experiments could not be extended beyond this period, and for the same reason no *in vivo* experiments were possible with the oleic acid derivative, which very readily renders the blood so clottable that it clots directly on opening the veins. The inhibition is not removed by mixing the cholesterol derivatives with lecithin, as is the case with free cholesterol. Cholesteryl benzoate and acetate are without action on phagocytosis, in which substances the free hydroxyl group no longer exists, and to this group is ascribed the inhibitory action of cholesterol and its derivatives on phagocytosis. Wright's theory of opsonins is discussed, and it is suggested that the opsonic index is not due to specific opsonins, but rather to the different states of the lipoids in the blood. S. B. S.

The Effect of Fatty Acids and Soaps on Phagocytosis HARTOG J. HAMBURGER and J. DE HAAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 1290—1297).—Propionic acid itself diminishes phagocytic action (as determined by Hamburger's charcoal method), whereas sodium propionate increases it, within wide limits of concentration of the salt. The former action is to be ascribed to the hydrogen ions, whereas the latter action is due to the action of the salt on the surface tension of the water. This constant is diminished, and this facilitates the pseudopodial action of the phagocytes. This action of sodium propionate and soaps is to be distinguished from the action of fat-dissolving substances, which exert their action owing to the fact that they dissolve in lipoids. S. B. S.

The Blood of Ascidians. III. MARTIN HENZE (*Zeitsch. physiol. Chem.*, 1913, **86**, 340—344).—The author's previous work has shown that organic vanadium compounds occur in the blood-corpuscles of Phallusia, and that these cells have an acid reaction due to sulphuric acid. It is now shown that vanadium also occurs in the blood of other ascidians (*A. mentula*, *A. fumigata*, *Ciona intestinalis*, and *Diazonia violacea*); in *Cynthia papillosa* its presence is uncertain.

Much of the present paper deals with the kinds of blood-corpuscle found, and their reactions with staining fluids. The nature of the pigment in the red cells of *Ascidia mentula* is uncertain; it is not a lipoid, and is insoluble in all common reagents.
W. D. H.

The Application of the Second Law of Thermodynamics to Processes in the Animal Organism. JULIUS BÁRON and MICHAEL PÓLÁNYI (*Biochem. Zeitsch.*, 1913, **53**, 1—20).—A knowledge of the changes of free energy in the animal organism can be arrived at by the application of Nernst's heat theorem. These changes of free energy were calculated for the individual products taking part in metabolism. It was found that the changes correspond very nearly with the heat production. The results indicate that the processes in the organism take place in accordance with the second law of thermodynamics only when the organism does not work with absorption of heat. The thermodynamical efficiency of mechanical work and of fat synthesis from sugar was calculated, and the trustworthiness of the theory from the point of view of the second law was confirmed.
S. B. S.

The Influence of the Character of the Nutrition on the Metabolism During a Succeeding Period of Starvation. ARTHUR SCHLOSSMANN and HANS MURSCHHAUSER (*Biochem. Zeitsch.*, 1913, **53**, 265—299).—Dogs were starved for some days, and then fed with different diets, in one case containing large amounts of fats, in another large amounts of carbohydrates, and in a third case, chiefly proteins. When the animals had attained their original weights again on these diets, a short period of starvation was interposed, during which the metabolism was investigated by the ordinary methods. As a result of these and earlier experiments, the conclusion was drawn that the metabolism during a period of starvation in both man and dogs depends to a large extent on the character of the nutrition ingested in the foregoing period, and this influence can be demonstrated even when the effects of the last meal taken have vanished. The organism has got accustomed to the utilisation of either fats, carbohydrates, and proteins, and the habit thus acquired still lasts even when the animal is deprived of food. This influence is demonstrated chiefly by the respiratory quotients, which remain similar during starvation to those obtained during the period of feeding. The influence of the fat diet lasts longer than that of the carbohydrate diet, as the reserve glycogen is soon used up. Thus, in the case of the dog fed on fats, on the fifth as well as on the second day of starvation about 90% of the calories are derived from the fat, and 3% from carbohydrates. In the case of the carbohydrate-fed dog, on the second day of starvation 21% of the calories are derived from carbohydrates, and 65% from fats; and on the fifth day, only 8% from carbohydrates and 79% from fats. The organism can therefore be "trained" to adapt itself to various diets.
S. B. S.

The Action of Carbohydrates on the Energy Metabolism. Paul Hári (*Biochem. Zeitsch.*, 1913, **53**, 116—139).—The experiments were carried out with the employment of the Tangl respiration calorimeter, and both the heat production and the nitrogen and carbon metabolism were investigated at the same time. When dextrose was subcutaneously administered to mice in 10% solution, in quantities corresponding with 10 grams per kilo. of body-weight, it caused a rise in the heat production of 8—13·2%. In quantities of 28—32 grams per kilo. of body-weight, when administered to starving rats, it caused a rise of 28—29·9%. This rise can be partly explained as a result of sugar intoxication. The heat thus produced is chiefly lost by radiation when the sugar is administered in concentrated solutions, but chiefly by water evaporation when given in dilute solution. S. B. S.

The Biochemical Synthesis of the Fatty Acids. (Miss) Ida Smedley and (Miss) Eva Lubrzynska (*Biochem. J.*, 1913, **7**, 364—374).—The hypothesis that pyruvic acid formed in the body from carbohydrates is the starting point for the synthesis of the fatty acids, is supported by a number of pieces of evidence, and equations are given to represent the series of reactions which occur W. D. H.

Fatty Acid Esters of Dextrose. W. R. Bloor (*Eighth Inter. Cong. App. Chem.*, 1912, **19**, 29—36).—Attention is called to the fact that fats are not completely metabolised in the absence of carbohydrates, as is witnessed by the fact that such products as β-hydroxybutyric acid, acetoacetic acid, etc., are excreted during starvation. The suggestion is made that sugars may act catalytically in the destruction of the fats in the animal body. It was therefore of interest to prepare dextrose esters of fatty acids and to investigate their action when administered to animals. These esters were prepared by the interaction of the acid chloride on dextrose in pyridine solution, and a preliminary account of several such esters is given. They readily form colloidal solutions with water. For physiological experiment a mixture of the esters prepared from the fatty acids of cocoa-nut oil was employed. When administered to cats by the mouth, these esters are readily absorbed (up to more than 80%). They do not appear to be adapted to administration either intraperitoneally or intravenously. In the former case, they act as an irritant foreign substance, and in the latter case they can act injuriously, even producing death of the animal. S. B. S.

Is Inulin a Glycogen Former? Alfred Oppenheim (*Chem. Zentr.*, 1913, ii, 371; from *Zentr. Physiol.*, 1913, **27**, 264—267).—Rabbits freed from glycogen by injections of strychnine were fed with inulin. Some glycogen was formed in the liver, and a good deal in the muscles. Since feeding with lævulose leads to the formation of glycogen in the liver, it is assumed that most of the inulin administered passes the liver and is converted into glycogen in the muscles. E. F. A.

Action of the Digestive Juices on Alicyclic Compounds. JUHO HÄMALÄINEN (*Chem. Zentr.*, 1913, i, 2052; from *Skand. Arch. Physiol.*, 1913, **29**, 60—67).—When alicyclic compounds are shaken for ten hours at 37° with gastric juice, they become partly hydrated—the hydrocarbons the most easily, and the ketones the least so. Menthene, limonene, terpinolene, pinene, nopinene, and dihydrocarveol give rise to menthanol, terpin, terpineol, etc. Only terpinene and fenchene proved resistant. E. F. A.

Influence of the Melting Point of Non-emulsified Fats on their Rate of Disappearance from the Stomach. A. VON FEJÉR (*Biochem. Zeitsch.*, 1913, **53**, 168—178).—Various fats were mixed with a standard diet and administered to dogs. After a given interval these test-meals were quantitatively removed from the stomachs by a form of stomach-tube, which is described and illustrated in the text, and the fat content of the vomit was then analysed. It was found that the higher the melting point and viscosity of the fat, the more slowly it disappeared from the stomach. The fats, after emulsification with food, disappear more rapidly than when administered in a non-emulsified form. When not administered with foods, these disappear even more slowly still, with the exception of the liquid olive oil. Fats also inhibit the disappearance of the other food constituents from the stomach, and the more viscous fats exert the greater inhibitory action in this respect. A fat added to foods readily separates from other food constituents in the stomach, and is afterwards digested independently of them in the intestine. S. B. S.

The Influence on Nitrogenous Metabolism of Feeding on Sodium Nitrate. ERICH GRAFE and H. WINTZ (*Zeitsch. physiol. Chem.*, 1913, **86**, 283—314).—Experiments on dogs and pigs are recorded with sodium nitrate similar to those previously published in relation to ammonium salts. In one of the four experiments there was no retention of nitrogen; in the other three, from 10—15% of the nitrogen was retained. Large doses exert a toxic action and increase the output of nitrogen. Hypotheses are advanced to explain the retention of nitrogen. W. D. H.

Utilisation of Individual Proteins by Man as Influenced by Repeated Fasting. PAUL E. HOWE and PHILIP B. HAWK (*Eighth Inter. Cong. App. Chem.*, 1912, **19**, 145—147).—The method of experiment was to administer to the same individual after a two days' fast, a standard diet containing 12·12 grams of nitrogen and 2500 cal. of energy. This diet was continued for two days, and was then increased for another two days, so that 18·18 grams of nitrogen and 3750 cal. were taken. Two days' fast then succeeded, and was followed by another five days of feeding with the quantities given above, but with nitrogen from another protein. By alternation of two fast days and five feeding days, in which various proteins were employed, the dietetic values of the latter

could be ascertained. The most efficiently utilised proteins were found to be meat and gliadin, of which 97·5% was absorbed, followed by plasmon, milk, and "standard" diet. The substances most efficient in maintaining a nitrogenous equilibrium (in both cases under the conditions of experiment, positive) were, however, meat and milk. It is noteworthy that in both cases the proteins were of animal origin. S. B. S.

Nuclein Metabolism. MAX DOHRN (*Zeitsch. physiol. Chem.*, 1913, **86**, 130—136).—The results of an experiment in which 10 grams of nucleic acid were consumed in addition to a diet consisting of bread, 300 grams; butter, 80 grams; apples, 250 grams; eggs, 200 grams, and milk, 2 litres, showed that the nitrogen in the form of carbamide is not increased during the nucleic acid period. The nitrogen in uric acid increased 50%, or 9·7% of the nitrogen in purine bases. The rest of the nitrogen as purine bases was not recovered. The phosphoric acid increased considerably, the amount found in the urine and fæces exceeding the amount supplied by 0·76 gram. The results indicate that almost all the nucleic acid underwent cleavage before resorption, and that the slight increase in uric acid is due to resorbed bases. N. H. J. M.

The Action of the Iron in Blood-powder on the Iron Metabolism when this Product is Administered to Animals. JULIUS GRÓH (*Biochem. Zeitsch.*, 1913, **53**, 256—258).—By the addition of blood-powder to a standard diet administered to pigs, no alteration was caused in the iron balance in the animal, the additional iron from the blood ingested being excreted in the fæces. S. B. S.

The Localisation and Detection of Peroxydases in the Digestive Tract. ARTHUR SCHEUNERT, WALTER GRIMMER, and PETER ANDRYEWSKY (*Biochem. Zeitsch.*, 1913, **53**, 300—319).—A trustworthy oxydase reagent is guaiacol tincture, to 100 c.c. of which have been added 0·1—0·2 c.c. of 3% hydrogen peroxide solution. This reagent is capable of detecting an oxydase in milk, saliva, etc., which contain a peroxydase, but not with blood, unless a superoxide solution, such as turpentine oil, ethyl hydroperoxide, etc., is also added. Rothenfusser's reagent (*p*-phenylenediamine +guaiacol) and the potassium iodide-starch reagents are not trustworthy for the detection of oxydases. The extracts of tonsils contain no oxydase, the sublingual glands contain large quantities of the ferment, whereas the submaxillary and parotid glands vary largely as to oxydase content in different animals; the same is true with reference to the mucous membrane of the stomach and the small intestine. Liver extracts are free from substances giving the blue reaction with guaiacum tincture. Furthermore, the ferment giving this reaction is not identical with the ferment causing the oxidation of formic acid, as several tissues give one reaction, but not the other. The guaiacol peroxydase of the submaxillary gland of the ox possesses a considerable but not complete resistance to digestion with trypsin. S. B. S.

Fluorine in the Animal Organism. III. Brain, Glands, Muscles, Blood, Milk, Excretions. ARMAND GAUTIER and PAUL CLAUSMANN (*Compt. rend.*, 1913, **157**, 94—100. Compare this vol., i, 677, 789).—Like phosphorus, fluorine exists in all animal organs and tissues, but in very varying proportions, the dental enamel having the highest content, 180—118 mg. per 100 grams of dry matter, and the muscle the lowest with 0·6—0·15 mg. per 100 grams. There is a fairly constant relation between the phosphorus and fluorine contents of the various organs, except in the case of the incompletely formed organs of young animals, the excretions, the dental enamel, and the blood. The fluorine increases with the phosphorus without being directly proportional to it. In the same organ the quantity of fluorine varies greatly with age. It increases generally up to the adult age, and then diminishes as the organ begins to degenerate. Muscular tissue is remarkably poor in fluorine. The fluorine content of human milk is very low, but, as in the case of phosphorus, it is about four times as great in cow's milk. About 1 mg. of fluorine per day is excreted by man, and since the amount of fluorine supplied by the food greatly exceeds this, the difference must be due to epithelial desquamation, loss of hair, growth of nails, etc. W. G.

The Lipocytic Constant. Content of the Tissues in Phosphorus-containing Lipoids. ANDRÉ MAYER and GEORGES SCHAEFFER (*Compt. rend.*, 1913, **157**, 156—159. Compare this vol., i, 424). —In different individuals of the same species the content of phosphorus in the lipoid form in a given organ is practically constant, but it varies from tissue to tissue in the same animal. For different animal species the values found for a given organ are very close. This phosphorus content of the different organs does not seem to vary during inanition, but rather appears to be the measure of a fundamental and permanent constituent of the cells. In certain cellular types the ratio, fatty acids/phosphorus in lipoid form, is remarkably constant, but in certain organs, for example, the muscles, the ratio has a value pointing to the presence of reserves of neutral fats in these organs. The content of a fresh tissue in phosphorus, in lipoid form, is characteristic of the tissue. In all the species examined the order of the different organs with respect to their phosphorus content relative to their fresh weight is the same, and this indicates that this content is proportional to the physiological activity. W. G.

The Application of Calorimetry to the Measurement of the Work of the Kidneys. FRANZ TANGL (*Biochem. Zeitsch.*, 1913, **53**, 36—40).—The energy metabolism of the kidneys was estimated by determining the heat production of rats placed in a calorimeter both before and after the extirpation of the kidneys. This was found to amount to 8·2% of the whole energy production of the body, and about 0·75 cal. per gram of kidney. This is the same as that found in the dog. Direct calorimetric measurements yield the same results as those obtained by Barcroft's method in the

analysis of the blood gases, and the author's own methods in the measurement of respiratory exchanges in curarised animals.

S. B. S.

The Magnitude of the Work of Diseased Kidneys. STEPHAN CSERNA and G. KELEMEN (*Biochem. Zeitsch.*, 1913, **53**, 41—68).—The respiratory method of Tangl was employed in these researches, the respiratory exchanges of the animal being measured both before and after extirpation of these organs in animals which had been treated with renal poisons. These results were compared with those obtained in the normal (unpoisoned) animals. Dogs were used in the experiments, and the following poisons were employed: uranyl acetate, potassium cantharidate, potassium dichromate. Experiments were also carried out on animals, in which the blood-supply to the kidneys had been ligatured. It was found that the work of the diseased kidneys was greater than that of healthy ones, the oxygen consumption and carbon dioxide production both being larger. Only when the poison had been sufficiently powerful to produce anuria were these factors below normal. When the kidney work is increased, both the absolute and relative carbon dioxide production is greater than normal in diseased kidneys. By injury to the parenchyma of the kidney tissue produced by the stoppage of the circulation, the gaseous metabolism in the other organs is also increased.

S. B. S.

The Magnitude of the Work of the Spleen. FRITZ VERZÁR (*Biochem. Zeitsch.*, 1913, **53**, 69—79).—No alteration can be detected with certainty in the respiratory exchange after extirpation of the spleen of curarised dogs. By the direct measurement of the gaseous exchange in the blood passing through the spleen of cats by Barcroft's method, the oxygen consumption was found to be 0·05 c.c. of oxygen per gram per minute. This is about the same as that of the resting submaxillary gland or anuric kidneys, according to the researches of Barcroft. Dextrose, intravenously injected, and soluble starch are readily burnt up in the body, even after extirpation of the spleen.

S. B. S.

The Changes in the Chemical Constitution of the Animal Body After Extirpation of the Spleen, Testis, and Thyroid. KARL DRÖGE (*Pflüger's Archiv*, 1913, **152**, 437—477).—The experiments were performed on dogs during the suckling period. Extirpation of the spleen delays growth, but whether this is the result of removing the organ or of the operation of laparotomy is uncertain. An increase of total ash (especially in calcium and to a smaller degree in phosphoric acid) was the only chemical change in the body noted. Extirpation of the thyroid does not affect growth, and causes a decrease in total ash. Extirpation of the testis does not affect growth, and a small decrease in the phosphoric acid of the ash occurs. Water, fat, fat- and ash-free substance, and proteins are not affected in all these classes of experiments.

W. D. H.

Muscle Chemistry. IV (Addendum). The Muscle Tissues of some Sea Animals when Dried by Heat. GIUSEPPE BUGLIA and A. COSTANTINO (*Zeitsch. physiol. Chem.*, 1913, **86**, 137—140. Compare this vol., i, 219).—When dried at 100—102°, the muscle tissues of some sea animals lose substances having an alkaline reaction, produced by the decomposition of extractive substances. At a temperature of 110—112°, acid substances are lost.

In the case of *Scyllium catulus* it was found that the loss is chiefly to be attributed to ammonia, produced by the decomposition of carbamide. N. H. J. M.

Catalase in Frogs' Muscles. EINAR HAMMERSTEN (*Chem. Zentr.*, 1913, i, 2051; from *Skand. Arch. Physiol.*, 1913, **29**, 46—59).—The action of a number of products of normal metabolism on the system catalase-hydrogen peroxide is investigated in a specially devised apparatus, frogs' muscles being used as the source of enzyme (compare Santesson, A., 1908, ii, 1061; 1910, ii, 331). The addition of creatinine causes a rapid increase in the rate of action at first; subsequently it falls owing to the using up of the peroxide. Creatinine decreases the rate of change similarly to Siegfried's "phosphor-meat acid." Choline hydrochloride and muscarine platinichloride have a direct harmful action on the enzyme. Acetaldehyde likewise lowers the activity, but reacts with hydrogen peroxide, fixing oxygen. Carbamide and alcohol are without effect. The muscle enzyme was more active in July and August than during December to June. When several substances act at once on the enzyme, the rate of change curves lie between those of the several constituents. E. F. A.

Influence of Various Substances on the Gaseous Interchange of Surviving Frog's Muscle. XI. Action of Aromatic and Other Cyclic Compounds. TORSTEN THUNBERG (*Chem. Zentr.*, 1913, i, 2054; from *Skand. Arch. Physiol.*, 1913, **29**, 1—28. Compare A., 1911, ii, 56, 627).—The behaviour of a number of benzene derivatives on the gas exchange of surviving muscles is described. Monobasic carboxylic acids, such as benzoic acid and the toluic acids, lessen the exchange; hippuric acid behaves similarly, but is weaker. The introduction of a second carboxyl group overpowers the adverse influence of the first. Phthalic acid is hardly poisonous, *iso*phthalic and terephthalic acids are slightly more so, and mellitic acid is very slightly poisonous. β-Phenylpropionic acid is as poisonous as phenylacetic acid. When the carboxyl group is in an unsaturated side-chain, the adverse effect on the exchange is much increased; this is exemplified by the behaviour of cinnamic, *allo*cinnamic, β-benzylidenepropionic, phenylpropiolic, and phenylmalonic acids. The salicylic acid grouping is more poisonous than the benzoic acid grouping. The para-compound is the least poisonous of the three hydroxytoluic acids. Anisic acid as a methoxy-compound is less poisonous than *p*-hydroxybenzoic acid. The presence of several hydroxy-groups does not greatly alter the action of the aromatic acids. The phenol-alcoholic acids, for

example, mandelic and phenylparaconic acids, are almost without effect.

Phenols are less poisonous than benzoic acid. It is considered that the benzene ring as such has a poisonous action on certain constituents of the cell concerned in the normal respiratory process. Nitration, as in mono- and di-nitrobenzoic acids, has little effect on the physiological action; sulphonation lessens the poisonous character of the ring. On the other hand, the hydrated six-membered ring in inositol and camphoric acid is inactive. The introduction of nitrogen into the ring, as in picolinic, nicotinic, and quinolinic acids, also counteracts the poisonous effect. Quinoline, which contains both pyridine and benzene nuclei, is strongly poisonous. Five-ring compounds are moderately poisonous.

E. F. A.

Organic Bases in the Roe of Herrings. KIYOHISA YOSHIMURA (*Zeitsch. physiol. Chem.*, 1913, **86**, 174—177).—The dry matter (92·093%) of the herring roe had the following composition: total N, 12·063; crude fat, 1·253; total P, 0·602; P as lecithin, 0·200; N as proteins, 0·601; N as ammonia and amines, 0·338; N as bases, 0·244%. One kilo. of the dried substance yielded 0·12 gram of trimethylamine, 0·02 gram of tetramethylenediamine, and 0·70 gram of choline.

N. H. J. M.

The Occurrence of Free Sulphuric Acid in the Mantle of Ascidia mentula. MARTIN HENZE (*Zeitsch. physiol. Chem.*, 1913, **86**, 345—346).—The cellulose mantle of *A. mentula* is acid, and this is due to sulphuric acid in the "bladder cells" of the mantle. Whether this is related to the acid cells of the blood is uncertain, for in *Phallusia mamillata*, although the blood-cells are acid, there is no acid in the mantle. There is less total sulphate in the expressed juice of *Phallusia* mantle than in the sea-water. The amount of chlorides in the two is equal.

W. D. H.

Presence of Carbamide in the Invertebrates and in their Excretion Products. ROBERT FOSSE (*Compt. rend.*, 1913, **157**, 151—154. Compare A., 1912, ii, 1203; this vol., i, 327, 432).—The author has proved the presence of carbamide in numerous invertebrates and their excretion products, and also in the water inhabited by them for any length of time, as follows:

Coelenterata: Actinia, and its products of excretion.

Echinoderm: Starfish, and products of excretion.

Worms: Sangsue officinale, cellular juice, and products of excretion.

Crustaceæ: Crayfish, cellular juice of the entire animal, of the flesh deprived of the organs, and of the liver; also in the products of excretion; spiny lobster, cellular juice, and excretion products; shrimp, cellular juice.

Insects: Silkworm, cellular juice; ant, eggs; fly, eggs.

Molluscs: Snail, entire animal, products of secretion and excretion; mussel, liquid in the shells; oyster, liquid in the shells.

W. G

The Mechanism of the Physiological Production of Light; Luciferase, Luciferin, and Luciferesceine. RAPHAEL DUBOIS (*Eighth Inter. Cong. App. Chem.*, 1912, **19**, 83—89).—Phosphorescence in organisms is due, according to the author, to the interaction of two substances, which he has isolated more especially from the molluscular lamellibranch, *Pholades dactylus*. One of the substances, to which the name *luciferin* is given, can be extracted from the secreting organs by water, after heating to 70°, at which temperature it is stable. The other substance, *luciferase*, is, however, destroyed at 60°. By the action of one on the other in the presence of air, a phosphorescence is produced. The luciferase is of ferment-like character (oxydase), and it can be replaced by an oxidising agent, such as potassium permanganate, and by the blood of various cold-blooded animals, such as molluscs and marine crustaceans. Solutions of both substances give protein reactions, and the luciferin contains phosphorus and can be precipitated by picric acid. The term luciferesceine is adopted for the fluorescent substances in other animals, such as the fire-fly (compare McDermott, A., 1911, i, 396). S. B. S.

Indian Edible Swallows' Nests. HEINRICH ZELLER (*Zeitsch. physiol. Chem.*, 1913, **86**, 85—106).—The substance, dried in a vacuum, contained 9·43% of total nitrogen, 1·35% of histidine, 1·20% of arginine, and 1·18% of lysine. When hydrolysed with 4% sulphuric acid, two reducing substances, not identified, were obtained. N. H. J. M.

The Ferments of the Milk Glands and of Milk. WALTHER GRIMMER (*Biochem. Zeitsch.*, 1913, **53**, 429—473).—Both in resting and active milk glands proteoclastic ferments are present, which can digest the proteins of the glands themselves, but not other proteins, such as fibrin, gelatin, egg-white. Glycine, leucine, and other products of hydrolysis were formed. Tryptophan was found as hydrolysis product of the active, but not of the resting gland. The expressed juices, saline extracts, and autolysates of both resting and acting glands contain a peptoclastic ferment, which can set free tyrosine from milk peptone. Reasons are given for supposing that the peptoclastic and proteoclastic ferment are not identical. The active and resting glands contain a monobutyrinase, the activity of which is considerably weakened by dialysis. The milk glands of the ox and pig possess an amylolytic ferment both when active and resting. In the case of the cow, the amylolytic ferment is more active in the resting than in the active gland, whereas the resting glands of sheep possess no marked amylolytic capacity. All glands (expressed juices and saline extract) possess a ferment capable of hydrolysing salol, and it is shown that this action is not due to the alkalinity of the medium. A guaiacum peroxydase was only found in the lactating glands of ruminants. This is apparently not identical with the *p*-phenylenediamine oxydase, as no parallelism was found between the two ferments in the various glands, etc., investigated. S. B. S.

The Quantity of Alcohol Excreted by the Animal Organism Under Various Conditions. IV. The Influence of Dose and External Temperature on the Excretion of Alcohol by the Urine and Expired Air; the Absorption of Alcohol from the Urinary Bladder. WILHELM VÖLTZ and AUGUST BAUDREXEL (*Pflüger's Archiv*, 1913, **152**, 567—578. Compare A., 1912, ii, 466). —In doses of 3 c.c. of alcohol per kilo. of body weight in dogs, from 92 to 98% is oxidised in the body; at a low external temperature the figure is higher (96% at 16°, and 92% at 26°). A certain amount of alcohol is absorbed from the bladder when the concentration in the urine is not greater than the quantity found there after its ingestion. W. D. H.

Respiration and Metabolism in Cardio-renal Disease. THOMAS LEWIS, JOHN H. RYFFEL, CHARLES G. L. WOLF, T. COTTON, G. L. EVANS, and JOSEPH BARCROFT (*Proc. physiol. Soc.*, 1913, liii—lv; *J. Physiol.*, **46**).—The fundamental factor in such cases is an increase in the proportion of acids (exclusive of carbon dioxide) in the blood. There is a fall in the alveolar carbon dioxide, and meionexy. W. D. H.

The Combustion of Sugar in Pancreas Diabetes. FRITZ VERZÁR and A. VON FEJÉR (*Biochem. Zeitsch.*, 1913, **53**, 140—167).—Experiments were carried out on curarised tracheotomised dogs, with the object of ascertaining whether, after extirpation of the pancreas, the intravenous injection of sugar still caused a rise in the respiratory quotient, which serves as an indication that the sugar is being burnt in the body. Such a rise occurred up to the fourth day after the operation, after which no sugar was burnt up. In certain cases, when the animal is thus rendered diabetic, sugar injection causes a rise in oxygen consumption, but in others it does not. Neither by blood transfusion from another animal, nor by infusion of ordinary blood or of blood from the pancreas, could a rise in the respiratory quotient after sugar injection be brought about in depancreatised dogs; nor could any constant changes in this factor be produced by the pancreatic hormone of Knowlton and Starling. S. B. S.

Blood-Dissociation Curves in Uræmia. EDWARD P. POULTON and JOHN H. RYFFEL (*Proc. physiol. Soc.*, 1913, xlvii—xlviii; *J. Physiol.*, **46**).—Four cases of uræmia were investigated; the alveolar carbon dioxide pressure is low (14 to 25 instead of 40 mm.), and the blood takes up oxygen with difficulty, so that the percentage saturation is from 37 to 43 instead of 52 to 63. The lactic acid of the blood was not increased except in one case. The urea in the blood was high in all (0·21 to 0·36 instead of 0·03%). The meionexy is not due to the urea; addition of urea to normal blood does not cause the shifting of the curve. W. D. H.

The Influence of Hydroxyl and Carboxyl Groups on the Pharmacological Action of Nitric Esters. CHARLES R. MARSHALL (*Eighth Inter. Cong. App. Chem.*, 1912, **19**, 211—215).—The experiments were carried out on cats and rabbits with the following

substances: glycerol dinitrate, glyceryl methyl ether dinitrate, mannitol tetramethyl ether dinitrate, mannitol dimethyl ether tetranitrate, mannitol pentanitrate, dulcitol pentanitrate, and the nitric esters of tartaric, citric, and lactic acids, and of their ethyl ethers. It was found generally that the presence of hydroxyl or methoxyl groups considerably diminishes the vaso-dilating action of the nitric esters. When compared with completely nitrated alcohols containing the same number of nitro-groups, most (but not all) of the esters containing hydroxyl or methoxyl groups are much less active. Carboxyl groups diminish the vaso-dilating power even more than these, and the nitric esters of tartaric, citric, and lactic acids, after neutralisation with sodium carbonate, were completely inactive as vaso-dilators. S. B. S.

The Biological Behaviour of 6-Chloro-*m*-hydroxytoluic Acid. ERNST SIEBURG (*Biochem. Zeitsch.*, 1913, **53**, 259—264).—The substance investigated [Me : OH : CO_2H : Cl = 1 : 3 : 4 : 6] acts antiseptically about six times more strongly than phenol, and thirty times more strongly than sodium salicylate. Kobert's method was employed, in which milk is mixed with sulphur, and the concentration of the drug just necessary to inhibit hydrogen sulphide formation was ascertained. Its antiseptic power was also confirmed when pure cultures in sterile human urine were employed. When administered to man, the acid is relatively non-toxic, and 2 grams can be tolerated when administered in one dose, without evil effects. It is excreted in the form of the sulphuric acid ester, which is crystalline, melts and decomposes above 200°, and can be synthetically prepared by Baumann's method, the synthetical substance and the substance isolated from urine after ingestion of the acid being identical. The acetyl ester is readily hydrolysed by ferments contained in beer-yeast, trypsin, taka-diastase, rabbit's pancreas, and rabbit's liver. S. B. S.

[Pharmacological] Investigation of Two Bromo-substituted Acidylcarbamides: Bromural and Adaline. Y. AIRILA (*Chem. Zentr.*, 1913, i, 2055; from *Skand. Arch. Physiol.*, 1913, **28**, 193—277).—The pharmacological behaviour of bromural (monobromo*iso*valerylcarbamide), $CHMe_2\cdot CHBr\cdot CO\cdot NH\cdot CO\cdot NH_2$, and of adaline ($\alpha$-bromo-$\alpha$-ethylbutyrylcarbamide),

$$CBrEt_2\cdot CO\cdot NH\cdot CO\cdot NH_2,$$

has been investigated. In rabbits both behave similarly, adaline being the more lethal; they cause a diminution in the blood pressure, but are without effect on the heart. E. F. A.

Action of Adrenaline on the Bronchioles. FREDERICK L. GOLLA and W. LEGGE SYMES (*Proc. physiol. Soc.*, 1913, xxxviii—xxxix; *J. Physiol.*, **46**).—In cat and rabbit, adrenaline causes constriction of the bronchioles, but after constriction has been established by other drugs, such as curare or muscarine, adrenaline then causes dilatation. The following drugs resemble adrenaline in this particular: epinine (3 : 4-dihydroxyphenylmethylethylamine), tyramine (*p*-hydroxyphenylethylamine), methyl-

amine, ethylamine, and *iso*amylamine. Ergamine (β-amino-4-ethylglyoxaline) never produces bronchial dilatation.

W. D. H.

The Pharmacological Action of Bromostrychnines. CHARLES R. MARSHALL (*Eighth Inter. Cong. App. Chem.*, 1912, **19**, 217—223).—The two monobromostrychnines act like strychnine, but are eight to nine times weaker. Dibromostrychnine, although it still possesses a slight convulsant action in frogs and rabbits, produces in the former animals chiefly a paralytic effect, mainly due to a depression of the motor nerve-endings. S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

Favourable Action Exercised by Manganese on Acetic Fermentation. GABRIEL BERTRAND and ROBERT SAZERAC (*Compt. rend.*, 1913, **157**, 149—151).—The addition of minute quantities of manganese has a marked accelerating influence on the conversion of alcohol into acetic acid by *B. aceti.* At first the acceleration increases with the proportion of manganese, then it reaches a maximum, and begins to decrease. Under the experimental conditions stated, 1 part of manganese sulphate in 10,000 had the optimum effect. W. G.

The Production of Acetaldehyde During the Anaerobic Fermentations of Dextrose by Bacillus coli communis (Escherich). EGERTON CHARLES GREY (*Biochem. J.*, 1913, **7**, 359—363). —By artificial selection of this bacillus by means of growth on sodium chloroacetate, strains have been obtained which produce little or no acetaldehyde. The formation of this product by the ordinary bacillus is related to the formation of alcohol, carbon dioxide, and hydrogen rather than to the other products. It is suggested that acetaldehyde is a primary product of the fermentation. W. D. H.

Products of the Lactic Fermentation of Sugars. ALAN A. CLAFLIN (*Eighth Inter. Cong. App. Chem.*, 1912, **25**, 343—345).— There are considerable discrepancies between the statements of different authors with reference to the amount of lactic acid produced by the lactic fermentation of sugars, but the statement of Mayer and of Kayser is usually accepted, that the yield is not over 84%, and that considerable quantities of volatile acids are formed.

A further study of this question has shown that maltose, hydrolysed starch, and inverted sucrose give identical results when fermented with the same bacteria under the same conditions. It has been found that 95—97% of the sugar may be converted into

lactic acid with formation of not more than 0·5% of volatile acids, the balance consisting of unfermented sugars. If all the sugar is fermented, the yield of lactic acid is reduced to 90%, and that of the volatile acids increased to 5%, the balance probably disappearing as water and carbon dioxide. The volatile acids are formic, acetic, propionic, and butyric acids, acetic and butyric being present in the largest quantities. The formic acid does not amount to more than 1% of the original sugar. The propionic acid occurs in the proportion of one part to ten parts of acetic acid. The percentage of acetic acid depends on the degree of aeration, and may attain to as much as 30 parts to 70 parts of lactic acid. E. G.

Influence of Some Colloids on Alcoholic Fermentation. Nicolaas L. Söhngen (*Chem. Zentr.*, 1913, i, 2167—2168; from *Folia Microbiol., Holländ. Beitr. gesamt. Microbiol.*, **2**).—Fermentation was effected between 38° and 40°, at which temperature the yeast no longer grows, but the fermentative function remains unchanged. The influence of a number of colloids on the process of alcoholic fermentation was investigated. Alkali humates have an adverse action. Colloidal iron, aluminium, or silicon oxides and humic acid have no measurable influence. Biocolloids, such as turf, blood-charcoal, garden soil, have a markedly favourable action. This is attributed to the low concentration of carbon dioxide in these liquids, which favours the rapid formation and dissipation of bubbles, so that the medium does not become supersaturated. The aggregation of the gas bubbles at the colloidal surfaces accelerates their liberation and escape. E. F. A.

Catalysts of Alcoholic Fermentation. Hans Euler and Henry Cassel (*Zeitsch. physiol. Chem.*, 1913, **86**, 122—129).—Whilst most of the substances known to accelerate fermentation have a comparatively slight effect—the maximum rarely exceeding 20%—it was found that addition of 0·04 gram of ammonium formate to 110 c.c. of water and 2 grams of sucrose resulted in an increase of 75%. Dry yeast was scarcely, if at all, influenced by ammonium formate.

Further experiments showed that the addition of ammonium formate affects the first phase of fermentation, in which an intermediate product, or products, are formed, more than the second phase (production of alcohol and carbon dioxide).

The effect of a given amount of organic salt is greater the less yeast is present. N. H. J. M.

Influence of the Yeasts and of the Initial Constitution of the Musts on the Acidity of Fermented Liquids. Jules Ventre (*Compt. rend.*, 1913, **157**, 154—156. Compare Fernbach, this vol., i, 231).—A study of the fermentation of sugar solutions by different yeasts in media of varying acidity, and of the effect of using different organic acids to produce the initial acidity. Each yeast produces a definite fixed and volatile acidity, the acidity increasing in neutral media, but diminishing in natural or artificial acid

media. Tartaric acid is preserved unchanged in original amount, but little being consumed by the different yeasts. Malic acid appears to be the most readily attacked by the yeasts. Each yeast has a power peculiar to itself of producing succinic acid. W. G.

Fermentations with Yeast in Absence of Sugar. XII. Changes During Fermentation by Yeast. CARL NEUBERG and JOHANNES KERB (*Ber.*, 1913, **46**, 2225—2228; *Biochem. Zeitsch.*, 1913, **53**, 406—419).—Pyruvic acid, $CH_3·CO·CO_2H$, is rapidly broken down by an enzyme in yeast into acetaldehyde and carbon dioxide (compare Neuberg and Kerb, A., 1912, ii, 973). The fermentation of a mixture of pyruvic acid and glycerol has been repeated on a large scale, using 100 litres of 1% pyruvic acid. Precautions were taken that the yeast had a high fermentative power, and allowance was made for the alcohol already present in the yeast used, and also for the alcohol formed by autofermentation. A considerable amount of alcohol is formed from pyruvic acid, and still more when both pyruvic acid and glycerol are present. It is considered that the influence of the glycerol is only indirect, in that it acts to protect the enzyme and increase its reducing power.

*iso*Butaldehyde and valeraldehyde are readily converted by yeast into the corresponding alcohols with a yield of 85% in the latter instance. E. F. A.

The Separation of Life and Fermentative Power. THOMAS BOKORNY (*Pflüger's Archiv*, 1913, **152**, 365—436).—Experiments on yeast show that by chemical reagents of appropriate strength it is possible to kill the cells, but leave the enzymic power intact; for instance, this is accomplished by sulphuric acid from 0·1 to 0·5% concentration. Details regarding a large number of chemical reagents (inorganic and organic) are given. The kind of yeast used is one factor in the process. W. D. H.

The Fat of Yeast. H. A. D. NEVILLE (*Biochem. J.*, 1913, **7**, 341—348).—The chief saturated acid in the fat of yeast is pentadecoic acid (Hinsberg and Roos, A., 1903, i, 56); arachidic acid and unsaturated acids with the formulæ $C_{16}H_{30}O_4$, $C_{18}H_{34}O_2$, and $C_{18}H_{32}O_2$ are also present. The cholesterol melts at 145—147°. W. D. H.

The Protein Substances of Yeast and their Products of Hydrolysis. PIERRE THOMAS and (Mme.) SOPHIE KOLODZIEJSKA (*Compt. rend.*, 1913, **157**, 243—246. Compare this vol., i, 942).—The authors have studied the products of hydrolysis of the two protein substances obtained from yeast (compare *loc. cit.*), one of which belongs to the casein group, and the other to the vegetable albumins. By hydrolysis with concentrated hydrochloric acid, followed by distillation with magnesium oxide, and then precipitation of the humic nitrogen by evaporation in acid solution, and of the amino-compounds with phosphotungstic acid, the nitrogen content has been determined as ammoniacal, humic, diamino- and

monamino-nitrogen. The figures are in fairly close agreement with Osborne's values for casein. Similar treatment of the cerevisine or vegetable albumin gives values agreeing well with Osborne's results for legumeline.

Hydrolyses have also been performed with sulphuric acid, and estimations made of the histidine, arginine, and lysine. W. G.

A Forgotten Investigator. A Contribution to the History of the Yeast Manufacture. F. G. WALLER (*Chem. Weekblad*, 1913, **10**, 635—644).—A review of the development of the manufacture of yeast, in which the author contends that a practical technical method for its production by the air process was first devised by Eusebius Bruun. A. J. W.

Potassium, Sulphur, and Magnesium in the Metabolism of Aspergillus niger. H. J. WATERMAN (*Proc. K. Akad. Wetensch, Amsterdam*, 1913, **15**, 1349—1355).—Deficiency of potassium chloride allows the production of mycelium, but not of spore formation. Only in the concentration of $M/37,500$ does spore formation commence after eight days. When potassium sulphate is added, larger quantities inhibit the formation of spore, which develop after two days, when potassium sulphate is absent. After forty days, all the moulds were covered with spores in all the concentrations of sulphate added. During the growth, sulphur accumulates in the cells, and is afterwards partly excreted. Relatively large quantities of magnesium are necessary to produce a perceptible growth of mycelium, as none visible to the naked eye appeared even in the concentration of $M/2,470,000$-$MgSO_4,7H_2O$ per litre. In the concentration $2M/247,000$, considerable growth only appeared after some days. S. B. S.

Amygdalase and Amygdalinase in Aspergillus niger and Some Allied Hyphomycetes. MAURICE JAVILLIER and (Mme.) HELENE TSCHERNORUTZKY (*Ann. Inst. Pasteur*, 1913, **27**, 440—449).—*Sterigmatocystis nigra* and most of the mosses examined contain unequal amounts of amygdalase and amygdalinase. The amounts of both diastases is diminished in absence of zinc. The diastases are active in solutions which are neutral or slightly acid to helianthin, and the optimum temperature is higher than that of the same diastases of almonds.

The percentage amount of the diastases in the plants varies with the age of the mycelium, and reaches its maximum at the time of sporulation. The two diastases pass into the culture medium very unequally. N. H. J. M.

Biological and Toxicological Studies on Penicillium stoloniferum (Thom.). CARL L. ALSBERG and OTIS F. BLACK (*Eighth Inter. Cong. App. Chem.*, 1912, **19**, 15—23).—Cultures of *Penicillium stoloniferum* were obtained by Thom from spoiled Italian maize. When grown on Raulin's medium, these were found to produce an acid, $C_{17}H_{20}O_6$, white needles, m. p. 140°, which was of phenolic character, almost insoluble in water, but soluble in

most organic solvents, to which the name *mycophenolic acid* is given. It gives with ferric chloride the colour which is characteristic of spoiled Italian maize, and resembles in many respects the lichen acids. S. B. S.

Sterigmatocystis nigra and Lactose. HENRI BIERRY and (Mlle.) F. COUPIN (*Compt. rend.*, 1913, **157**, 246—247).—By cultivation of *Sterigmatocystis nigra* on Raulin's liquid for three days, then on a similar liquid deprived of all carbohydrate, and finally on this liquid with the sucrose replaced by lactose, lactase is produced in the plant, but in an endocellular form, and in consequence it does not pass into water when the crop is macerated with it. W. G.

The Influence of the Chemical Constitution of Certain Organic Hydroxyl and Aminic Derivatives on their Germicidal Power. GILBERT T. MORGAN and E. ASHLEY COOPER (*Eighth Inter. Cong. App. Chem.*, 1912, **19**, 243—257).—The antiseptic value of several series of substances was investigated by Chick and Martin's modification of the Rideal-Walker process. The antiseptic value of the following classes of substances was ascertained. The aliphatic alcohols: The "carbolic acid coefficients" of these were all low. Certain phenols: The influence of the addition of alcohol to these was also investigated, and found to vary in different cases. The carbolic acid coefficients of the dihydroxybenzenes were as follows. (With *B. Typhosus*) Resorcinol, 0·29; catechol, 0·48; quinol, 1·1. The results with the nitrophenols were as follows (*Staphylococcus py. aur.*): *p*-Nitrophenol, 2·3; potassium *p*-nitrophenoxide, 0·52; *m*-nitrophenol, 3·5; picric acid, 7·5. The coefficients for coumarin, the coumaric acids and salts were low. The coefficients for the dihydroxynaphthalenes were, for the 2:3-derivative, 4·4, and for the 2:7-derivative, 2·8. The coefficients of several series of both aliphatic and aromatic amines were also determined. The chief results are the following (with *B. Typhosus*), ethylamine, 1·27; *iso*amylamine, 2·8; *n*-heptylamine, 24·3; *ac*-tetrahydro-β-naphthylamine, 5·3; aniline, 0·57; the toluidines, ortho-, 1·00; meta-, 1·30; para-, 1·25; pyridine, 0·18. S. B. S.

Compounds Obtained from Plant Seeds by the Methods for Extracting Lecithin. I. Introduction: Bean Seeds. GEORG TRIER (*Zeitsch. physiol. Chem.*, 1913, **86**, 1—32).—A summary is given of previous work on plant phosphatides, and the opinion is expressed that the apparent differences between plant and animal phosphatides is due to the incomplete investigation of the former and to incorrect interpretation of the experimental results. The preparation and purification of the lecithin contained in *Phaseolus vulgaris* is described. E. F. A.

Compounds Obtained from Plant Seeds by the Methods for Extracting Lecithin. II. Hydrolysis of Egg-albumin. III. Oat Seeds. GEORG TRIER (*Zeitsch. physiol. Chem.*, 1913, **86**, 141—152, 153—173).—Previous experiments having shown that

aminoethyl alcohol is obtained by hydrolysing the lecithin of bean seeds, it became desirable to ascertain whether the compound could be obtained from other lecithins. Egg-lecithin, when hydrolysed, yielded, in addition to choline, small amounts of aminoethyl alcohol and glycerolphosphoric acid. Evidence was obtained that the aminoethyl alcohol is attached to the lecithin by the hydroxyl group, the amino-group being free.

Further experiments, with oats, showed that the phosphatides of the seeds of cereals are very similar to egg-lecithin and the lecithins of leguminous seeds. N. H. J. M.

Quantitative Experiments on the Effect of Formaldehyde on Living Plants. SARAH M. BAKER (*Ann. Bot.*, 1913, **27**, 411—442).—The results of experiments on the growth of seeds in atmospheres containing known amounts of formaldehyde showed that in presence of light, formaldehyde is utilised to some extent for the synthesis of food materials. In absence of light, formaldehyde is not assimilated; it seemed, however, to stimulate respiration.

Acetaldehyde is not assimilated in presence of light. The change in the dry weight of the cultures, when compared with the carbon dioxide respired, gave a ratio closely agreeing with that calculated for the complete oxidation of a carbohydrate. With cultures kept in darkness, no change occurred in the relations between loss in dry weight and the respired carbon dioxide. Formaldehyde was therefore not converted into carbon dioxide, and was not used as a source of food materials in absence of light.

It is probable that formaldehyde may function as a stage in photosynthesis; but the production of sugars and other food materials requires light energy. N. H. J. M.

Action of Sulphites, Thiosulphates, and Sulphur in Soils on the Growth of Plants. WALTER THALAU (*Landw. Versuchs-Stat.*, 1913, **82**, 161—209).—The results of pot experiments with different plants showed that, in a loamy soil, ammonium sulphite has the same effect as ammonium sulphate; in sand, ammonium sulphite has somewhat less effect than the sulphate; whilst in peat the yield was much less with sulphite.

In water cultures, ammonium sulphite is very injurious; germination is retarded in 0·4% solutions.

When exposed to air for a short time, ammonium sulphite is oxidised to sulphate; the rate of oxidation is increased by dissolving the salt in water, and still more in presence of soil.

Calcium sulphite was found to have no injurious action in loamy and sandy soils; in water cultures, and perhaps in peat, it reduced the yields. Sodium thiosulphate had no injurious effect. Flowers of sulphur had no very appreciable effect, and further experiments will be necessary. N. H. J. M.

Presence of Hemicelluloses in Root-stock, Rhizomes, and Tubers. ANTON STIEGER (*Zeitsch. physiol. Chem.*, 1913, **86**, 270—282).—The investigation of root-material from a number of

plants showed that in every case hemicellulose was present, a mixture of galactose and arabinose in approximately equal quantities being obtained on hydrolysis, whilst in no instance was either mannose or fructose present. The root and rhizome of *Asparagus officinalis* yielded only arabinose. The presence of much or little starch in the roots had no apparent effect. It is left undecided whether the hemicelluloses act as a reserve or as a skeletal material in the vegetative parts of plants. E. F. A.

Distribution of Asparagine, Glutamine, Arginine, and Allantoin in Plants. ANTON STIEGER (*Zeitsch. physiol. Chem.*, 1913, **86**, 245—269).—Asparagine and glutamine were sought for in the roots, underground shoots, portions above ground, or in the seedlings of a large variety of plants. It is characteristic of some families that they contain asparagine alone; in others only glutamine is present, whilst a few contain both amides. The last may contain either amide in excess or both in equal proportions. The results show a remarkable parallelism between the morphological-anatomical classification of the plants and their chemical behaviour. Certain irregularities are recorded where plants, in which normally only asparagine is present, sometimes contain more or less glutamine as well. Such variations are attributed to the altered conditions of environment.

Arginine almost always accompanies asparagine, but is less often present with glutamine. It is found when neither amide is present, where it probably acts as a reserve material.

The presence of allantoin in a number of plants is established.

E. F. A.

Antiaris Latex. HEINRICH KILIANI (*Ber.*, 1913, **46**, 2179—2188. Compare this vol., i, 381).—A fresh supply of preserved Antiaris latex was received from Mid-Borneo. It contained a deposit of the protein in the form of well-defined, short columns. The latex is therefore a saturated solution of the protein, which must be an original ingredient, and not the product of subsequent fermentation. On this occasion, the most exhaustive extraction, full details of which are described, failed to yield more than one-sixth of the amount of glucosides which was previously obtained, and only β-antiarin (0·1% of the latex), but no α-antiarin could be isolated. The crude glucoside contained, however, a new active substance, which is easily soluble in water, and is designated *γ-antiarin.*

Ether extracted from the alcoholic solution of the glucosides a new *acid*, $C_{16}H_{14}O_7$ (?), which forms pale yellow, glistening crystals, sinters at 178—184°, is strongly acid, gives a *calcium* salt, and develops a green coloration with ferric chloride, changing to deep red with a drop of ammonia. The alkaline solutions rapidly darken in the air, from which it appears that the acid is a pyrogallol derivative, probably metameric with lecanoric acid.

J. C. W.

Alcohol From the Fruit of Arbutus unedo (Ellerone). GIOVANNI SANI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 884—885).—Fermentation of this fruit yields a product containing 9·15—9·75% of alcohol. The alcohol recovered from it by distillation had an acidity of 0·132 gram per litre (as acetic acid), contained esters (1·757 grams per litre, as ethyl acetate), furfuraldehyde, methyl alcohol, and fusel oil (2·321 grams per litre), but no free or combined hydrogen cyanide. R. V. S.

Chemical Examination of the Seeds of the Cacao Tree. L. REUTTER (*Compt. rend.*, 1913, **156**, 1842—1844).—Ground cocoa beans were treated with steam at 110°, deprived of oil, and extracted with warm dilute methyl alcohol. On spontaneous evaporation, the reddish-violet solution deposits white, microscopic crystals, m. p. 184—185°. This substance, termed *cacaorine*, $C_{16}H_{20}O_3N_8$, yields a neutral solution in water, which is optically inactive. On hydrolysis, it yields theobromine and a small quantity of a reddish-brown precipitate.

The mother liquor from cacaorine, when further concentrated, yields *cacao-red*, $C_{40}H_{60}O_{27}N$, reddish-violet leaflets, which slowly oxidise on exposure to air, becoming brown. It is soluble in water and in methyl alcohol. The aqueous solution is coloured yellowish-brown by alkalis, bright red by acids. It reduces Fehling's solution, but is optically inactive. When hydrolysed by dilute sulphuric acid, it yields carbon dioxide, a dextrorotatory sugar, and *cacao-brown*, $C_{76}H_{78}O_{34}N$. H. W.

Ash of the Castor Bean. MARSTON LOVELL HAMLIN (*Biochem. Bull.*, 1913, **2**, 410—411).—The following were the results obtained:

	SiO_2.	CaO.	MgO.	P_2O_5.	Mn.	Total ash.
Per cent. in dry oil-free kernel...	0·04	0·28	1·51	3·52	0·00056	7·3
Per cent. in ash	0·5	3·9	20 7	48·2	0·0076	—

Schulze and Godet obtained the following figures from dry, but not oil-free, kernels:

	CaO.	MgO.	P_2O_5.	Total ash.
Per cent. in dry substance ...	0·15	0·72	1·16	3·64
Per cent. in ash	4·0	19 8	31·9	—

W. D. H.

The Composition of Coffee Essence; Presence of Pyridine. GABRIEL BERTRAND and GUSTAVE WEISWEILLER (*Compt. rend.*, 1913, **157**, 212—213).—The authors have proved the presence of pyridine in the infusion of freshly roasted and ground coffee, by precipitation with silicotungstic acid and subsequent preparation of its platinichloride. Pyridine is present to the extent of 200—250 mg. per kilo. of freshly roasted coffee. W. G.

Nitrogenous Constituents of the Fungus, Cortinellus shiitake (P. Henn.). KIYOHISA YOSHIMURA and M. KANAI (*Zeitsch. physiol. Chem.*, 1913, **86**, 178—184).—The sample examined contained 87·355% of dry matter of the following composition:

Nitrogen.			Crude		
Total.	As proteins.	As ammonia.	fat.	Ash.	P_2O_5.
3·993	2·406	0·085	0·641	5·781	0·804

The following substances were obtained from 2 kilos. of the air-dried fungus: adenine, 0·40; choline, 0·41; alanine, 1·60; leucine, 2·30; copper glutamate, 0·50; proline, 0·30; mannitol, 50·00 grams: also a trace of trimethylamine and a little phenylalanine.

N. H. J. M.

Latex of Ficus coronata; an Incomplete Vegetable Pancreatic Juice Containing a Proteolytic Enzyme, but no Amylase. C. GERBER (*Compt. rend.*, 1913, **156**, 1917—1919. Compare A., 1911, ii, 647; 1912, ii, 801, 977).—The latex has no action on starch paste or soluble starch, and consequently contains no amylase. Judging from its action on egg-yolk, it contains a lipase twice as active as that in the latex of *Ficus carica* (*loc. cit.*), and slightly more resistant to the influence of heat and of acids. It also contains a very active proteolytic ferment, which from its activity in coagulating milk appears to be four times as active as the similar ferment in *Ficus carica* latex, and more resistant to heat than the latter. The rennet of *Ficus coronata* is affected by acids and salts in the same way as that of *Ficus carica*. The latex is like that of *Morus nigra*, an incomplete vegetable pancreatic juice, but differs from this in containing a rennet more active towards boiled than raw milk. T. A. H.

The Influence of the Carbonates of the Rare Earths (Cerium, Lanthanum, Yttrium) on Growth and Cell Division in Hyacinths. WILLIAM HOWEL EVANS (*Biochem. J.*, 1913, **7**, 349—355).—The concentration of the carbonates of the rare earths necessary to produce physiological effects is very small. Lanthanum and cerium are favourable to growth and cell-division; yttrium is unfavourable. The lanthanum ion has a special effect on the flower-stalk, causing an increase in length. W. D. H.

Value of Caoutchouc in Kickxia-elastica. DAVID SPENCE and WILLIAM F. RUSSELL (*Kolloid. Zeitsch.*, 1913, **13**, 41—46).—The authors have worked up six specimens of indiarubber latex by different methods with the object of ascertaining whether the kickxia caoutchouc could be converted into a good commercial product. They conclude that when carefully worked, this substance, as far as its physical properties are concerned, gives a good caoutchouc, but as far as its composition and other properties are concerned, the kickxia latex is inferior to the Plantagen-Hevea latex. J. F. S.

Analyses of Some Wyoming Larkspurs. I. FREDERICK W. HEYL, F. E. HEPNER, and SYLVESTER K. LOY (*J. Amer. Chem. Soc.*, 1913, **35**, 880—885).—Analyses are given of the various parts of *Delphinium Nelsonii*, *Delphinium glaucum*, and *Delphinium geyeri*.

The leaves of all three varieties were found to contain *d*-mannitol, whilst the last variety is found to yield the highest proportion of mixed alkaloids. D. F. T.

Constituents of the Berries of Kuko (Lycium chinense). T. FURUYA (*Chem. Zentr.*, 1913, i, 1823; from *Arb. Pharm. Inst. Univ. Berlin*, **9**, 117—120).—The berries of Kuko (*Lycium chinense*) yield 0·0912% of betaine. E. F. A.

Constituents of the Roots of Stemona sessilifolia. T. FURUYA (*Chem. Zentr.*, 1913, i, 1823—1824: from *Arb. Pharm. Inst. Univ. Berlin*, **9**, 112—116).—The powdered roots contain an alkaloid *hodorine*, $C_{19}H_{31}O_5N$, which was not obtained crystalline. The *hydrobromide* forms a colourless, odourless, crystalline powder, m. p. 258—259°. The *hydrochloride* has m. p. 244—247° (decomp.). E. F. A.

Manketti Seed Oil. HERMANN THOMS (*Chem. Zentr.*, 1913, i, 1823; from *Arb. Pharm. Inst. Univ. Berlin*, **9**, 225—227).—Manketti seeds yield a pale yellow oil of nutty odour and agreeable flavour. The oil becomes cloudy at −2°. It is optically inactive, and has the following constants: Saponification number, 195·2; Reichert-Meissl, 1·085; Polenske, 0·6; iodine number, 130·4; Hehner number, 98·5; m. p. of the fatty acids, 40°; iodine number of these, 140·7; acetyl number, 163·2. The crude oil consists of the above oil, a half solid fat, m. p. 33°, and a watery fluid. E. F. A.

"Tannin Masses" in the Persimmon Fruit. ERNEST D. CLARK (*Biochem. Bull.*, 1913, **2**, 412—418).—On hydrolysis of tannin masses from the persimmon, tannin, phloroglucinol, and much colloidal residue are obtained, but no hexose or pentose. The union between the two first-mentionel substances is probably similar to that of phloroglucintannoids in various plants. The colloidal residue is cellulose-like. In the presence of phloroglucinol, the ferric chloride test for tannin is untrustworthy. W. D. H.

Investigation of Puccinia graminis Persoon. A. VON POMARSKI (*Chem. Zentr.*, 1913, ii, 288; from *Sep. Zoot. Lab.*, 1912, **8**, 85—120).—The air-dried spores of *Puccinia graminis* contain 12·1% of moisture, 3·25% of nitrogen, 5·1% of fat, and 9·15% of cell membrane. The last yields dextrose, formic and acetic acids on hydrolysis, it contains about 7% of nitrogen, and is analogous to chitin or chitosan.

The fat contains lauric acid, heptoic acid, oleic acid, and glycerol, also 32% of a wax and dioleinlecithin.

Dextrose, mannitol, and an unknown disaccharide are present, also the enzymes, invertase, catalase, diastase and lipase, as well as brownish-red and green pigments. E. F. A.

Arsenic and Manganese in Some Seaweeds. HENRI MARCELET (*Chem. Zentr.*, 1913, ii, 278; from *Bull. Sci. Pharmacol.*, 1913, **20**, 271—275).—Seaweeds contain from 0·005 to 0·5 mg. of

arsenic per 100 grams of dry material. Apparently the proportion of arsenic is greatest when that of chlorophyll is least; this is the opposite of the relation in land plants. In *Posidonia* the leaves contain 0·045 mg.; the roots, 0·035 mg.; and the whole plant, 0·04 mg. of arsenic per 100 grams. E. F. A.

Occurrence of Trehalose in Selaginella lepidophylla. OTTO ANSELMINO and E. GILG (*Ber. deut. Pharm. Ges.*, 1913, **23**, 326—330). —On extraction with alcohol, *Selaginella lepidophylla* furnished trehalose, which was identified by means of its melting point, composition, etc. *S. Galeottii* and *S. Kraussiana* yielded no trehalose. T. A. H.

The Unsaponifiable Constituents of Sesame Oil. ALFRED HEIDUSCHKA (*Eighth Inter. Cong. App. Chem.*, 1912, **11**, 13—16).—Sesame oil contains three unsaponifiable substances, namely, phytosterol, sesamin, and a thick yellow oil. The phytosterol, m. p. 136·2—136·8°, is a definite compound, and cannot be separated, by fractional crystallisations, into fractions having different melting points. Sesame oil yields about 0·17% of sesamin; this contains 67·36% of carbon and 5·43% of hydrogen, and has a molecular weight of 341·8. From these figures the formula $C_{20}H_{19}O_6$ is deduced for the substance. The yellow oil could not be separated into any characteristic or definite substances. W. P. S.

Chemical Examination of Wheat Germ. FREDERICK B. POWER and ARTHUR H. SALWAY (*Pharm. J.*, 1913, **91**, 117—120).—Wheat germ was found to contain sitosterol, choline, betaine, allantoin, sucrose, dextrose, and raffinose; no evidence was obtained of the presence of asparagine, which has been recorded as a constituent of wheat germ by Frankfurt (A., 1897, ii, 67). About 7% of fatty oil was obtained from the wheat germ under examination, the oil consisting of the glycerides of stearic, palmitic, and linolic acids; the quantity of linolic acid was about three times as much as that of the total solid acids. The amount of resinous substance present was 0·04%, as was also a small quantity of an amorphous glucosidic substance. It was ascertained that wheat germ contains a very small amount of sinapic acid, probably present as sinapine, a choline ester of sinapic acid. W. P. S.

Influence of the Lime-Magnesia Ratio. P. L. GILE and C. N. AGETON (*J. Ind. Eng. Chem.*, 1913, **5**, 564—567).—Experiments are described in which bush beans were grown for three years on plots 30 × 60 dcm., the soil of which contained varying proportions of lime and magnesia.

The results indicate that bush beans are independent of lime-magnesia ratio in the soils employed; and that the amount of lime in the plants remained the same, with increasing amounts of lime in the soil.

The conclusion is drawn that whilst the ratios of different salts,

including lime and magnesia, affect plant growth under certain conditions, the hypothesis of the lime-magnesia ratio cannot be considered as applying to all soil conditions. N. H. J. M.

Unfermentable Sugar (Pentose) and the Formation of Furfuraldehyde in Wine. RUDOLF HAID (*Chem. Zentr.*, 1913, i, 2170; from *Zeitsch. Gärungsphysiol*, 1913, **2**, 107—109. Compare Pasquero and Cappa, A., 1912, ii, 103).—The furfuraldehyde formed on the distillation of wine cannot be derived from *l*-arabinose, since this pentose, when distilled with malic or tartaric acid, does not yield furfuraldehyde. An unknown pentose is assumed to be the source of the aldehyde. E. F. A.

The Advance and Prospects of the Newer Agricultural Chemistry (Chiefly Land Chemistry) since the Discoveries of Modern Physical Chemistry and Colloidal Chemistry Have been Employed. HANS BREHM (*Kolloid. Zeitsch*, 1913, **13**, 19—35).—The author considers the work which has been done in connexion with agricultural soil and the processes taking place in it, from the colloidal chemistry point of view. The various substances occurring in the soil are individually considered, and a long bibliography of the chief researches on the subject from 1901 to the present time is given. J. F. S.

Mineralogical Soil Analysis. WILLIAM J. MCCAUGHEY (*J. Ind. Eng. Chem.*, 1913, **5**, 562—564).—The potassium minerals usually present in soils are orthoclase, microcline, muscovite, and biotite. Muscovite is the most resistant, and probably contributes very little to the soil solution; biotite is the most readily decomposed. Orthoclase is the commonest, and occurs in amounts varying from 3 to 30%.

The commonest calcium minerals are epidote, hornblende, plagioclase, and garnet. Epidote is a normal constituent of most soils, whilst garnet, which is formed by contact metamorphism, occurs less frequently. Hornblende is the common calcium mineral, and weathers generally, forming chlorite.

Quartz crystals occur so frequently in limestone soils and are so exceptional in others, that their presence seems to indicate origin from limestone. N. H. J. M.

Quantitative Investigations on the Reaction of Aqueous Extracts of Soils. TEODOR SAIDEL (*Bull. Acad. Sci. Roumaine*, 1913, **2**, 38—44).—An electrical method for estimating the reaction of soil extracts is described with sketch of the apparatus employed. The difficulty due to loss of carbon dioxide when hydrogen is passed through the solution can be overcome by mixing the hydrogen with a definite amount of carbon dioxide, or else by boiling off the carbon dioxide.

The results of estimations obtained with several soils shows that there is a considerable difference in reaction between forest soils and the soils of the steppes on the one hand, and podsol soils on the other. N. H. J. M.

Alkaline Reactions Caused by Acids and their Acid Salts in Soils. GIULIO MASONI (*Chem. Zentr.*, 1913, i, 1999; from *Staz. sperim. agrar. ital.*, 1912, **46**, 219—240. Compare A., 1912, ii, 677).—Organic and mineral acids and their acid salts are able to cause an alkaline reaction in soils. In calciferous soils, calcium carbonate is formed, which in aqueous solution, on the addition of acid, parts with hydroxyl. The alkaline reaction may also be due to the action of acids on basic salts of magnesium, calcium, or aluminium. Acid alkali salts will give rise to alkali carbonates. The influence of the alkaline reaction on the biological function of the roots is discussed. E. F. A.

Behaviour of Amino-acids in the Soil. SAMUEL L. JODIDI (*Eighth Inter. Cong. App. Chem.*, 1912, **26**, 119—134. Compare A., 1911, ii, 820; 1912, ii, 292).—In connexion with a study of the proteins contained in soils, experiments have been undertaken to ascertain the rate at which amino-acids in the soil eliminate their nitrogen in the form of ammonia and whether the process is quantitative. In these experiments, definite quantities of various amino-acids were mixed thoroughly with weighed portions of soil and kept in covered vessels at 22—27°; after the lapse of some days the quantity of ammoniacal nitrogen formed was estimated. The various amino-acids yielded under these conditions the following maximum proportions of ammonia: glycine, 81·03%; alanine, 75·58%; leucine, 59·62%; aspartic acid, 72·74%; glutamic acid, 72·19%; phenylalanine, 54·31% tyrosine, 59·65% asparagine, 77·47%.

The results do not show whether amino-acids can be quantitatively de-aminated in the soil. It is possible that during the course of the process, some of the ammonia produced is oxidised to nitrites and nitrates. There are also other factors to be taken into consideration. It has been demonstrated, however, that the amino-acids examined readily lose nitrogen in the form of ammonia, and that the rate of the change is greatly influenced by the structure of the acids, acids of similar structure yielding about the same proportion of ammonia. E. G.

Normal and Abnormal Constituents of Soil Organic Matter. ELBERT C. LATHROP (*Eighth Inter. Cong. App. Chem.*, 1912, **15**, 147—151).—The following compounds may be considered as normally present in soils: pentosans, pentoses, histidine, xanthine, hypoxanthine, cytosine, and, perhaps, creatinine. Arginine and adenine only occur infrequently, whilst dihydroxystearic and picolinecarboxylic acids, being injurious to plants, must be classed as abnormal soil constituents.

It is uncertain whether agroceric, lignoceric, paraffinic and monohydroxystearic acids, agrosterol, phytosterol, and hentriacontane should be considered as normal or abnormal constituents of soils. N. H. J. M.

Organic Chemistry.

Determination of the Critical Constants of Methane. ETTORE CARDOSO (*Arch. Sci. phys. nat.*, 1913, [iv], **36**, 97—100).—Preliminary details are given of the apparatus employed in the determination of critical constants; the following values are found for methane: critical temperature, 82·85°; critical pressure, 45·60 atm.; critical density, 0·1623. J. F. S.

Preparation of Erythrene and Isoprene. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 261876).—When the hydrochlorides of δ-dimethylamino-Δ^{α}-*iso*amylene and of δ-dimethylamino-Δ^{α}-butylene (this vol., i, 342) are heated at 200—240°, they decompose into dimethylamine and isoprene or erythrene respectively. F. M. G. M.

Preparation of Halogenated Propanes. HENDRIK JACOBUS PRINS (D.R.-P. 261689).—Compounds of general formulæ C_3X_7H, $C_3X_6H_2$ and $C_3X_5H_3$ (where X is Cl or Br), are readily prepared from a mixture of halogenated methane and halogenated ethylenes (of formulæ CX_2:CHX and CHX:CHX) by mixing together in the required proportions in the presence of aluminium chloride or bromide at about 20°.

ααα βγγ-Hexachloropropane, CCl_3·CHCl·$CHCl_2$, obtained from chloroform (or carbon tetrachloride) and dichloroethylene, is a colourless liquid, b. p. 216°; when treated with alcoholic potassium hydroxide at the ordinary temperature, it gives rise to *ααβγγ-pentachloropropylene*, CCl_2:CCl·$CHCl_2$, b. p. 184°, from which *αββ-trichloroacraldehyde*, CCl_2:CCl·CHO, b. p. 164°, is obtained by the action of concentrated sulphuric acid, which latter can further be converted into *αβ-dichloroacrylic acid*, CHCl:CCl·CO_2H, and its *amide*, CHCl:CCl:CO·NH_2, m. p. 132°.

αααβγγγ-Heptachloropropane, CCl_3·CHCl·CCl_3, is an oil with a penetrating odour, m. p. 11—12°, b. p. 164—166°/90 mm., D^4 1·9, $n_D^{16·5}$ 1·5418, and in a similar manner furnishes *hexachloropropylene*, C_3Cl_6, b. p. 210°, and *trichloroacrylic acid.*

ααβγγ-Pentachloropropane, $CHCl_2$·CHCl·$CHCl_2$, a colourless liquid, b. p. 198—200°, gives rise to *αβγγ-tetrachloropropylene*,

CHCl:CCl·$CHCl_2$,

b. p. 165°, and the *aldehyde*, OH·CH:CCl·CHO, m. p. 145°.

ααβγγ-Pentabromopropane, $CHBr_2$·CHBr·$CHBr_2$, has b. p. 163—165°/18 mm. F. M. G. M.

Catalytic Action of Certain Manganese Salts on Alcohols (Spirits) in the Presence of Hydrogen Peroxide. A. C. CHAUVIN (*Ann. Falsif.*, 1913, **6**, 463—466).—The addition of 1% of hydrogen peroxide solution (perhydrol) to crude alcohol, spirits, and liqueurs, produces, after thirty days' contact, an increase in the quantities of the usual impurities (aldehydes, esters, higher alcohols, etc.), which were

present originally, but the furfuraldehyde tends to disappear. The action of the peroxide is augmented by the addition of about 0·01% of manganese salts, the acetate having the greatest effect. In the case of kirsch liqueur the hydrocyanic acid is decomposed by the treatment, whilst the essential oils present in absinthe are resinified. W. P. S.

Preparation of Esters from Alcohols and Organic Acids. OTTO HAUSER and ADOLF KLFOTZ (D.R.-P. 261878).—An account of work previously described (Hauser and Klotz, this vol., i, 246). tert.-*Butyl* n-*nonoate* has b. p. 242°, and tert.-*butyl* n-*octoate*, b. p. 231°.

F. M. G. M.

Alkylation of Ethyl Cyanoacetate. JOHN C. HESSLER (*J. Amer. Chem. Soc.*, 1913, **35**, 990—994).—The ethylation of ethyl cyanoacetate has already been studied (Hessler, A., 1908, i, 182; 1904, i, 830; Hadley, A., 1912, i, 699), and the author has now turned his attention to the substitution of other alkyl groups into this ester.

Crude ethyl α-cyanopropionate, obtained by the action of sodium ethoxide and methyl iodide on an alcoholic solution of ethyl cyanoacetate (Henry, A., 1887, 796), after shaking with 10% sodium hydroxide solution and subsequent fractionation yielded about 12% of ethyl α-cyano-α-methylpropionate, b. p. 77°/9 mm., 185°/ord. pressure, D^{26} 0·971. The sodium hydroxide extract contained α-cyanopropionic acid, b. p. 142—145°/11 mm., D^{20} 1·14, from the silver salt of which pure ethyl α-cyanopropionate, b. p. 89—90°/20 mm., 192—193°/ord. pressure, D^{22} 0·998, was obtainable by the action of ethyl iodide.

Crude ethyl α-cyano*iso*valerate, prepared in a similar manner to the above methyl derivative, was submitted to like treatment with sodium hydroxide; it yielded about 10% of ethyl α-cyano-α-*iso*propyl-*iso*valerate, b. p. 240°, $D^{29 \cdot 4}$ 0·918, and also cyano*iso*valeric acid, b. p. 166—168°/28 mm.; the silver salt of the latter reacted vigorously with ethyl iodide, giving pure ethyl α-cyano*iso*valerate, b. p. 113°/25 mm., 211°/739 mm., $D^{29 \cdot 2}$ 0·962.

Crude ethyl α-cyano-α-*iso*heptoate contained 28% of ethyl α-cyano-α-*iso*amyl*iso*heptoate, b. p. 158—159°/16 mm., D^{22} 0·909, which was unaffected by long standing with cold 10% sodium hydroxide solution; the sodium hydroxide extract yielded α-cyano*iso*heptoic acid, m. p. 47—48°, which was converted through the ammonium salt into the silver salt; this reacts with ethyl iodide, giving ethyl α-cyano*iso*-α-heptoate, b. p. 125°/12 mm., 241°/749 mm., D^{21} 0·939, which is readily hydrolysed by 10% sodium hydroxide solution.

α-Cyano-α-*iso*heptoamide, m. p. 142°, obtained by the action of concentrated ammonia solution on the ester, when heated in a vacuum with phosphorus pentachloride to 120—130° undergoes conversion into α-cyano-α-*iso*heptonitrile, b. p. 121—122°/18 mm., D^{25} 0·899.

D. F. T.

Glycerol Esters of Benzoic and Myristic Acids, and the Partial Saponification of Triglycerides. ANDREAS LIPP and P. MILLER (*J. pr. Chem.*, 1913, [ii], **88**, 361—394).—The author reviews

previous work on the hydrolysis of fats, and points out that, although it is now generally accepted that the hydrolysis of triglycerides takes place in stages with the intermediate formation of diglycerides and monoglycerides, only in the case of sulphuric acid as a hydrolytic agent has this view been placed beyond all doubt by the isolation of the intermediate products (compare Thieme, A., 1912, i, 333; Grün and Corelli, *ibid.*, 409). The work described in the present paper deals with the hydrolysis of tribenzoin and trimyristin by means of water and alkali hydroxides in aqueous, alcoholic and acetone solutions. It is definitely proved by the isolation of the corresponding di- and monoglycerides from the product obtained by partial saponification of the triglycerides, that in these cases also a similar hydrolysis in stages takes place.

When heated in sealed tubes at 225° in an atmosphere of carbon dioxide an equimolecular mixture of benzoic acid and glycerol yields as main product α-monobenzoin, which is freed from the accompanying αα-dibenzoin by taking advantage of its solubility in water; the latter compound forms the chief product if the benzoic acid is in excess (2 mols.).

In agreement with the observations of Thieme (A., 1912, i, 333) on the simultaneous formation of mono- and di-glycerides by the interaction of the sodium salts of acids and glycerol α-monochlorohydrin, the authors find that the latter compound reacts at 175° with sodium benzoate, yielding a mixture of α-mono- and αα-dibenzoin.

Glycerol αγ-dichlorohydrin and sodium benzoate at 190° give rise to α-monobenzoin, αα-dibenzoin, and tribenzoin. αα-Dibenzoin is an oil; the solid dibenzoin, described by Baumann (A., 1887, 229) and Grün (this vol., i, 157), probably consists of impure tribenzoin. The latter compound is obtained by shaking glycerol with benzoyl chloride (5 mols.) and aqueous sodium hydroxide at a low temperature. If less than this amount of benzoyl chloride is used, it is accompanied by varying amounts of mono- and di-benzoin (compare Baumann, *loc. cit.*, and Balbiano, A., 1903, i, 547).

The separation of mono-, di-, and tri-benzoin can be accomplished by taking advantage of the solubility of the monobenzoin in water and the greater solubility of the dibenzoin in alcohol as compared with that of the tribenzoin. When treated in alcoholic solution with 5% of the amount of potassium hydroxide, theoretically necessary for complete hydrolysis, and the mixture maintained for twenty-four hours at the ordinary temperature, tribenzoin undergoes complete decomposition into glycerol, ethyl benzoate, and potassium benzoate; if the reaction is allowed to proceed for only two minutes and the excess of potassium hydroxide at once neutralised by the addition of hydrochloric acid, then monobenzoin and dibenzoin are also formed.

The latter compounds were also isolated from the product obtained by partly hydrolysing the tribenzoin by means of potassium hydroxide in acetone at the ordinary temperature, and by heating with water in sealed tubes at 200°, both the water and potassium hydroxide being present in insufficient amount for complete hydrolysis. Partial saponification with 10% aqueous sodium hydroxide gave only di-

benzoin; the absence of the monobenzoin is referred to its solubility in water and consequent rapid hydrolysis by the sodium hydroxide.

When heated at 250° in sealed tubes in an atmosphere of carbon dioxide, a mixture of myristic acid and glycerol in equimolecular proportions yields trimyristin, *αα*-dimyristin and *α*-monomyristin, the latter compound forming the main product. The method adopted in separating the three compounds is based on the sparing solubility of the monomyristin in cold light petroleum, and the greater solubility in alcohol of the dimyristin in comparison with that of the trimyristin. Monomyristin (Krafft, A., 1904, i, 136) has m. p. 68°; when heated to 70° and allowed to cool slowly it solidifies at 54°; if the temperature is allowed to fall to 44° and the substance again heated, it has m. p. 55°; on further heating it solidifies at about 60° and then shows the original m. p. of 68°.

αα-Dimyristin has m. p. 64·5° (compare Grün and Theimer, A., 1907, i, 463; also *ibid.*, 464, and this vol., i, 159).

Trimyristin exists in two forms of m. p. 56·5° and 49° (compare Reimer and Will, A., 1885, 1197).

The results obtained in the partial hydrolysis of trimyristin resemble those described above in the case of tribenzoin. F. B.

The Glycerides of Butter Fat. CONRAD AMBERGER (*Zeitsch. Nahr. Genussm.*, 1913, **26**, 65—85).—Glycerides of definite composition were isolated from butter fat by subjecting the latter to fractional solution and crystallisation in ether. The most insoluble glyceride was found to consist of tristearin in the case of some butters; with other butters it was palmityldistearin.

Stearyldipalmitin was also obtained from butter fat, proving the presence of stearic acid. W. P. S.

Tripropionin. RUDOLF W. SEUFFERT (*Zeitsch. Biol.*, 1913, **61**, 551—553).—*Tripropionin* is readily obtained by the gradual addition of the calculated amount of propionic anhydride to glycerol heated at 150—165°. It has b. p. 177—182°/ca. 20 mm., n_D^{19} 1·43175. The compound is not formed by heating glycerol with propionic acid in the presence of sodium acetate, whilst, when propionyl chloride is employed under varying conditions, the product obtained invariably contains chlorine. H. W.

Catalytic Decomposition of Esters of Dibasic Organic Acids by Alumina. LOUIS MICHIELS (*Bull. Soc. chim. Belg.*, 1913, **27**, 227—230).—Senderens (this vol., i, 342) has observed that ethylene, carbon dioxide, carbon monoxide, and hydrogen are formed by the decomposition of ethyl succinate in the presence of alumina at 390° and 420°, and has surmised that a diketone may also be formed under these conditions. The author has investigated this action at 260°. The main gaseous product is ethylene mixed with some carbon dioxide. The distillate consists almost entirely of succinic anhydride. Diketones or their condensation products are only present in very small quantity, since the crude distillate is almost completely soluble in alkalis.

Similarly, ethyl glutarate under the influence of alumina at 270° yields mainly ethylene and glutaric acid. In one experiment, ethyl hydrogen glutarate was also isolated. In like manner, ethyl adipate at 300—320° yields an acid distillate. The general course of the reactions is shown by the equation :

$$CO_2Et{\cdot}[CH_2]_x{\cdot}CO_2Et = CO_2H{\cdot}[CH_2]_x{\cdot}CO_2H + 2C_2H_4.$$

H. W.

The Nitrogenous Constituent of Kephalin. A. BAUMANN (*Biochem. Zeitsch.*, 1913, **54**, 30—39).—The kephalin was hydrolysed with dilute hydrochloric or sulphuric acid at 60°. From the aqueous solution, after separation of the insoluble products and the glycerophosphates (by means of lead acetate), the salt of an organic base could be separated by means of alcohol, which contains the amino-groups pre-existent in kephalin. This could be identified by means of the auri- and platini-chlorides as hydroxyethylamine. S. B. S.

Catalytic Acceleration of the Absorption of Oxygen by Lecithin with Iron Salts. TORSTEN THUNBERG (*Zeitsch. physiol. Chem.*, 1913, **87**, 82); OTTO WARBURG (*Ibid.*, 83—84).—A claim for priority. Thunberg (A., 1910, ii, 323) had previously noticed that the oxidation of lecithin was accelerated by the presence of iron salts (compare Warburg and Meyerhof, this vol., i, 698). Thunberg also claims priority with reference to the influence of freezing and finely powdering the cells. Warburg denies this; he comes to precisely the opposite conclusions to Thunberg. E. F. A.

Preparation of Acetic Acid. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 261589).—The oxidation of acetaldehyde to acetic acid by air or oxygen proceeds satisfactorily at 70—100° or at lower temperatures (30—80°) in the presence of a catalyst, such as ferrous oxide, uranium oxide, acetic anhydride, or acetyl chloride.

F. M. G. M.

Decomposition of Trichloroacetic Acid by Mercuric Oxide. KURT BRAND (*J. pr. Chem.*, 1913, [ii], **88**, 342—357).—When mercuric oxide is added to a concentrated solution of trichloroacetic acid and the mixture heated to boiling, a vigorous reaction occurs, resulting in the formation of carbon monoxide, carbon dioxide, chloroform, hydrogen chloride, mercuric and mercurous chlorides; at 60° the reaction proceeds according to the equation :

$$2CCl_3{\cdot}CO_2H + 5HgO = 4CO_2 + 4HgCl + HgCl_2 + H_2O.$$

The author considers that the mercuric trichloroacetate first produced decomposes into dichloromethylene, carbon dioxide, and mercuric chloride, thus: $Hg(CCl_3{\cdot}CO_2)_2 = 2CCl_2 + 2CO_2 + HgCl_2$, the dichloromethylene being converted by the action of water into dihydroxymethylene, which is transformed at 60° into formic acid, and at 100° into formic acid and carbon monoxide. The formic acid is then oxidised by the mercuric chloride to carbon dioxide. The formation of chloroform during the reaction is referred to the decomposition of free trichloroacetic acid, formed from the mercuric trichloroacetate, either by hydrolysis or by the action of hydrochloric acid. F. B.

Cholic Acid. III. MARTIN SCHENCK (*Zeitsch. physiol. Chem.*, 1913, **87**, 59—73. Compare A., 1910, i, 10; 1911, i, 10).—A re-investigation of cilianic acid and its methyl ester (compare Pregl, A., 1903, i, 318) establishes it as a tetrabasic acid, $C_{24}H_{34}O_{10}$ or $C_{24}H_{32}O_{10}$, the ester being a tetramethyl derivative. Cilianic acid is accordingly an oxidation and not a degradation product of cholic acid. The carbon dioxide formed during the oxidation is derived from the decomposition of part of the cilianic acid. E. F. A.

Senecioic Acid. YASUHIKO ASAHINA (*Arch. Pharm.*, 1913, **251**, 355—356).—Senecioic acid, $C_5H_8O_2$, the unsaturated acid obtained from the rhizomes of *Ligularia tussilaginea* (*Senecio kaempferi*) is proved to be identical with $\beta\beta$-dimethylacrylic acid by the direct comparison of the two acids, m. p. 69—70°, and of their calcium salts, $(C_4H_7\cdot CO_2)_2Ca,4H_2O$. C. S.

Action of Cyanides on Aldehydes and Ketones. HARTWIG FRANZEN and WALTER RYSER (*J. pr. Chem.*, 1913, [ii], **88**, 293—306). —It has been shown previously (A., 1909, i, 804) that ethyl acetoacetate, ethyl benzoylacetate, and acetylacetone, when shaken with aqueous solutions of calcium, barium, strontium, and magnesium cyanides, yield crystalline salts, which were considered to be metallic derivatives of cyanohydrins, having a similar structure to that of the calcium derivative of mandelonitrile, obtained by the action of calcium cyanide on benzaldehyde.

The authors now find that the products are not nitriles, but the metallic derivatives of the ketonic esters and diketone.

The preparation of the calcium, barium, strontium, and magnesium derivatives of ethyl acetoacetate, and the *calcium*, *strontium*, and *magnesium* derivatives of acetylacetone is described.

The metallic derivatives of ethyl benzoylacetate decompose very rapidly, and, therefore, could not be isolated in a pure condition.

The calcium derivative of mandelonitrile, $Ca(O\cdot CHPh\cdot CN)_2$, has been obtained in a state of purity by using an aqueous solution of calcium cyanide, prepared from calcium hydroxide and hydrocyanic acid, instead of the mixture of calcium chloride and potassium cyanide employed previously (*loc. cit.*). Its constitution has been established by its conversion into the benzoyl derivative of madelonitrile by the action of benzoyl chloride.

The *calcium* derivative of *o*-chloromandelonitrile, prepared from *o*-chlorobenzaldehyde and aqueous calcium cyanide, forms a light yellow powder.

The *calcium* derivatives of *p*-methylmandelonitrile and *p*-methoxymandelonitrile are also described.

The colourless, crystalline substance obtained by Kohn (A., 1900, i, 205) by the action of calcium cyanide on formaldehyde in aqueous solution is considered to have the constitution

$$Ca[O\cdot CH(CN)\cdot Ca\cdot OH]_2.$$

Acetaldehyde yields a similar crystalline compound,

$$Ca[O\cdot CMe(CN)\cdot Ca\cdot OH]_2.$$

The action of potassium cyanide on acetaldehyde in aqueous solution results in the formation of alanine and α-iminodipropionic acid.

F. B.

The Action of Silicon Tetrachloride on Aldehydes and Ketones. JAMES N. CURRIE (*J. Amer. Chem. Soc.*, 1913, **35**, 1061).—It has been observed that a mixture of pure acetone with silicon tetrachloride in a few hours sets to a gelatinous mass, which when broken up with water gives a brown oil consisting mainly of mesityl oxide.

Analogous results were obtained in qualitative experiments with other aldehydes and ketones. D. F. T.

Photochemical Synthesis of Carbohydrates. JULIUS STOKLASA, JOHANN ŠEBOR, and WENZEL ZDOBNICKÝ (*Biochem. Zeitsch.*, 1913, **54**, 330—332. Compare this vol., i, 18).—A further reply to the criticisms of Walther Löb (this vol., i, 250).

Behaviour of Cellulose Towards Pure Nitric Acid. II. CARL HAEUSSERMANN (*Zeitsch. angew. Chem.*, 1913, **26**, 456. Compare *Zeitsch. angew. Chem.*, 1910, **23**, 1761).—"Sulphite cellulose" is converted by cold concentrated nitric acid into nitrates without undergoing marked structural change. Treatment with nitric acid, D 1·495, 1·48, 1·47, 1·46 and 1·40, leads to the formation of nitrates containing 11·1%, 9·6%, 8·0%, 7·5%, and 2·3% of nitrogen respectively. "Sulphite cellulose" dissolves readily in warm concentrated nitric acid, and the solution, when poured into cold water, yields an amorphous product, part of which is soluble in a mixture of alcohol and ether.

Hydrocellulose prepared from cotton when treated with nitric acid, D 1·5, 1·485, 1·48, and 1·40, yields hydrocellulose nitrates containing 13·0%, 9·5%, 8·9%, and 2·3% of nitrogen respectively, whilst hydrocellulose nitrates containing 11·2%, 8·8%, 6·6%, and 2·1% of nitrogen are obtained by the action of nitric acid, D 1·495, 1·48, 1·45 and 1·40 respectively, on hydrocellulose prepared from "sulphite cellulose."

The esters derived from "sulphite cellulose" closely resemble those derived from cotton in their behaviour towards solvents, but the higher cellulose and hydrocellulose nitrates prepared from "sulphite cellulose" are not completely soluble in acetone. W. H. G.

Benzoyl Esters of Cellulose. HERMANN OST and F. KLEIN (*Zeitsch. angew. Chem.*, 1913, **26**, 437—440. Compare Hauser and Muschner, this vol., i, 363; Briggs, this vol., i, 594).—An investigation on the benzoylation of cellulose, carried out primarily with the object of preparing a tribenzoate corresponding with the triacetate and trinitrate of cellulose.

Cellulose when treated with alkali hydroxide and benzoyl chloride yields a mixture of benzoates, the benzoic acid content of which is between 0 and 77%, and is dependent mainly on the proportions in which the reacting substances interact and to a slight degree on the physical state of the cellulose employed. A maximum yield of 218% of product is obtained by using a 22·4% sodium hydroxide solution in

the molecular proportions of 30 of sodium hydroxide to 1 of cellulose and 3 of benzoyl chloride to 4 of sodium hydroxide, whilst by using a 31·4% potassium hydroxide solution a maximum yield of 211% of product is obtained, the molecular proportions being the same as those just cited. The yields of product increase regularly with increase in the concentrations of the alkali up to the strengths quoted; at higher concentrations of the alkali the yields gradually decrease, and curves representing the relationship between alkali concentration and percentage of benzoic acid in the product do not show a "break" as do curves connecting alkali concentrations with the proportion of sodium combined with the cellulose (compare Vieweg, A., 1907, i, 893). A second and third treatment with alkali and benzoyl chloride increases the yield to 224% and 226% respectively, but it has not been found possible by the Schotten-Baumann method to pass beyond these values; the portion of the latter product soluble in chloroform contained 72·7% of benzoic acid, corresponding approximately with 2·5 benzoyl groups to the $C_6H_{10}O_5$ complex.

The crude benzoates may be fractionally separated by solvents; chloroform extracts 5 to 10% of a mixture containing 68 to 70% benzoic acid; aniline extracts from the portion insoluble in chloroform a mixture containing 61 to 65% of benzoic acid, whilst aniline-phenol (1 : 1) extracts from the residue a mixture containing 59 to 60% of benzoic acid.

Benzoates containing up to 77% of benzoic acid (a tribenzoate would contain 77·2%) are obtained by treating cellulose with benzoyl chloride in the presence of nitrobenzene and pyridine at 110—130°; the highest esters are formed when the quantity of pyridine employed is insufficient to keep the solution basic or neutral.

Solutions of cellulose benzoates in chloroform are dextrorotatory; the following values are given: tribenzoate, $[\alpha]_D$ 26—27°; ester with 70—72% of benzoic acid, $[\alpha]_D$ 20—22°.

Mercerised cellulose does not react more readily than finely divided cotton. Cellulose regenerated from "young" viscose is more reactive than that from "old" viscose; the benzoate from the former gave elastic films, whilst the benzoate from the latter gave films which were very brittle.

The yield of benzoate from hydrocellulose is less than that from cellulose, but 50% of the product containing 71—72·4% of benzoic acid is soluble in chloroform. W. H. G.

Chemical Reactions Induced by Bacteria aceti. H. J. WATERMAN (*Chem. Weekblad*, 1913, **10**, 718—730).—*B. aceti* isolated at low temperature rapidly transform aldoses, such as dextrose and galactose, into the corresponding monobasic acids, but has no action on ketoses. *B. aceti* isolated at high temperature does not react with either aldoses or ketoses. A summary of previous work on the action of *B. aceti* is given. A. J. W.

***d*-Ribose.** W. ALBERDA VAN EKENSTEIN and JAN J. BLANKSMA (*Chem. Weekblad*, 1913, **10**, 664).—*d*-Ribose has been synthesised by converting *d*-gluconic acid into *d*-arabinose by the action of hydrogen peroxide, transformation of the pentose into *d*-arabonic acid by means

of bromine water, and conversion of this acid into *d*-ribonic acid by heating with pyridine. The ribonic acid was separated from arabonic acid by fractional crystallisation of the phenylhydrazides, and had m. p. 80° and $[\alpha]_D$ $+18{\cdot}4°$. On reduction with sodium amalgam, it yielded *d*-ribose, purified by conversion into its *p*-bromophenylhydrazone, m. p. 164°. The hydrazone was transformed into *d*-ribose by the action of benzaldehyde. It forms colourless, hygroscopic crystals, m. p. 95°, $[\alpha]_D$ $-21{\cdot}5°$. A. J. W.

The Oxidation of *d*-Glucose in Alkaline Solution by Air as Well as by Hydrogen Peroxide. J. W. E. GLATTFELD (*Amer. Chem. J.*, 1913, **50**, 135—157).—The author has repeated the oxidation of α-glucose by hydrogen peroxide and air in potassium hydroxide solution, and finds that in addition to glycollic acid, formic acid and carbon dioxide, isolated by Spoehr (A., 1910, i, 221) from the oxidation product, *d*-erythronic, *l*-threonic and *dl*-glyceric acids are produced.

Spoehr's α-hydroxymethyl-*d*-arabonic acid is found to be identical with *d*-arabonic acid.

The formation of the latter acid proves that glucose in the form of its $\alpha\beta$-dienol, $HO{\cdot}CH{:}C(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}OH$, dissociates into hydroxymethylene, $HO{\cdot}CH{:}$, and the methylenenol of *d*-arabinose, ${:}C(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}OH$, which is then oxidised to *d*-arabonic acid. Oxidation of the dissociation products of the $\beta\gamma$-dienol,

$$HO{\cdot}CH_2{\cdot}C(OH){:}C(OH){\cdot}CH(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}OH,$$

gives rise to glycollic, *d*-erythronic and *l*-threonic acids, whilst the glyceric acid is formed by the dissociation and subsequent oxidation of the $\gamma\delta$-dienol, $HO{\cdot}CH_2{\cdot}CH(OH){\cdot}C(OH){:}C(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}OH$ (compare Nef, A., 1908, i, 5).

For details of the method employed in separating the oxidation products, the original must be consulted.

The following new salts are described: *cinchonine* d-*arabonate*, m. p. 170—180°, $[\alpha]_D^{20}$ $+120{\cdot}3°$ in water, and the corresponding *strychnine* salt, decomp. 167—170°, $[\alpha]_D^{20}$ $-26{\cdot}08°$, *quinine* salt, m. p. 172—173°, $[\alpha]_D^{20}$ $-106{\cdot}2°$, and *brucine* salt, m. p. 167—170°, $[\alpha]_D^{20}$ $-26{\cdot}33°$.

The *strychnine* salt of *d*-erythronic acid has m. p. 198—199°, $[\alpha]_D^{20}$ $-16{\cdot}84°$; the *quinine* salt, m. p. 166°, $[\alpha]_D^{20}$ $-106{\cdot}9°$. F. B.

Biochemical Synthesis of Galactosides of Alcohols. V. β-*iso*Butylgalactoside. ÉMILE BOURQUELOT and MARC BRIDEL (*J. pharm. chim.*, 1913, [vii], **8**, 108—109).—A mixture of 95 parts of *iso*butyl alcohol by weight and 5 parts of water was kept for four months with galactose and emulsin. β-iso*Butylgalactoside* was obtained in colourless needles of bitter taste, $[\alpha]_D$ $-11{\cdot}23°$. E. F. A.

Phosphates of Magnesium and Amines. LÉONCE BARTHE (*Bull. Soc. chim.*, 1913, [iv], **13**, 821—824).—The only double phosphate of magnesium and amines that has been prepared is magnesium methylamine phosphate (Barthe, A., 1905, i, 546; François, A., 1908,

i, 505). Unsuccessful attempts to prepare the corresponding salt from ethylamine are now described.

When ethylamine is added to a solution of magnesium hydrogen phosphate in dilute phosphoric acid in quantity more than sufficient for saturation, a colloidal precipitate is formed which becomes crystalline after several hours and consists entirely of magnesium phosphate. The mother liquors, when concentrated, deposit ethylamine phosphate and a further quantity of magnesium phosphate. If an excess of ethylamine is avoided, a crystalline precipitate is obtained after some hours, analysis of which shows it to be a mixture of magnesium ethylamine phosphate and magnesium phosphate or of ethylamine phosphate and magnesium phosphate. When the phosphoric acid is replaced by hydrochloric or sulphuric acids, magnesium phosphate is similarly precipitated. Analogous results are obtained by the solution of magnesium hydrogen phosphate in ethylamine hydrochloride and subsequent addition of the free amine.

Magnesium hydrogen phosphate, $MgHPO_4,7H_2O$, is most readily obtained by mixing equal volumes of 2% magnesium sulphate solution and 3% disodium hydrogen phosphate solution. A gelatinous precipitate is immediately obtained, which is rapidly transformed into a mass of fine needles. H. W.

Preparation of the Nitrites of the Primary, Secondary, and Tertiary Amines by the Interaction of the Hydrochlorides of the Bases and Alkali Nitrites. PANCHANAN NEOGI (*Chem. News*, 1913, **108**, 53—55, 62—65).—A full account of work of which an abstract has already appeared (P., 1913, **29**, 112). W. G.

The Double Cadmium and Mercuric Iodides of Substituted Ammonium Bases. RASIK LAL DATTA (*J. Amer. Chem. Soc.*, 1913, **35**, 949—955).—The following cadmium compounds were prepared either by adding cadmium chloride to an excess of the substituted ammonium iodide (compare T., 1913, **103**, 426), or by mixing solutions of cadmium iodide and the ammonium iodide in the requisite proportions. Two types of salts are obtained, namely, $2NR_4I,CdI_2$ and NR_4I,CdI_2, of which the latter is produced only in exceptional cases. The salts are white powders, sparingly soluble in water.

The double salts of cadmium iodide with *tetramethylammonium*, *tetraethylammonium*, p-*tolyltrimethylammonium*, *pyridinium*, *a-picolinium*, and *quinolinium* iodides are of the type $2NH_4I,CdI_2$; *tetrapropylammonium iodide* gives the salt NPr_4I,CdI_2.

When an aqueous solution of mercuric chloride is added to an excess of alkylammonium iodide, a white to yellowish-white precipitate is formed, of the type $2NR_4I,HgI_2$. If the addition of mercuric chloride be continued, the precipitate changes to yellow and the salt is of the type $2NR_4I,3HgI_2$; further addition of mercuric chloride gives mercuric iodide. A solution of mercuric iodide in potassium iodide may be used instead of mercuric chloride; when the interacting solutions are strong, the type $2NR_4I,HgI_2$ is produced, but this is decomposed by water and changed to the type $2NR_4I,3HgI_2$, which is the most stable of all, and is prepared by the interaction of dilute

solutions, using an excess of potassium mercuric iodide solution. The following substituted ammonium iodides give salts of both types: *Tetramethylammonium*, *tetraethylammonium*, and *trimethylsulphonium* (compare Smiles, T., 1900, **77**, 160) *iodides*. The following iodides give salts of the type $2NR_4I,HgI_2$: *tetrapropylammonium*, p-*tolyltrimethylammonium*, *pyridinium* and *quinolinium iodides*. p-*Tolyltrimethylammonium iodide* also gives the salt, $C_6H_4Me\cdot NMe_2I,HgI_2$.

The above salts, for the most part, vary in colour from a pale to a bright lemon yellow. They are all decomposed quantitatively into mercuric iodide on boiling with dilute nitric acid. T. S. P.

Platini-iodides of Substituted Ammonium and Sulphonium Bases. RASIK LAL DATTA (*J. Amer. Chem. Soc.*, 1913, **35**, 1185—1188).—It is found that although the platini-iodides of sodium and of the alkaline-earth metals cannot be obtained as precipitates by the interaction of chloroplatinic acid with concentrated solutions of the iodides (Datta, T., 1913, **103**, 426), this method proves very convenient for the preparation of the platini-iodides of potassium, ammonium, and the amines. The method failed with hydrazine hydriodide on account of the reduction of the chloroplatinic acid to metallic platinum. In other cases the condition necessary to success is the employment of an excess of the iodide of the metal or base.

The following substances were prepared: potassium platini-iodide, very soluble, black, crystalline powder; ammonium platini-iodide, black powder; *dipropylammonium platini-iodide*, black; *tetrapropylammonium platini-iodide*, chocolate coloured; *a-picolinium platini-iodide*, black; *quinolinium platini-iodide*, jet black; *trimethylsulphonium platini-iodide*, black powder; *triethylsulphonium platini-iodide*, chocolate coloured.

D. F. T.

Non-equivalence of the Five Valencies of Nitrogen. EMIL FROMM (*Annalen*, 1913, **399**, 366—370).—By reason of the great importance of the subject, Meisenheimer's recent proof (this vol., i, 595) of the non-equivalence of the five valencies of the nitrogen atom must be submitted to searching criticism before being accepted. The author is of opinion that Meisenheimer's experiments can be interpreted in another, and more probable, manner. Meisenheimer assumes that hydrogen chloride and methyl iodide both attack trimethylamine oxide at the same point and in the same manner, yielding the additive compounds $NMe_3{<}^{OH}_{Cl}$ and $NMe_3{<}^{OMe}_{I}$ respectively. From the former by the action of sodium methoxide, and from the latter by moist silver oxide, are obtained the substances $NMe_3{<}^{OH}_{OMe}$ and $NMe_3{<}^{OMe}_{OH}$; the different behaviour of the two substances during decomposition is the foundation of Meisenheimer's proof of the difference of the fifth "uniqne" valency of nitrogen from the other four. The author takes exception to this. The two substances $NMe_3{<}^{OH}_{OMe}$

and $NMe_3<^{OMe}_{OH}$, being alcoholates of a very feeble base, $NMe_3(OH)_2$, must both be hydrolytically dissociated by water, and yield MeOH and $NMe_3(OH)_2$ if they have the constitutions given above. He is of opinion that hydrogen chloride and methyl iodide do not attack trimethylamine oxide in the same manner. With methyl iodide the oxide forms the methiodide, $NMe_3{:}O<^{Me}_{I}$; the product of the action of moist silver oxide is then $NMe_3{:}O<^{Me}_{OH}$, which would be expected to yield trimethylamine, formaldehyde, and water by its decomposition, as is actually the case.

The formula $NMe_3{:}O<^{Me}_{I}$ has been discussed and rejected by Meisenheimer (*loc. cit.*); the author, however, shows that the reasons for its rejection are insufficient. C. S.

Non-equivalence of the Five Valencies of Nitrogen. JAKOB MEISENHEIMER (*Annalen*, 1913, **399**, 371—376).—The author replies to Fromm's criticisms (preceding abstract). In answer to his contention that two isomeric compounds should be produced by the addition of hydrogen chloride at the double linking of trimethylamine oxide if the fourth and the fifth valencies of the nitrogen atom are fundamentally different, the author claims that the whole behaviour of ammonium compounds proves that four of the valencies of the nitrogen atom are negative and the fifth is positive; therefore, in the addition of hydrogen chloride to trimethylamine oxide, the negative chlorine will become attached only to the fifth positive valency of the nitrogen atom, and only one additive compound will be produced.

To Fromm's criticism that the two isomerides, $NMe_3<^{OH}_{OMe}$ and $NMe_3<^{OMe}_{OH}$, should both be hydrolysed by water, the author replies that only one, namely, that in which the methoxy-group is attached to the fifth positive valency of the nitrogen atom, should be hydrolytically dissociated; the other isomeride, in which the methoxy-group is bound by a negative valency, should be as little affected by water as is methoxylamine, $OMe{\cdot}NH_2$.

The author also criticises adversely Fromm's reasons for ascribing oxonium formulæ to substances of the types $NMe_3Cl{\cdot}OMe$ and $NMe_3(OEt){\cdot}OMe$. C. S.

[Non-equivalence of the Five Valencies of Nitrogen.] EMIL FROMM (*Annalen*, 1913, **399**, 377).—The author agrees with Meisenheimer (preceding abstract) that in ammonium compounds the fifth "positive" valency of the nitrogen atom is different from the other four "negative" valencies, but is of opinion that the results of observations on ammonium compounds cannot be applied to the case of the amino-oxides without further consideration. He claims that in amino-oxides there are two "positive" valencies which differ from the other three "negative" valencies. C. S.

Decomposition of Glucosamine by Bacteria. EMIL ABDERHALDEN and ANDOR FODOR (*Zeitsch. physiol. Chem.*, 1913, **87**, 214—219).—Glucosamine hydrochloride, when decomposed by micro-organisms of the *B. subtilis* group, yields propionic acid and *d*-lactic acid. E. F. A.

Fermentative Decomposition of Creatinine. DANKWART ACKERMANN (*Zeitsch. Biol.*, 1913, **62**, 208—216).—Creatinine, mixed with a little dextrose and peptone, was inoculated with bacteria from a decomposing pancreas. Neither methyl- nor dimethyl-guanidine was formed, the main product of the change being 1-methylhydantoin, $CO<\begin{matrix}NH-CO\\ NMe\cdot CH_2\end{matrix}$. E. F. A.

The Changes Produced in Asparagine by Heating its Aqueous Solutions. FELIX EHRLICH and FRITZ LANGE (*Biochem. Zeitsch.*, 1913, **54**, 256—276).—By heating the ordinary asparagine with water for twelve hours and allowing the substance to crystallise out in fractions, a very small amount was obtained which has $[\alpha]_D^{20}$ 46·2°; this apparently *d*-asparagine (compare Erlenmeyer, this vol., i, 836). The authors also show that when asparagine solutions are heated, ammonia is evolved, and on crystallisation, crystals together with a non-crystallising syrup are obtained. The longer the heating takes, the smaller is the amount of crystals, the larger the amount of syrup obtainable, and the larger is the quantity of ammonia evolved. The uncrystallisable syrup is not readily freed from ammonia, and the evidence obtained indicates that it contains ammonium aspartate. The latter substance readily crystallises from water, but if its solution is heated, an uncrystallisable syrup is also obtained. It appears, therefore, to be an intermediate product produced by the action of heat on asparagine solutions. The actual nature of the final products has not yet been ascertained. S. B. S.

Resolution of *dl*-Aminohexoic Acid (Norleucine) into the Optically Active Components by means of the Formyl Compound. Polypeptides Derived from α-Aminohexoic Acid. EMIL ABDERHALDEN, C. FROEHLICH, and DIONYS FUCHS (*Zeitsch. physiol. Chem.*, 1913, **86**, 454—468).—*dl*-α-Aminohexoic acid, which E. Fischer resolved by means of the brucine salt, is readily resolved when the brucine salts of the formyl derivatives are crystallised. The acid, for which the name norleucine is proposed, has been combined with glycine and leucylglycine to form polypeptides in the usual manner.

Formyl-dl-*α-aminohexoic acid* crystallises in lustrous needles, which soften at 110—111°, m. p. 114°. The optical antipodes resemble each other very closely, crystallising in slender, lustrous, short or long needles aggregated in bunches. They soften at 111°, m. p. 114°, and have $[\alpha]_D^{20}$ − 15·85° and + 15·53° respectively.

Chloroacetyl-d-*norleucine* crystallises in colourless, transparent lamellæ, which soften at 70°, m. p. 104—106°, $[\alpha]_D^{20}$ + 3·56°.

Glycyl-d-*norleucine*, $CH_3\cdot[CH_2]_3\cdot CH(CO_2H)\cdot NH\cdot CO\cdot CH_2\cdot NH_2$, forms

prisms growing into long needles, which become brown at 220°, sinter at 230°, m. p. 239—240°; they have $[\alpha]_D^{20}$ $-8.71°$.

Glycyl-l-*norleucine* is almost identical in crystalline form and behaviour on heating; it has $[\alpha]_D^{20}$ $+8.24°$.

Chloroacetyl-dl-*norleucine* forms long prisms, m. p. 104—107°.

Glycyl-dl-*norleucine* separates in fatty plates or bundles of prisms; it sinters at 210°, decomp. 215°.

α-*Bromo*iso*hexoylglycyl*-dl-*norleucine* crystallises in platelets, m. p. 140°.

dl-*Leucylglycyl*-dl-*norleucine* separates as a crystalline skin. It sinters at 220°, decomp. 250°. It could not be hydrolysed by means of yeast juice with any certainty. The same applies to glycyl-*dl*-norleucine. E. F. A.

Preparation of Derivatives of α-Bromo*iso*valeric Acid. ARTHUR LIEBRECHT (D.R.-P. 261877).—α-*Bromo*iso*valerylmethylamide*, needles, m. p. 103°, is obtained when α-bromo*iso*valeryl bromide is slowly dropped into a cooled 20% aqueous solution of methylamine (2 mols.); the corresponding *ethylamide*, needles, m. p. 120°, is prepared in a similar manner with ethylamine. F. M. G. M.

Action of Hydrazine Hydrate on Dicyanodiamide and Biuret. ROBERT STOLLÉ and K. KRAUCH (*J. pr. Chem.*, 1913, [ii], 88, 306—314).—The authors have investigated the action of hydrazine hydrate on dicyanodiamide under various conditions, and find that in addition to guanazole, obtained by Hofmann and Ehrhart (A., 1912, i, 919), the following substances may be formed: aminodicyanodiamidine, 1-amino-2:5-dehydrazino-1:3:4-triazole, carbohydrazide, aminodiguanide, mono-, di- and tri-aminoguanidine.

With the exception of guanazole and the triazole, all the above-mentioned substances were isolated in the form of their benzylidene derivatives by acidifying the product of the reaction with hydrochloric acid and shaking with benzaldehyde.

The action of hydrazine hydrate on dicyanodiamide, both at 40° and at the ordinary temperature, results in the formation of guanazole, diaminoguanidine and triaminoguanidine; if the reaction is carried out at 50°, these compounds are accompanied by aminoguanidine and *aminodiguanide*, which forms a *benzylidene* derivative, m. p. 287°, $NH:C(NH_2)\cdot NH(NH)\cdot NH\cdot N:CHPh$.

Guanazole is best prepared by heating a mixture of dicyanodiamide (1 mol.) and hydrazine hydrate ($2\frac{1}{2}$ mol.) at 60—70°; if the temperature is raised to 100—110°, carbohydrazide is formed simultaneously.

Nitrosoguanazole, $C_2H_4ON_6$, obtained as canary-yellow precipitate by the addition of sodium nitrite to a solution of guanazole in dilute acetic acid, is insoluble in the ordinary solvents, and on reduction with zinc dust and sulphuric acid yields guanazole and probably guanazine. When a large excess of hydrazine hydrate (5 mols.) is employed and the reaction carried out at 40°, dicyanodiamide yields guanazole and aminodicyanodiamidine (Thiele and Uhrfelder, A., 1899, i, 119); at the ordinary temperature, guanazole, mono-, di- and tri-aminoguanidine are formed, whilst at 70° 1-amino-2:5-hydrazino-1:3:4-triazole

(Stollé and Bowles, A., 1908, i, 474) is the main product. Excess of hydrazine hydrate at 100—110° leads to the formation of carbohydrazide.

When heated with hydrazine hydrate (4 mols.) at 108—118°, biuret yields the *hydrazine* salt of hydrazidicarboxylimide [2 : 5-diketotetrahydro-1 : 3 : 4-triazole], $\begin{matrix} NH\cdot CO \\ | \\ NH\cdot CO \end{matrix}\!\!>NH,N_2H_4$, which crystallises in needles, m. p. 195°, and is converted by shaking with benzaldehyde and dilute hydrochloric acid into benzalazine and hydrazidicarboxylimide (compare Pellizzari, A., 1895, i, 73); if the reaction is carried out at 80—85°, the hydrazine salt is accompanied by aminobiuret, which was isolated in the form of its benzylidene derivative, m. p. 207° (compare Thiele and Uhrfelder, A., 1899, i, 118). F. B.

Some Hydrazine Derivatives of Chloral and Trichloroacetic Acid. ROBERT STOLLÉ and FR. HELWERTH (*J. pr. Chem.*, 1913, [ii], 88, 315—318).—Chloralhydrazine (Knöpfer, A., 1911, i, 704; this vol., i, 703) is readily obtained by the gradual addition of hydrazine hydrate to a well cooled ethereal solution of chloral hydrate. It separates from alcohol in white needles, m. p. 100° (Knöpfer gives 85°), and decomposes when kept, yielding hydrazine hydrochloride. With benzaldehyde in aqueous solution it forms the *benzylidene* derivative, $CCl_3\cdot CH(OH)\cdot NH\cdot N\!:\!CHPh$, crystallising in small needles, m. p. 65° (decomp.).

s-Bistrichloroacetylhydrazide, m. p. 195°, $N_2H_2(CO\cdot CCl_3)_2$, prepared by heating hydrazine monohydrochloride with trichloroacetyl chloride on the water-bath (compare L. and P. Spiegel, A., 1907, i, 507), reacts with alcoholic silver nitrate and ammonia, yielding a yellow *silver* derivative, and when heated with phosphorus pentachloride or thionyl chloride is converted into 2 : 5-*bistrichloromethyl*-1 : 3 : 4-*oxadiazole*, $CCl_3\cdot C\!<\!\begin{matrix} N\!:\!N \\ O \end{matrix}\!>\!C\cdot CCl_3$, which has m. p. 121°/9 mm., and separates from ether in long prisms, m. p. 48°. F. B.

isoButyl Ester of Phosphorous Acid. I. ALEXANDER E. ARBUZOV and A. A. IVANOV (*J. Russ. Phys. Chem. Soc.*, 1913, 45, 681—690).—*Di*iso*butylphosphorous acid*, $P(O\cdot C_4H_9)_2OH$, obtained by Arbuzov's method for obtaining esters of this type (A., 1907, i, 8, 174, 275), is a colourless, mobile liquid with a pleasant, fruity odour, b. p. 117·5°/14 mm., 235—236°/760 mm., D_0^0 0·9941, D_{20}^{20} 0·9776, D_4^0 0·9940, D_4^{20} 0·9759. With metallic sodium it yields a sodium salt stable at high temperatures; the *silver* salt, $P(OC_4H_9)_2OAg$, was analysed.

iso*Butyl phosphite*, $P(O\cdot C_4H_9)_3$, separated from its mixture with the preceding compound (A., 1907, i, 8) by converting the latter into sodium salt and distilling, is a colourless, mobile liquid with an intense peculiar odour, b. p. 100·5°/4·5 mm., 234—235°/760 mm., D_0^0 0·9193, D_{20}^{20} 0·9052, D_4^0 0·9193, D_4^{20} 0·9036. It reacts with bromine according to the equations:

$$P(O\cdot C_4H_9)_3 + Br_2 = PBr_2(O\cdot C_4H_9)_3 = 2C_4H_9Br + PO_2\cdot O\cdot C_4H_9.$$

With cuprous iodide it forms the *compound*, $CuI,P(O\cdot C_4H_9)_3$, m. p. about 48°.

It is evident that the impossibility of separating the two esters, $P(O\cdot C_4H_9)_2\cdot OH$ and $P(O\cdot C_4H_9)_3$, by fractional distillation is due to the fact that the two liquids and mixtures of them have almost identical boiling points. T. H. P.

Isomeric Change of $P(OC_4H_9)_3$ into $C_4H_9\cdot PO(OC_4H_9)_2$. II. ALEXANDER E. ARBUZOV and A. A. IVANOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 690—694).—When heated with *iso*butyl iodide, *iso*butyl phosphite (see preceding abstract) undergoes isomeric change in accordance with the equations:

$$C_4H_9I + P(O\cdot C_4H_9)_3 = I\cdot P(C_4H_9)(O\cdot C_4H_9)_3 = PO(C_4H_9)(OC_4H_9)_2 + C_4H_9I.$$

The iso*butyl* iso*butylphosphite* thus obtained is a colourless, mobile liquid, b. p. 133·5—134°/10 mm., 258—259°/760 mm., D_0^0 0·9630, D_{20}^{20} 0·9475, D_4^0 0·9628, D_4^{20} 0·9459. The corresponding *iso*butylphosphorous acid was obtained in crystals, $2O{:}P(C_4H_9)(OH)_2,H_2O$, m. p. 124°; this acid was originally prepared by Hofmann (A., 1873, 883) as a waxy and evidently impure mass, m. p. 100°. T. H. P.

Compounds of Boric Acid and Mannitol. FERNANDO AGENO and ELENA VALLA (*Gazzetta*, 1913, **43**, ii, 163—174).—Solubility measurements indicate that the combination of boric acid and mannitol takes place in equimolecular proportions. The stability constant at 25° is 0·598; it decreases when the temperature increases. The concentration of the hydrogen ions in solutions of mannitoboric acid has been determined, the dissociation constant being of the same order of magnitude as those of the monobasic organic acids, and it is proportional to the concentration of the mannitol. The rotatory power of solutions of sodium metaborate and mannitol is proportional to the concentration of the mannitol. R. V. S.

Preparation of Readily Soluble Stable Compounds of Perborates. VEREINIGTE FABRIKEN FÜR LABORATORIUMSBEDARF (D.R.-P. 261633).—The following complex salts are prepared by mixing the required proportions of the components in aqueous solution and evaporating to dryness: *sodium borotartrates*, $C_4H_4O_6(BONa)$ or $C_4H_3NaO_6(BONa)$; *sodium borocitrates*, $(C_6H_5O_7)_2(BONa)_3$ or $(C_6H_4NaO_7)_2(BONa)_3$; *aluminium sodium tartrates*, $NaOAl(C_4H_4O_6)_2Na_2$ or $Al(C_4H_4O_6)_3Na_3$ When moist they are of a syrupy consistency, but can be dried to masses resembling water glass and then reduced to powder. F. M. G. M.

Preparation of Chlorobenzenedisulphonic Acid. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 260563).—When *p*-chlorobenzenesulphonyl chloride is heated with fuming sulphuric acid (4 parts) at 160—180° with continual stirring, it furnishes a chlorobenzenedisulphonic acid (compare A., 1892, 331). F. M. G. M.

Preparation of *meso***Halogenanthracene-β-sulphonic Acids.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 260562).—*Dichloroanthracenesulphonic acid*, a yellow powder, somewhat soluble in and exhibiting a blue fluorescence in water, is obtained when dichloroanthracene (1 part) in chloroform (100 parts) at 30° is treated with chlorosulphonic acid and the temperature subsequently maintained at 40° for four hours; the reaction can also be carried out in fuming sulphuric acid.

Dibromoanthracenesulphonic acid is obtained in a similar manner from dibromoanthracene. F. M. G. M.

Preparation of Iodo-derivatives of *p***-Hydroxy-β-phenylethylamine and of its** *N***-Alkyl Derivatives.** F. HOFFMANN-LA ROCHE & Co. (D.R.-P. 259193).—The iodo-derivatives of *p*-hydroxy-β-phenylethylamine have an enhanced therapeutic value. *Di-iodo*-p-*hydroxy-β-phenylethylamine*, glistening, colourless needles, m. p. 189—190°, is obtained when an aqueous solution of *p*-hydroxy-β-phenylethylamine is slowly treated with iodine and sodium hydroxide; any great excess of alkali is to be avoided during the reaction; the *hydriodide* separates in yellowish-brown leaflets, and is decomposed with sodium carbonate in the usual manner.

N-*Benzyl*-p-*hydroxy-β-phenylethylamine hydrochloride*,

$$OH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot NH\cdot CH_2Ph,HCl,$$

needles, m. p. 216°, is prepared from benzaldehyde and *p*-hydroxy-β-phenylethylamine with subsequent reduction (with sodium amalgam) of the Schiff *base*, $OH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot N\colon CHPh$; when treated with iodine, it furnishes N-*benzyldi-iodo*-p-*hydroxy-β-phenylethylamine*, yellow needles, m. p. 159—160° (decomp.).

Piperonyl p-*hydroxyphenylethylamine*, m. p. 115° (the *hydrochloride* has m. p. 219°), on similar treatment gives rise to a N-*piperonyldi-iodo*-p-*hydroxyphenylethylamine*, decomp. m. p. 165°. F. M. G. M.

Preparation of *N***-Alkylaryl Derivatives of** *p***-Hydroxy-β-phenylethylamines.** F. HOFFMANN-LA ROCHE & Co. (D.R.-P. 259874). —The Schiff base obtained from benzaldehyde and *p*-hydroxy-β-phenylethylamine (compare preceding abstract) has m. p. 148°; N-*benzyl*-p-*hydroxy-β-phenylethylamine* forms colourless needles, m. p. 143°; whilst the Schiff *base* (*loc. cit.*) prepared from piperonaldehyde and *p*-hydroxy-β-phenylethylamine has m. p. 151°.

When *p*-hydroxy-β-phenylethylamine is combined with veratraldehyde it furnishes a Schiff *base*, m. p. 114°, which on reduction gives rise to N-*veratryl*-p-*hydroxy-β-phenylethylamine*, m. p. 118°; the *hydrochloride* has m. p. 215°, whilst with salicylaldehyde it yields a Schiff *base*, yellow needles, m. p. 145°, and on reduction *N*-o-*hydroxybenzyl*-p-*hydroxy-β-phenylethylamine*, colourless needles, m. p. 115°.

F. M. G. M.

The Condensation of Vanillin and Piperonal with Certain Aromatic Amines. ALVIN S. WHEELER (*J. Amer. Chem. Soc.*, 1913, **35**, 976—978. Compare A., 1909, i, 673; 1908, i, 332; 1903, i, 246). —An extension of the earlier investigations. In boiling toluene

solution, vanillin slowly condenses with *p*-aminobenzoic acid with formation of *4-hydroxy-3-methoxybenzylidene*-p-*aminobenzoic acid*, deep yellow plates, m. p. 211—212°, which on recrystallisation from water separates as a brilliant red substance with one molecule of water; on expelling the water at 100° the original yellow colour is restored.

Vanillin condenses with ethyl *p*-aminobenzoate in boiling benzene solution, giving *ethyl 3-methoxy-4-hydroxybenzylidene*-p-*aminobenzoate*, thin, yellow plates, m. p. 145° (corr.).

Under similar conditions to the last, vanillin and *p*-anisidine produce *4-hydroxy-3-methoxybenzylidene*-p-*anisidine*, pale yellow crystals forming radiating clusters, m. p. 133·5° (corr.); with piperonal and *p*-anisidine, 3:4-*methylenedioxybenzylidene*-p-*anisidine*, very pale yellow needles, m. p. 117·5° (corr.), is obtained.

Piperonal and *p*-aminobenzoic acid condense slowly in boiling toluene solution, yielding 3:4-*methylenedioxybenzylidene*-p-*aminobenzoic acid*, pale yellow prisms, 233—234°. If the heating is less prolonged, or if an excess of the acid is taken, a *substance*, m. p. 171—173°, is obtained in considerable quantity.

When heated together in boiling benzene solution, piperonal and ethyl *p*-aminobenzoate undergo condensation to *ethyl* 3:4-*methylenedioxybenzylidene*-p-*aminobenzoate*, long, pale yellow needles, m. p. 109° (corr.). D. F. T.

Preparation of Benzoylchloroamide. RASIK LAL DATTA and TARAPADA GHOSH (*J. Amer. Chem. Soc.*, 1913, **35**, 1044—1045).—Benzoylchloroamide is conveniently prepared by passing chlorine into an aqueous suspension of powdered benzamide until a sample of the solid, after separation and recrystallisation, has m. p. 116°; the process usually occupies several hours.

If the method used by Bender (*Ber.*, 1882, **15**, 410) for the preparation of this substance is modified by adding acetic acid and then a concentrated solution of bleaching powder to an aqueous suspension of benzamide, the product is a *substance*, m. p. 153—163°.

D. F. T.

Molecular Rearrangements of Carbon Compounds. II. Aromatic (*N*)-Acylamines and the Beckmann Rearrangement. CLARENCE G. DERICK and J. H. BORNMANN (*J. Amer. Chem. Soc.*, 1913, **35**, 1269—1289. Compare Derick, A., 1910, i, 805).—Further experimental evidence is produced in favour of the decision in the earlier investigation that non-reversible intramolecular rearrangements of carbon compounds take place in the direction to decrease the ionisation constant. For the purpose of determination of the small ionisation constants of acylamines, a colorimetric method based on the colours produced with suitable indicators has been developed, by means of which the ionisation constant of sufficiently soluble acids and bases may be estimated with a mean error of 2%.

In accord with the view expressed above it is found that each of such substances as acetanilide, propionanilide, benzanilide, and chloroacetanilide, which do not rearrange to monoacylaminoketones, has a

lower ionisation constant (basic) than the corresponding isomeride of the latter type. On the other hand, the aromatic diacylamides, for example, diacetanilide and dipropionanilide, which can undergo rearrangement (Chattaway, T., 1904, 386, 1181, etc.), are found to have higher ionisation constants (acidic) than their isomerides, *p*-acetylaminoacetophenone and *p*-propionylaminopropiophenone, which ionise as bases.

The results generally indicate that acyl radicles derived from acids with ionisation constants between $1{\cdot}4 \times 10^{-5}$ and $1{\cdot}55 \times 10^{-3}$ at 25° must be twice substituted at the nitrogen atom of aniline before isomeric change will be possible.

In the case of the Beckmann rearrangement, which has been studied with acetophenoneoxime and benzophenoneoxime, it is again found that the ionisation constants (basic) of these substances are greater than those of acetanilide and benzanilide, into which they pass by isomeric change.

p-*Propionylaminopropiophenone*, long, colourless needles, m. p. 151° (corr.), was obtained by the action of propionyl chloride on *p*-aminopropiophenone, and also by warming propionylanilide with propionyl chloride and aluminium chloride in carbon disulphide. The method adopted by Čech (A., 1878, 51) proved unsatisfactory for the preparation of chloroacetanilide, and it was found that much better results were obtainable by allowing aniline and chloroacetic acid to react in cooled ethereal solution and keeping the resulting aniline chloroacetate with the calculated quantity of phosphoric oxide in a well stoppered bottle for several weeks. D. F. T.

A New Method of Synthesising the Higher Phenols. TREAT B. JOHNSON and WILLARD W. HODGE (*J. Amer. Chem. Soc.*, 1913, **35**, 1014—1023).—It is found that mixed ketones containing hydroxyl or alkyloxyl radicles in the benzene nucleus are readily and smoothly reducible by zinc amalgam and hydrochloric acid to form the corresponding alkyl-substituted phenols or ethers. The reaction appears to be a general one. Only those products which are described for the first time are mentioned below.

1-Acetyl-2 : 4-dihydroxybenzene is reduced by the above agent to 2 : 4-*dihydroxy*-1-*ethylbenzene*, prismatic crystals, m. p. 98—99°. The corresponding propionyl compound gives 2 : 4-*dihydroxy*-1-*propylbenzene* prisms, m. p. 82—83°.

2-Propionyl-1 : 4-dihydroxybenzene becomes converted into 1 : 4-*dihydroxy*-2-*propylbenzene*, microscopic needles, m. p. 86°. 2-*Propionyl*-1 : 4-*dimethoxybenzene*, a pale yellow oil, b. p. 167—169°/13 mm., obtained by the action of propionyl chloride and aluminium chloride on a solution of quinol dimethyl ether in light petroleum, on reduction yields 1 : 4-dimethoxy-2-propylbenzene (Thoms, A., 1903, i, 415).

It is noteworthy that whereas the reduction of 1-chloroacetyl-3 : 4-dihydroxybenzene by this new method proceeds satisfactorily giving a good yield of 3 : 4-dihydroxy-1-ethylbenzene, the action of zinc and hydrochloric acid, as has already been shown (Dziergowski, A., 1894, i, 73), leads only to the formation of 1-acetyl-3 : 4-dihydroxybenzene.

D. F. T.

Triphenylmethyl. XXIII. Tautomerism of the Hydroxytriphenylcarbinols. MOSES GOMBERG (*J. Amer. Chem. Soc.*, 1913, **35**, 1035—1042).—The conflicting results as to the properties of *p*-hydroxytriphenylcarbinol (Bistrzycki and Herbst, A., 1903, i, 639; 1904, i, 44; Baeyer and Villiger, A., 1903, i, 813; Auwers and Schröter, A., 1903, i, 820) are readily explicable when it is borne in mind that tautomerism has been observed with such related compounds as triphenylmethyl and the triarylcarbinyl haloids (A., 1909, i, 144). There exist two forms of hydroxytriphenylcarbinol, probably of the benzenoid structure, $OH\cdot CPh_2\cdot C_6H_4\cdot OH$, and the quinonoid structure, $CPh_2:C_6H_4<^{H}_{OH}$, respectively.

The hydroxycarbinol is best prepared by demethylating *p*-anisyldiphenylcarbinol with aluminium chloride in benzene. The product is digested with 3% sodium hydroxide solution, when, after filtration, the addition of excess of acetic acid precipitates the yellow quinonoid modification; this, after recrystallisation from 40—50% acetic acid, has m. p. 139—140°, whilst separation of the carbinol from the alkaline solution by addition of ammonium chloride solution gives the colourless benzenoid form, which, after crystallisation from aqueous alcohol containing a little ammonia, forms needles or plates, m. p. 157—159°, or sometimes 162—163° (compare Auwers and Schröter, *loc. cit.*).

The two forms are not physical isomerides, for a solution of each crystallises only in the original form even when inoculated with a crystal of the other. On heating the solids, the quinonoid modification commences to undergo dehydration below 60°, whilst the benzenoid modification begins to turn yellow in the neighbourhood of 100°, probably due to isomerisation, and simultaneously commences to lose water.

The yellow modification is always obtained when either form is crystallised from acetic acid, whilst the colourless modification is invariably the result if an alkaline solution is treated with ammonium chloride or if crystallisation is effected from alcohol containing some ammonia. Recrystallisation of either form from alcohol containing hydrochloric acid usually gives a mixture of yellow and colourless crystals, whilst alcohol alone induces tautomerisation but slowly.

Exposure to sunlight or ultraviolet radiation causes a fairly rapid and complete change of the colourless benzenoid to the yellow quinonoid tautomeride, so that, from analogy to the stereoisomeric ethylenic compounds, the latter is presumably the labile modification.

Hydrogen chloride is absorbed by both isomerides in the solid state with formation of the same chloride, $CPh_2:C_6H_4<^{Cl}_{OH}$, a deep red, iridescent solid apparently identical with the product of the action of hydrogen chloride on fuchsone; when treated with molecular silver this *p*-hydroxytriphenylcarbinyl chloride loses hydrogen chloride and gives rise to fuchsone.

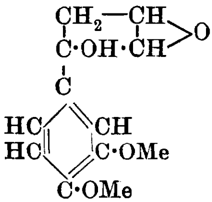
It is found that this behaviour is apparently general for the *p*-hydroxytriphenylcarbinols, and that, also, *o*-cresyldiphenylcarbinol (compare Bistrzycki and Zurbriggen, A., 1904, i, 44) gives two modifications which can be best isolated by the methods applied above;

there exists similar relations between the modifications of high and low m. p., as regards colour and behaviour towards light. D. F. T.

Identification of "Jambulol" as Ellagic Acid. FREDERICK B. POWER and THOMAS CALLAN (*Pharm. J.*, 1913, **91**, 245).—Further examination of the substance present in jambul seeds, to which the name "jambulol" was given previously by the authors (A., 1912, ii, 480) shows that it is identical with ellagic acid (compare T., 1905, **87**, 1412). W. P. S.

The Crystalline Deposit Occurring in the Timber of the "Colonial Beech" [Gmelina Leichhardtii, F.v.M.]. HENRY G. SMITH (*J. Roy. Sci. New South Wales*, 1913, **46**, 187—200).—The author has examined the white deposit which frequently fills the cells of the wood and accumulates in the cracks of *Gmelina Leichhardtii*; he proposes to name this, *gmelinol.* It separates from hot water in needle prisms or plates. In the crystalline state it has m. p. 122° (corr.) and, after cooling, solidifies to a transparent, resin-like substance, m. p. 62—63°. The latter m. p. remains unchanged after many weeks if the material is preserved in the glassy condition in the lump, but, if the fused substance is powdered, the m. p. immediately commences to rise, and, after a comparatively short time, has reached about 120—121°, but does not appear to revert quite to the m. p. of the original crystals. It has $[\alpha]_D$ $+123{\cdot}3°$ when dissolved in chloroform. It dissolves in 1470 parts of water at 22°. Analyses and determination of molecular weight indicate the formula $C_{12}H_{14}O_4$. Nitric acid converts it into a *dinitro*-compound, $C_{12}H_{12}O_4(NO_2)_2$, m. p. 128—129°. Sodium acetate and acetic anhydride transform it into a *monoacetyl* derivative, m. p. 110°.

When an excess of bromine water is added to an aqueous solution of the substance, a light drab *substance*, $C_{12}H_{13}O_4Br$, is formed, which is not distinctly crystalline, and melts at about 100°, after much darkening at about 90°. The bromine atom must have been introduced into the side-chain, since it can be eliminated by boiling with alcoholic silver nitrate solution. Zeisel determinations indicate the presence of two methoxy-groups, and this is confirmed by the production of veratric acid when the substance is oxidised by a solution of chromic acid in glacial acetic acid, or by alkaline permanganate. When fused with potassium hydroxide at a temperature not exceeding 200°, phenolic substances are formed, whilst, at 210—225°, protocatechuic acid is produced, together with small quantities of a volatile acid.



From the above experiments, and from the red and green colorations given by the vapour of the substance to pine wood moistened with hydrochloric acid, the author is led to propose tentatively the annexed formula for gmelinol. H. W.

Preparation of *N*-Monoalkyl Derivatives of *p*-Aminophenols. EMMANUEL MERCK (D.R.-P. 260234. Compare A., 1909, i, 222).—*N*-Alkyl derivatives of *p*-aminophenols are readily prepared by the

action of primary aliphatic amines on the alkali derivatives of quinol at a temperature of 200—250° for five to twenty hours, either in the presence or absence of condensing agents; this reaction, moreover, can be carried out in aqueous solution or in the absence of a solvent.

Details are given of several modifications of these methods for preparing *N*-methyl-*p*-aminophenol from methylamine and quinol in the presence of sodium ethoxide, or of sodium carbonate either with or without the addition of zinc chloride or other condensing agents. F. M. G. M.

Derivatives of Phenacyl Sulphide and their Stereoisomerism. EMIL FROMM and WILHELM SCHÖMER (*Annalen*, 1913, **399**, 353—365).—*Dibenzylidenediphenacyl sulphide*, $S(CBz{:}CHPh)_2$, m. p. 270°, leaflets, is obtained from phenacyl sulphide, benzaldehyde, and sodium hydroxide in 50% alcohol. Diphenacyl sulphide and bromine in chloroform at 0° yield at first a yellow precipitate of the unstable *diphenacyl sulphide dibromide*, but ultimately *dibromodiphenacyl sulphide*, $C_{16}H_{12}O_2SBr_2$, m. p. 107°, white crystals, is obtained. The *di-iodide*, $I_2S(CH_2{\cdot}COPh)_2$, m. p. 121°, red needles, is more stable, and is prepared in a similar manner.

Equal molecular quantities of diphenacylsulphoxide and phenylhydrazine in neutral or in acid solution yield *diphenacylsulphoxidephenylhydrazone*, $C_{22}H_{20}O_2N_2S$, m. p. 186°. Diphenacylsulphoxide and hydroxylamine hydrochloride, with or without sodium carbonate, yield *diphenacylsulphoxidedioxime*, $C_{16}H_{16}O_3N_2S$, m. p. 206°; no other oxime or dioxime has been obtained.

Dimethyldiphenacylsulphone has the symmetrical formula,

$$SO_2(CHMe{\cdot}COPh)_2,$$

since it is decomposed by boiling dilute sodium hydroxide into benzoic acid and diethylsulphone. Unlike diphenacylsulphone itself, dimethyldiphenacylsulphone does not condense with phenylhydrazine, semicarbazide, or hydroxylamine in acid, neutral, or alkaline solution. This inactivity apparently must be due to steric hindrance; it is not to be attributed to the existence of the sulphone in the form $SO_2(CMe{:}CPh{\cdot}OH)_2$, because the substance does not react with acetic anhydride, benzoyl chloride, or sodium and chlorodinitrobenzene.

Diphenacylsulphone and aqueous bromine in daylight yield *dibromodiphenacylsulphone*, $C_{16}H_{12}O_4Br_2S$, m. p. 186°, prisms, after eight days, and *tetrabromodimethylsulphone*, $SO_2(CHBr_2)_2$, m. p. 151°, and benzoic acid after three months. Dibromodiphenacylsulphone forms a *dioxime*, $C_{16}H_{14}O_4N_2Br_2S$, m. p. 184°, needles, by boiling with hydroxylamine hydrochloride (two equivalents) and sodium carbonate, and an *oxime*, $C_{16}H_{13}O_4NBr_2S$, m. p. 158°, white needles, by boiling with alcohol and hydroxylamine hydrochloride; isomeric oximes cannot be isolated.

The behaviour of the oximes and the dioximes of diphenacylsulphone has been partly described by Fromm and Flaschen. The dioxime, m. p. 204°, has the *syn.*-configuration (see below). It yields only an acetyl derivative with acetic anhydride, but by treatment with benzoyl chloride and sodium hydroxide is converted into a *dibenzoyl* derivative, $C_{30}H_{24}O_6N_2S$, m. p. 150°. The *anti*-dioxime has m. p. 209°, not 190°, as stated previously; it forms a *diacetyl* derivative, $C_{20}H_{20}O_6N_2S$,

m. p. 152°, and a *dibenzoyl* derivative, $C_{30}H_{24}O_6N_2S$, m. p. 168°. Its *anti*-configuration is proved by the behaviour of the dioxime with phosphorus pentachloride in boiling ether, whereby, after treatment with water, a *substance*, $C_{16}H_{16}O_4N_2S$, m. p. 215°, is obtained, which must be *sulphonediacetanilide*, $SO_2(CH_2{\cdot}CO{\cdot}NHPh)_2$, since it is decomposed into aniline and sulphuric and acetic acids by aqueous sodium hydroxide. Consequently the dioxime, m. p. 204°, must have the *syn.*-configuration, since the dioxime-anhydride, m. p. 167°, being formed from each of the phenacylsulphoneoximes, must have the *amphi*-configuration.

The configurations of the diphenacylsulphoneoximes follow from the preceding. The *syn.*-dioxime can only result from the *syn.*-oxime; the latter, therefore, must be the oxime, m. p. 144°, since this yields the *syn.*-dioxime by treatment with hydroxylamine hydrochloride and calcium carbonate. The oxime, m. p. 173°, must therefore have the *anti*-configuration.

syn.-Diphenacylsulphonedioxime is unchanged by rapid treatment with phosphorus pentachloride and ether. When the mixture is kept for many days, it yields, after treatment with water, a *substance*, $C_{16}H_{13}O_2N_2Cl_3S$, m. p. 174°, yellow crystals, which is probably trichlorodiphenacylsulphonedioxime or its transformation product, trichlorosulphonediacetanilide; the substance, which can also be obtained from the *anti*-dioxime, is receiving further examination. C. S.

Preparation of Condensation Products from Phenolsulphonic Acids. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 260379).—An account of the preparation of *compounds*, colourless powders, soluble in water, which are obtained by heating a mixture of *o*- and *p*-phenolsulphonic acids during twenty-four to seventy-two hours at 130—140° under 20 mm. with condensing agents, such as phosphorus trichloride or thionyl chloride. F. M. G. M.

α-Hydroxy-γ-phenylcrotonic Acid. J. BOUGAULT (*Compt. rend.*, 1913, **157**, 377—379).—The author puts forward an alternative constitution for the γ-hydroxyphenylcrotonic acid obtained from the α-hydroxy-acid by boiling in aqueous solution with oxalic acid (compare this vol., i, 727). From the behaviour of the new isomeride he is unable to decide between the two formulæ:

(I.) $HO{\cdot}CPh{:}CH{\cdot}CH_2{\cdot}CO_2H$ (II.) $HO{\cdot}CHPh{\cdot}CH{:}CH{\cdot}CO_2H$,

but is now inclined to support formula II, by reason of the behaviour of the acid on oxidation with potassium permanganate. Further, he notes that the original transformation is reversible. W. G.

Isomerisation of the α-Hydroxy-βγ-unsaturated Acids to γ-Ketonic Acids. J. BOUGAULT (*Compt. rend.*, 1913, **157**, 403—405. Compare Thiele, A., 1902, i, 152; Erlenmeyer, A., 1904, i, 1015).—The author considers that the transformation of α-hydroxyphenylcrotonic acid into *p*-benzoylpropionic acid takes place in two stages, namely: $CHPh{:}CH{\cdot}CH(OH){\cdot}CO_2H \longrightarrow HO{\cdot}CHPh{\cdot}CH{:}CH{\cdot}CO_2H \longrightarrow COPh{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$.

The first stage has already been shown to take place under the

influence of dilute acids (compare preceding abstract), and since the second step can be brought about equally well by acids and alkalis, the intermediate formation of lactones (compare Thiele and Erlenmeyer, *loc. cit.*) is not necessary. W. G.

Action of Light on Esters of α-Cyanocinnamylideneacetic Acid. II. MARIE REIMER and ELEANOR KELLER (*Amer. Chem. J.*, 1913, 50, 157—171).—In continuation of previous work (A., 1911, i, 447), the authors have examined the behaviour of the methyl, ethyl, propyl, *iso*propyl, and *iso*butyl esters of α-cyanocinnamylideneacetic acid on exposure to light, both in the solid condition and also in solution. Without solvent all the esters polymerise to a dimeric form, the reaction being practically quantitative, except in the case of the stable ethyl ester, which is considerably oxidised. In alcoholic solution only the methyl ester undergoes polymerisation; the ethyl ester is transformed into an unstable isomeride, whilst the remaining esters undergo slight oxidation. Similar results were obtained in benzene solution. The behaviour of the isomeric ethyl and *iso*butyl esters has also been studied. On exposure to light without solvent, the isomeric ethyl esters polymerise to dimeric forms, which are not identical but structurally isomeric (compare *loc. cit.*); at the same time the stable form is partly oxidised, whilst the unstable form is not.

In benzene and alcoholic solution the stable ethyl ester is transformed into the unstable isomeride; the reverse reaction does not take place. The isomeric *iso*butyl esters behave in a similar manner.

From these results the conclusion is drawn that the action of light on ethylenic compounds is determined, not only by the nature of the groups, but also by the spatial configuration of the molecule.

The anomalous behaviour of the cinnamylidene compounds described by Stobbe (this vol., i, 177) may be explained on the assumption that in this series, compounds of different configuration were compared.

The unstable ethyl α-cyanocinnamylideneacetate crystallises in flat, straw-coloured needles, m. p. 113°.

Propyl α-cyanocinnamylideneacetate, prepared by the condensation of cinnamaldehyde with propyl cyanoacetate by means of potassium propyloxide in propyl-alcoholic solution, forms long, flat, orange crystals, m. p. 107°, and is converted by light into *propyl* 1 : 3-*diphenyl*cyclo*butane*-2 : 4-*di-α-cyanoacrylate*,

$$CO_2Pr^{\alpha}\cdot C(CN){:}CH\cdot HC{<}{\begin{matrix}CHPh\\CHPh\end{matrix}}{>}CH\cdot CH{:}C(CN)\cdot CO_2Pr^{\alpha},$$

which crystallises in white needles, m. p. 107—108°, and is oxidised by potassium permanganate in acetone solution to α-truxillic, benzoic and oxalic acids.

iso*Propyl α-cyanocinnamylideneacetate*, prepared in a similar manner, forms lemon-yellow plates, m. p. 111—112°, and on exposure to light yields iso*propyl* 1 : 3-*diphenyl*cyclo*butane*-2 : 4-*di-α-cyanoacrylate*, crystallising in needles, m. p. 136°. The stable form of iso*butyl α-cyanocinnamylideneacetate*, prepared by esterifying the acid by the hydrogen chloride method, forms yellow plates, m. p. 114°, and is converted by light into iso*butyl* 1 : 3-*diphenyl*cyclo*butane*-2 : 4-*di-α-cyanoacrylate*, crystallising in glistening, white needles, m. p. 123°.

The unstable iso*butyl* ester is prepared by the condensation of cinnamaldehyde with *iso*butyl cyanoacetate. It forms yellow plates, m. p. 110—111°, and by boiling with an *iso*butyl-alcoholic solution of hydrogen chloride is transformed into the stable form. On exposure to light, it polymerises to a dimeric form, $C_{32}H_{34}O_4N_2$, m. p. 114—115°, the constitution of which has not yet been established. F. B.

Phototropy. II. FERDINANDO GRAZIANI and F. BOVINI (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 32—41. Compare this vol., i, 984).—The hydrazones described in the present paper of the type

R′R″N·N:CHR

are not phototropic, resembling in this respect those of the type R′R′N·N:CHR previously investigated. The phenomenon is therefore associated only with hydrazones of the type R′NH·N:CHR, and these must not contain a substituent in the ortho-position of the nucleus of the group R′. The explanation of the phototropy of the hydrazones would then be the mobility of the hydrazinic hydrogen atom, which is displaced to the ortho-position of the nucleus of the group R′ by waves of short length, whilst those of great length, including those of heat, reproduce the original, stable form of the hydrazone. Of the hydrazones mentioned in this paper, the following have not previously been prepared:

Cuminaldehydephenylmethylhydrazone, $MePhN·N:CH·C_6H_4·CHMe_2$, forms pale yellow needles, m. p. 54°.

Cinnamaldehydephenylmethylhydrazone, MePhN·N:CH·CH:CHPh, crystallises in intensely yellow needles, m. p. 114°.

Salicylaldehydephenylmethylhydrazone has m. p. 74° (Labhardt and V. Zembruski, A., 1900, i, 125, gave 71°).

Piperonaldehydephenylmethylhydrazone has m. p. 88° (Goldschmidt, A., 1897, i, 54, gave 85°).

p-*Tolualdehydephenylmethylhydrazone*, $MePhN·N:CH·C_6H_4Me$, crystallises in soapy, yellowish-green leaflets, m. p. 122°.

Vanillinphenylmethylhydrazone, $MePhN·N:CH·C_6H_4(OH)·OMe$, forms colourless needles, m. p. 122°.

Cinnamaldehydephenylbenzylhydrazone,

$CH_2Ph·NPh·N:CH·CH:CHPh$,

is a lemon-yellow, crystalline powder, m. p. 167—168°.

Piperonalphenylbenzylhydrazone, $CH_2Ph·NPh·N:CH·C_6H_3:O_2:CH_2$, forms pale yellow needles, m. p. 124°.

p-*Tolualdehydephenylbenzylhydrazone*, $CH_2Ph·NPh·N:CH·C_6H_4Me$, crystallises in colourless, silky needles, m. p. 123—124°.

Phenyl-β-naphthylhydrazine may be prepared by reducing the corresponding nitrosoamine with zinc and acetic acid.

Benzaldehydephenyl-β-naphthylhydrazone, $C_{10}H_7·NPh·N:CHPh$, forms yellow needles, m. p. 92—93°.

Anisaldehydephenyl-β-naphthylhydrazone,

$C_{10}H_7·NPh·N:CH·C_6H_4·OMe$,

crystallises in almost colourless, prismatic needles, m. p. 116—117°.

Cuminaldehydephenyl-β-naphthylhydrazone,

$C_{10}H_7·NPh·N:CH·C_6H_4·CHMe_2$,

forms colourless needles, m. p. 118°.

Cinnamaldehydephenyl-β-naphthylhydrazone,

$$C_{10}H_7\cdot NPh\cdot N:CH\cdot CH:CHPh,$$

forms pale yellow, acicular crystals, m. p. 156°.

p-*Tolualdehydephenyl-β-naphthylhydrazone* forms yellow, acicular crystals, m. p. 154°. R. V. S.

Reduction of Aromatic Ketones. JACOB BÖESEKEN and W. D. COHEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 91—99).—The authors have made an approximate quantitative study of the reduction of benzophenone by zinc dust and aluminium amalgam in neutral, faintly acid, faintly alkaline, and strongly alkaline alcoholic solutions. For this purpose, quantities of 5 grams of benzophenone were boiled under reflux for definite intervals, with the requisite amount of reducing agent in 50 c.c. of 80% alcohol, filtered hot, made up to 100 c.c., and shaken at 25° for a day. Benzopinacone, being practically insoluble, was then filtered off, if produced at all, and some of the filtrate was evaporated and the residue weighed and examined.

In a neutral solution, zinc dust had no action, but aluminium amalgam produced 32% of pinacone and 68% of pure benzhydrol. In a very faintly acid solution, in a current of carbon dioxide or in presence of ammonium chloride, zinc dust gave rise exclusively to the pinacone. In acetic acid solution both metals produced the pinacone, together with some pinacoline and diphenylmethane, but no benzhydrol. In presence of free ammonia the product was almost exclusively the hydrol, although a small amount of the pinacone was obtained. In a strongly alkaline solution the sole product with zinc dust was benzhydrol (compare Montagne, A., 1907, i, 14), whilst aluminium and magnesium amalgams and sodium gave, in addition, traces of diphenylmethane.

The chief controlling factor is therefore the reaction of the medium. As long as it is acid the pinacone is the sole product, but as soon as hydroxyl ions are present the hydrol appears. In the case of aluminium amalgam in aqueous alcohol it is assumed that a slight excess of these ions occurs at the surface of the metal. As the excess of hydroxyl ions increases, the pinacone can no longer exist, since it is easily converted into a mixture of benzophenone and benzhydrol,

$$[Ph_2COH]_2 \rightarrow Ph_2CH\cdot OH + Ph_2CO.$$

The first product of the reduction is assumed to be, in all cases, the half-pinacone, Ph_2COH; this would polymerise at once to the pinacone, which would remain unchanged, unless the concentration of hydroxyl ions were such that it would be resolved into the hydrol and the ketone with appreciable velocity. In alkaline solution the half-pinacone might also be reduced directly to the hydrol, but the above assumption would account for the occurrence of a little pinacone in solutions with very low hydroxyl-ion concentration.

The latter point was verified by the reduction of several substituted benzophenones by means of aluminium amalgam in 80% alcohol. The methoxy- and methyl groups appear to favour the formation of pinacone, but halogens in the nucleus, and especially a number of them, have the opposite effect; thus *pp'*-dichlorobenzophenone gave 96% of hydrol and 4% of pinacone. In dilute acetic acid solution with zinc

dust, however, it gave a quantitative yield of *tetrachlorobenzopinacone*, $C_{26}H_{18}O_2Cl_4$, m. p. 180°. J. C. W.

Action of Magnesium Phenyl Bromide on Di-α-bromo*iso*propyl Ketone. (Mlle.) ANNA I. UMNOVA (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 881—884).—From a study of the products obtained by the interaction of magnesium methyl bromide (or iodide) and di-α-bromo*iso*propyl ketone (this vol., i, 7), it is supposed that the reaction is represented by the equation:

$$CMe_2Br\cdot CO\cdot CMe_2Br + 2MgMeX = CH_3X + MgBrX + CMe_3\cdot CO\cdot CMe_2\cdot MgBr,$$

the action of water then yielding *iso*propyl *tert.*-butyl ketone. This supposition is supported by the liberation of a gas burning with a green flame when methyl bromide is employed, and by the formation of silver iodide when the ethereal extract of the products obtained with methyl iodide is treated with silver nitrate; the formation of methyl iodide was not, however, directly proved.

If, however, magnesium phenyl bromide is used in the reaction in place of the magnesium methyl compound, bromobenzene is found to be liberated. In one case, the complex magnesium ketonic compound was treated with water so as to yield α-phenyl*iso*propyl *iso*propyl ketone, and in another with carbon dioxide to give the corresponding β-ketonic acid.

*α-Phenyl*iso*propyl* iso*propyl ketone*, $CPhMe_2\cdot CO\cdot CHMe_2$, b. p. 118—119°/12 mm., 243—244°/760 mm., could not be obtained quite free from diphenyl. Its *bromo*-derivative, $C_{13}H_{17}OBr$, forms stout prisms, m. p. 64—65°, apparently containing alcohol of crystallisation, and has the normal molecular weight in freezing benzene.

The *ketonic acid*, $CPhMe_2\cdot CO\cdot CMe_2\cdot CO_2H$, m. p. 90—91° (decomp.), exhibits marked association in freezing benzene. Its *silver* salt was analysed. T. H. P.

Condensation Products of *m*-Methoxybenzaldehyde. HUGO BAUER and P. VOGEL (*J. pr. Chem.*, 1913, [ii], **88**, 329—342).—It has been shown previously (A., 1903, i, 479; 1904, i, 385; 1911, i, 881) that the introduction of alkyloxy-groups in the ortho- and para-position of the benzene nucleus in compounds of the type

$$CHPhBr\cdot CHBr\cdot R$$

is accompanied by a marked increase in the reactivity of the bromine atom adjacent to the aromatic group; the bromine atom is readily replaced by alkyloxy-groups when the dibromides are boiled in alcoholic solution.

The reactivating influence of the alkyloxy-groups is apparently confined to the ortho- and para-positions, for the dibromides of *m*-methoxystyryl methyl ketone and phenyl *m*-methoxystyryl ketone may be boiled with alcohol without undergoing change.

m-*Methoxystyryl methyl ketone*, $OMe\cdot C_6H_4\cdot CH:CH\cdot COMe$, obtained as an oil, b. p. 173°/8 mm., by the condensation of *m*-methoxybenzaldehyde with acetone in the presence of aqueous sodium hydroxide, forms a *semicarbazone*, slender, yellow needles, m. p. 197—198°, and a yellow, crystalline *phenylhydrazone*, m. p. 116—117°, which decomposes when kept and is converted by boiling in glacial acetic acid solution

into 1-*phenyl*-5-m-*methoxyphenyl*-3-*methylpyrazoline*,

$$\begin{matrix} CMe\cdot CH_2 \\ \| \\ N\text{——}NPh \end{matrix}\!\!>\!CH\cdot C_6H_4\cdot OMe,$$

m. p. 93—94°. It reacts with bromine (2 mols.), yielding *αβ-6-tribromo-α-3-methoxyphenylbutan-γ-one*, $OMe\cdot C_6H_3Br\cdot CHBr\cdot CHBr\cdot COMe$. This forms slender, white crystals, m. p. 112°, and when heated with pyridine loses hydrogen bromide with the formation of *β-6-dibromo-α-3-methoxyphenyl-Δ^{α}-buten-γ-one*, $OMe\cdot C_6H_3Br\cdot CH{:}CBr\cdot COMe$, which crystallises in extremely slender, colourless, down-like needles, m. p. 64°. The position of the bromine atom in the benzene nucleus of the preceding compounds has been established by the formation of 6-bromo-3-methoxybenzoic acid (Pschorr and others, A., 1912, i, 775) on oxidising the dibromo-compound with aqueous permanganate.

Phenyl m-*methoxystyryl ketone*, $OMe\cdot C_6H_4\cdot CH{:}CH\cdot COPh$, prepared by the condensation of *m*-methoxybenzaldehyde and acetophenone in alcoholic solution by means of sodium hydroxide has b. p. 247°/12 mm., m. p. 65°, and is converted by phenylhydrazine in boiling alcoholic solution into 1 : 3-*diphenyl*-5-m-*methoxyphenylpyrazoline*, which crystallises in slender, green needles, m. p. 98°, yields green, fluorescent solutions in alcohol and acetone, and is oxidised by aqueous potassium permanganate to 1 : 3-*diphenyl*-5-m-*methoxyphenylpyrazole*, $C_{22}H_{18}ON_2$, crystallising in large, yellow needles, m. p. 140°.

It reacts with bromine in glacial acetic acid solution, yielding *αβ-6-tribromo-β-3-methoxyphenylpropiophenone* (*phenyl αβ-6-tribromo-β-3-methoxyphenylethyl ketone*), $OMe\cdot C_6H_3Br\cdot CHBr\cdot CHBr\cdot COPh$. This forms stout, colourless crystals, m. p. 140°, and is oxidised by potassium permanganate to 6-bromo-3-methoxybenzoic acid. When heated with pyridine or alcoholic ammonia, it is converted into *phenyl α-6-dibromo-3-methoxystyryl ketone*, $OMe\cdot C_6H_3Br\cdot CH{:}CBr\cdot COPh$, which forms slender needles, m. p. 105°. With alcoholic sodium ethoxide it forms *phenyl α-6-dibromo-β-ethoxy-β-3-methoxyphenylethyl ketone*,

$$OMe\cdot C_6H_3Br\cdot CH(OEt)\cdot CHBr\cdot COPh,$$

m. p. 109—110°.

Ethyl m-*methoxybenzylidenemalonate*, $OMe\cdot C_6H_4\cdot CH{:}C(CO_2Et)_2$, prepared by maintaining a mixture of *m*-methoxybenzaldehyde and ethylmalonate, containing a little pyridine, for eight days at the ordinary temperature has m. p. 47°, b. p. 204—206°/10 mm., and is hydrolysed by aqueous sodium hydroxide to the corresponding *acid*, m. p. 163°, which forms a crystalline *barium* and amorphous *silver* salt, and reacts with bromine (1 mol.) in ethereal solution, yielding *α-bromo-α-*m-*methoxyphenylmethylenemalonic acid*, $OMe\cdot C_6H_4\cdot CBr{:}C(CO_2H)_2$, slender, yellow needles, m. p. 188°.

The *ethyl* ester of the last-mentioned acid is obtained as a viscid oil, b. p. 208°/10 mm., by the addition of bromine to ethyl *m*-methoxybenzylidenemalonate in glacial acetic acid.

m-Methoxybenzylidenemalonic acid reacts with bromine (2 mols.) in acetic acid solution, yielding *α-6-dibromo-α-3-methoxyphenylmethylenemalonic acid*, $OMe\cdot C_6H_3Br\cdot CBr{:}C(CO_2H)_2$, slender, pale yellow needles, m. p. 167°. When heated at 180°, it loses carbon dioxide with the formation of *m*-methoxycinnamic acid, m. p. 117° (compare Tiemann and Ludwig, A., 1883, 188), which is successively converted by the

action of bromine in glacial acetic acid solution into *β-bromo-m-methoxycinnamic acid*, slender, colourless needles, m. p. 186°, and *β-6-dibromo-3-methoxycinnamic acid*, $OMe\cdot C_6H_3Br\cdot CBr{:}CH\cdot CO_2H$, white needles, m. p. 160°.

6-Bromo-3-methoxybenzoic acid is readily prepared by shaking *m*-methoxybenzaldehyde with water and the theoretical amount of bromine.

If excess of bromine is used, it is accompanied by a *dibromo-m-methoxybenzoic acid*, which crystallises in slender, felted needles, m. p. 201—202°, and is separated from the monobromo-acid by taking advantage of its sparing solubility in water. F. B.

Some Acetylenic Compounds. ÉMILE ANDRÉ (*Ann. Chim. Phys.*, 1913, [viii], **29**, 540—596).—The paper is mainly a résumé of work previously abstracted (A., 1910, i, 563; 1911, i, 269, 277, 545; 1912, i, 628). The following points are, however, new.

Unsuccessful attempts have been made to prepare phenylpropinene, $CH_2Ph\cdot C{:}CH$, by the elimination of hydrogen bromide from allylbenzene dibromide.

Phenylbutinene has b. p. 189—191°/760 mm., D^0 0·9375.

iso*Heptylene*, b. p. 84—85°/762 mm., D^0 0·7087, is obtained by the addition of an ethereal solution of allyl iodide to a solution of magnesium *iso*butyl chloride in the same solvent. It unites with bromine, yielding a *dibromide* which, when heated with solid potassium hydroxide at about 130°, is converted into iso*heptinene*, $CHMe_2\cdot CH_2\cdot CH_2\cdot C{:}CH$, b. p. 92—93°, D^0 0·7515.

α-Propionyl-δ-phenylbutinene, $CH_2Ph\cdot CH_2\cdot C{:}C\cdot COEt$, is prepared by the gradual addition of a suspension of the potassium compound of δ-phenylbutinene in benzene to a solution of propionyl chloride in benzene. It is a pale yellow liquid, b. p. 162—163°/15 mm., D^0 1·0156; the *piperidyl* compound has m. p. 44°.

*Propionyl*iso*heptinene*, b. p. 100—101°/15 mm., D^0 0·8902, is obtained in a similar manner, the benzene, however, being replaced by anhydrous ether.

ε-Diethylamino-β-methyl-Δ^ε-nonen-η-one, b. p. 163°/13 mm., is obtained by mixing its constituents at a low temperature.

α-Propionyl-δ-phenylbutan-β-one, $CH_2Ph\cdot CH_2\cdot CO\cdot CH_2\cdot COEt$, has b. p. 166°/13 mm., D^0 1·0460, and *α-propionyl*iso*heptan-β-one*,

$$CHMe_2\cdot CH_2\cdot CH_2\cdot CO\cdot CH_2\cdot COEt,$$

b. p. 106°/14 mm., D^0 0·9262.

Ethylenic β-substituted amino-ketones react with hydroxylamine in a complex manner. Thus diethylaminobenzoylstyrene yields a small quantity of 3 : 5-diphenyl*iso*oxazole, $O<\begin{matrix}N{=}CPh\\ CPh{:}CH\end{matrix}$, m. p. 142°, together with two other *substances*, one of which has m. p. 163°.

Hexoylphenylacetylene and *iso*valerylphenylacetylene react with hydroxylamine to yield *5-phenyl-3-amyl*iso*oxazole*, m. p. 25—26°, b. p. 186—187°/13 mm., and *5-phenyl-3-*iso*butyl*iso*oxazole*, b. p. 172°/13 mm., respectively, neither of which regenerates hydroxylamine when heated with dilute hydrochloric acid.

3-*Phenyl*-5-*amylpyrazole*, plates, m. p. 77—78°, is formed by the action of hydrazine on hexoylphenylacetylene.

Reduction of ethylenic β-substituted amino-ketones by sodium or sodium amalgam in alcoholic solution, or by aluminium amalgam in neutral solution, causes a quantitative separation of the amine. A regular hydrogenation of the remainder of the molecule has not yet been achieved. H. W.

Action of Ethyl Oxalate on Cyclic Ketones. ARTHUR KÖTZ and J. MEYER (*J. pr. Chem.*, 1913, [ii], **88**, 261—272).—In previous papers (A., 1906, i, 88, 666, 667, 668), Kötz and others have shown that cyclic ketones condense with ethyl oxalate under the influence of sodium alkyloxides, yielding ketonic esters of the formula

$$R<\begin{matrix}CO \\ | \\ CH\cdot CO\cdot CO_2Et\end{matrix}$$

It is now found that in the case of certain derivatives of *cyclo*-hexanone, alcohol may be eliminated from the ketonic esters during the condensation, resulting in the formation of lactones derived from the following formulæ:

$$\begin{matrix}CH_2\cdot CH{=}C\cdot O\cdot CO \\ CH_2\cdot CH_2\cdot CH{-}CO\end{matrix} \quad \text{or} \quad \begin{matrix}CH_2\cdot CH{=}C\cdot O\cdot CO \\ CH_2\cdot CH_2\cdot C{=}C\cdot OH\end{matrix}.$$

One example of the formation of a lactone of this type has already been recorded (this vol., i, 179).

From the authors' results it would appear that ketonic esters are produced when the time during which the reaction is allowed to proceed is short and the temperature low, whilst a high temperature and a more prolonged action favour the formation of lactones.

Ethyl suberone-2-*oxalate* (*ethyl* 2-cyclo*heptanonylglyoxylate*), prepared from *cyclo*heptanone, ethyl oxalate, and alcoholic sodium ethoxide, has b. p. 146—148°/13 mm.

3-Methyl-Δ^2-*cyclo*hexen-2-ol-1-glyoxylolactone (this vol., i, 179) yields with acetic anhydride an *acetyl* derivative,

$$\begin{matrix}CH_2\cdot CMe{:}C\cdot O\cdot CO \\ CH_2\cdot CH_2{-}C{=}C\cdot OAc\end{matrix},$$

m. p. 78°.

The methyl derivative of the lactone (*loc. cit.*) is hydrolysed by aqueous potassium hydroxide (1 mol.) to 3-*methyl*cyclo*hexan*-2-*onylidene-methoxyacetic acid*, m. p. 139°, $CH_2<\begin{matrix}CHMe\cdot CO \\ CH_2{-}CH_2\end{matrix}>C{:}C(OMe)\cdot CO_2H$ or $CH_2<\begin{matrix}CMe{:}C(OH) \\ CH_2{-}CH_2\end{matrix}>C{:}C(OMe)\cdot CO_2H$.

2-Methoxy*cyclo*hexanone condenses with ethyl oxalate, yielding 3-*methoxy*-Δ^2-cyclo*hexen*-2-*ol*-1-*glyoxylolactone*,

$$\begin{matrix}CH_2\cdot C(OMe){:}C\cdot O\cdot CO \\ CH_2\cdot CH_2{-}CH{-}CO\end{matrix}, \quad \text{or} \quad \begin{matrix}CH_2\cdot C(OMe){:}C\cdot O\cdot CO \\ CH_2\cdot CH_2{-}C{=}C\cdot OH\end{matrix},$$

which has m. p. 51°.

3:6-*Dimethyl*-Δ^2-cyclo*hexen*-2-*ol*-1-*glyoxylolactone*, from 1 : 4-dimethyl-*cyclo*hexan-3-one, has m. p. 158—159°.

6-*Methyl*-3-iso*propyl*-Δ^2-cyclo*hexen*-2-*ol*-1-*glyoxylolactone*,

$$\begin{array}{l} CH_2\text{–}CMe\text{:}C\text{——}CO \\ \vert \qquad\qquad\quad \vert \qquad \vert \\ CH_2\cdot CPr^{\beta}\text{:}C\cdot O\cdot CO \end{array},$$

prepared from menthone, ethyl oxalate, and sodium in the presence of light petroleum, has m. p. 142·5° (decomp.), and decomposes on exposure to air.

In addition to ketonic esters and lactones, the condensation of ethyl oxalate with *cyclo*hexanone and its methyl derivatives gives rise to triketones or pyrone derivatives, which are found in the higher boiling fractions of the condensation product.

Thus, the condensation of 2-methyl*cyclo*hexanone and ethyl oxalate yields, as a by-product, *bis*-3-*methyl*cyclo*hexan*-2-*onyl ketone*,

$$CH_2{<}{\begin{array}{l} CHMe\cdot CO \\ CH_2\text{—}CH_2 \end{array}}{>}CH\cdot CO\cdot CH{<}{\begin{array}{l} CO\cdot CHMe \\ CH_2\text{—}CH_2 \end{array}}{>}CH_2,$$

which has b. p. 170°/13 mm., and gives a reddish-violet coloration with ferric chloride.

*Bis*cyclo*hexan*-2-*onyl ketone*, from *cyclo*hexanone, has b. p. 181°/14 mm.

3-Methyl*cyclo*hexanone yields the *pyrone* derivative, m. p. 121°,

$$\begin{array}{l} CHMe\cdot CH_2\cdot C\text{–}O\text{–}C\cdot CH_2\cdot CHMe \\ \vert \qquad\qquad\quad \Vert \qquad \Vert \qquad\quad \vert \\ CH_2\cdot CH_2\text{——}C\cdot CO\cdot C\cdot CH_2\cdot CH_2 \end{array}$$

; the *pyrone* derivative from 4-methyl*cyclo*hexanone has m. p. 91°.

The formation of the above-mentioned products is probably due to the intermediate formation of tetraketones of the type:

$$CH_2{<}{\begin{array}{l} CH_2\text{—}CO \\ CH_2\cdot CH_2 \end{array}}{>}CH\cdot CO\cdot CO\cdot CH{<}{\begin{array}{l} CO\text{—}CH_2 \\ CH_2\cdot CH_2 \end{array}}{>}CH_2,$$

by the condensation of one molecule of the ester with two molecules of the ketone, the tetraketone being subsequently converted into the triketone and pyrone derivatives by loss of carbon monoxide and water. F. B.

Unsaturated β-Diketones. I. HUGH RYAN and JOHN M. DUNLEA (*Proc. Roy. Irish Acad.*, 1913, **32**, 1—8).—Some typical unsaturated β-diketones have been prepared by condensing cinnamic esters with saturated ketones in presence of sodium or sodamide. All attempts to prepare similar compounds by condensing acetic and benzoic esters with unsaturated ketones have, however, failed, and consequently the chief aim of the research, the formation of the parent substance of curcumin, $CH_2(CO\cdot CH\text{:}CHPh)_2$, from a cinnamic ester and styryl methyl ketone, could not be realised.

For the preparation of *a-phenyl-Δ^{a}-hexene-$\gamma\epsilon$-dione*,

$$CHPh\text{:}CH\cdot CO\cdot CH_2\cdot COMe,$$

sodium wire was added during the course of some hours to a cold mixture of acetone and methyl cinnamate, and the sodium salt of the diketone was dissolved in water and decomposed by carbon dioxide. The compound crystallises in faintly yellow needles, has m. p. 83—84°, gives a yellow solution in concentrated sulphuric acid, and a red coloration with alcoholic ferric chloride, and dyes mordanted wool. On heating with hydroxylamine hydrochloride in alcohol, it yields

*3-styryl-5-methyl*isooxazole, $\mathrm{CHPh{:}CH{\cdot}C}\Big\langle\substack{\mathrm{CH{:}CMe}\\ |\\ \mathrm{N{-}O}}$, which forms pearly plates from alcohol or colourless needles from light petroleum, m. p. 88°. *$\alpha\epsilon$-Diphenyl-Δ^{α}-pentene-$\gamma\epsilon$-dione*, $\mathrm{CHPh{:}CH{\cdot}CO{\cdot}CH_2{\cdot}COPh}$, from acetophenone and ethyl cinnamate in the presence of sodamide, forms long, pale yellow needles, m. p. 109°, and yields *5-phenyl-3-styryl*iso*oxazole*, $\mathrm{CHPh{:}CH{\cdot}C}\Big\langle\substack{\mathrm{CH{:}CPh}\\ |\\ \mathrm{N{-}O}}$, in small, colourless needles, m. p. 137—138°.

α-Phenyl-Δ^{α}-heptene-$\gamma\epsilon$-dione, $\mathrm{CHPh{:}CH{\cdot}CO{\cdot}CH_2{\cdot}COEt}$, from methyl cinnamate and methyl ethyl ketone, requires a stronger acid than carbon dioxide for the decomposition of its sodium compound. It forms small, colourless prisms, which soften at 154° and melt to a yellow liquid at 161—163°. Similarly, *α-phenyl-Δ^{α}-*iso*octene-$\gamma\epsilon$-dione*, $\mathrm{CHPh{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CHMe_2}$, crystallises in thin plates which are probably rhombic, and softens at 165° and melts to a yellow liquid at 173—175°. These diketones are soluble in potassium hydroxide, but do not give coloured solutions in sulphuric acid or colorations with ferric chloride, nor do they dye mordanted wool. That their constitution is not represented by the alternative formulæ was proved by methylating α-phenyl-$\Delta\alpha$-hexene-$\gamma\epsilon$-dione, when it was found that *α-phenyl-δ-methyl-Δ^{α}-hexene-$\gamma\epsilon$-dione*, $\mathrm{CHPh{:}CH{\cdot}CO{\cdot}CHMe{\cdot}COMe}$, was not identical with the above α-phenyl-Δ^{α}-heptene-$\gamma\epsilon$-dione, but formed long, pale yellow needles, m. p. 88—89°, and gave a dark brown coloration with alcoholic ferric chloride, a yellow solution in sulphuric acid, and a pale brown colour to wool mordanted with iron.

J. C. W.

Unsaturated β-Diketones. II. HUGH RYAN and JOSEPH ALGAR (*Proc. Roy. Irish Acad.*, 1913, **32**, 9—16).—Although unsaturated ketones did not yield definite compounds on condensation with acetic or benzoic esters (compare preceding abstract), such a result has been attained with the oxalic esters. *Methyl $\alpha\gamma$-diketo-ϵ-phenyl-Δ^{δ}-hexenoate* (*methyl benzylideneacetoneoxalate*),

$$\mathrm{CHPh{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CO_2Me},$$

from styryl methyl ketone and methyl oxalate in the presence of sodium, forms pale yellow, acicular prisms, m. p. 70° (compare the ethyl ester, Schiff and Gigli, A., 1898, i, 490). It gives a yellow solution in potassium hydroxide, an orange solution in concentrated sulphuric acid, and a yellow solution with greenish fluorescence in alcohol. Ferric chloride imparts a dark red colour to an alcoholic solution, and the substance dyes wool orange-red or brown, according to the mordant employed. *$\alpha\gamma$-Diketo-ϵ-phenyl-Δ^{δ}-hexenoic acid*, $\mathrm{CHPh{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CO_2H}$, may readily be obtained by hydrolysis of the esters, in pale yellow needles, m. p. 139—140°. When the methyl ester is heated with hydroxylamine hydrochloride in methyl alcohol, *methyl 3-styryl*iso*oxazole-5-carboxylate*,

$$\mathrm{CHPh{:}CH{\cdot}C}\Big\langle\substack{\mathrm{CH{:}C{\cdot}CO_2Me}\\ |\\ \mathrm{N{-}O}},$$

is formed in long, colourless needles, m. p. 142—143°. When ethyl

alcohol is employed, however, a transformation occurs, and the *ethyl* ester is produced, in colourless crystals, m. p. 111°. The free *acid*, $C_{12}H_9O_3N$, is white, and has m. p. 190—192°. The above methyl ester also absorbs bromine, yielding *methyl δε-dibromo-αγ-diketo-ε-phenyl-hexoate*, $CHPhBr{\cdot}CHBr{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CO_2Me$, in almost colourless prisms, m. p. 134°.

Similar compounds were obtained by condensing *p*-methoxystyryl methyl ketone with methyl oxalate. *Methyl αγ-diketo-ε-*p*-methoxy-phenyl-Δ^δ-hexenoate*, $OMe{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CO_2Me$, forms yellow needles, m. p. 127·5°, and with bromine yields *methyl δε-dibromo-αγ-diketo-ε-*p*-methoxyphenylhexoate*, $C_{14}H_{14}O_5Br_2$, in pale yellow needles, m. p. 106—108° (decomp.). The free *acid* crystallises with water in bright yellow, slender needles, whilst the anhydrous substance is deep orange, and has m. p. 150—151°. *Ethyl* 3-p-*methoxystyryl*-iso*oxazole-5-carboxylate*, $C_{15}H_{15}O_4N$, from the above methyl ester with hydroxylamine hydrochloride in ethyl alcohol, forms long, colourless needles, m. p. 76—77°. J. C. W.

Alkylation of Ketones by means of β-Ketoneoxalic Esters.

ARTHUR KÖTZ and K. BLENDERMANN (*J. pr. Chem.*, 1913, [ii], **88**, 257—260).—The method previously employed (this vol., i, 179) to convert 1-methyl*cyclo*hexan-3-one into 1 : 4-dimethyl*cyclo*hexan-3-one is found to be of general application for alkylating both aliphatic and hydroaromatic ketones. It consists in condensing the ketone with ethyl oxalate by means of sodium methoxide or ethoxide, heating the sodium derivative of the resulting ketonic ester (I) with an alkyl haloid, and hydrolysing the product (II) with aqueous alkali hydroxides:

$$R{<}{\begin{matrix}CO\\ |\\ CH_2\end{matrix}} \longrightarrow \text{(I.)}\ R{<}{\begin{matrix}CO\\ |\\ CH{\cdot}CO{\cdot}CO_2Et\end{matrix}} \xrightarrow{R'I}$$

$$\text{(II.)}\ R{<}{\begin{matrix}CO\\ |\\ CR'{\cdot}CO{\cdot}CO_2Et\end{matrix}} \longrightarrow R{<}{\begin{matrix}CO\\ |\\ CHR'\end{matrix}} + EtOH + H_2C_2O_4.$$

Thus, acetone can be converted into methyl ethyl ketone by condensing it with ethyl oxalate and alcoholic sodium ethoxide, heating the ethyl sodioacetoneoxalate thus formed with methyl iodide, and hydrolysing the resulting methyl derivative with the calculated amount of 10% aqueous sodium hydroxide.

Ethyl 1 : 3-dimethyl*cyclo*hexan-2-onylglyoxylate,

$$CH_2{<}{\begin{matrix}CHMe{\cdot}CO\\ CH_2{-}CH_2\end{matrix}}{>}CMe{\cdot}CO{\cdot}CO_2Et,$$

obtained from 1-methyl*cyclo*hexan-2-one, ethyl oxalate, and methyl iodide, yields, on hydrolysis, 1 : 3-dimethyl*cyclo*hexan-2-one (Kötz and Schaeffer, A., 1912, i, 603).

On treatment with ethyl iodide and subsequent hydrolysis, the sodium derivative of ethyl 4-methyl*cyclo*hexan-2-onylglyoxylate, obtained from 1-methyl*cyclo*hexan-3-one and ethyl oxalate, yields *1-methyl-4-ethyl*cyclo*hexan-3-one*, a strongly refractive, colourless liquid, b. p. 81—82°/17 mm., having an odour resembling that of menthone.

*4-Benzyl-1-methyl*cyclo*hexan-3-one*, prepared in a similar manner, using benzyl chloride, has b. p. 176°/15 mm.

*Ethyl methyl*iso*thujoneoxalate* (*ethyl* 1 : 3 : 4-*trimethyl*-5-iso*propyl*-Δ³-

cyclo*hexen-2-onylglyoxylate*), $\begin{matrix}\text{CMe}\text{——CO}\\ \|\qquad\qquad \\ \text{CMe·CHPr}^{\beta}\end{matrix}\!\!>\text{CMe·CO·CO}_2\text{Et}$, obtained by heating the product of the condensation of *iso*thujone and ethyl oxalate with methyl iodide, has b. p. 183°/11 mm., and is hydrolysed by aqueous sodium hydroxide to *methyl*iso*thujone* (1 : 3 : 4-*trimethyl-5-*iso*propyl*-Δ^3-cyclo*hexen-2-one*), $\begin{matrix}\text{CMe}\text{——CO}\\ \|\qquad\qquad \\ \text{CMe·CHPr}^{\beta}\end{matrix}\!\!>\text{CHMe}$, which has b. p. 229—231°, and has also been prepared by the reduction of hydroxymethylene*iso*thujone (Schaeffer, *Diss.*, Göttingen, 1903). F. B.

Isolation of Lapachol from the Heart-wood of Avicennia tomentosa. Konrad Bournot (*Arch. Pharm.*, 1913, **251**, 351—354).—The residue left after the evaporation of the ethereal extract of the powdered heart-wood of *Avicennia tomentosa* yields to 3% aqueous sodium carbonate a substance, lapachol, $C_{15}H_{14}O_3$, m. p. 140—141°, truncated, yellow plates, which is shown by its m. p., crystalline form, solubilities, and formation of a diacetyl derivative, m. p. 130°, to be identical with Paternò's and with Hooker's lapachoic acid (2-hydroxy-3-$\omega\omega$-dimethylallyl-α-naphthaquinone). C. S.

The Anthraquinone Series. I. Halogenated 2-Aminoanthraquinones. Walter Junghans (*Annalen*, 1913, **399**, 316—330).—1-*Chloro-2-acetylaminoanthraquinone*, m. p. 241—242° (corr.), faintly yellow needles, obtained by the chlorination of 2-acetylaminoanthraquinone in acetic acid containing sodium acetate on the water-bath, yields, by hydrolysis by acids or alkalis, 1-*chloro-2-aminoanthraquinone*, m. p. 237°, orange needles or reddish-brown leaflets. The latter reacts with *p*-toluenesulphonamide, potassium acetate, and a trace of copper acetate in boiling amyl alcohol to form 1-p-*toluenesulphonylamino-2-aminoanthraquinone*, m. p. 239° (corr.), yellowish-red leaflets. In a similar manner, 1-chloro-2-acetylaminoanthraquinone yields 1-p-*toluenesulphonylamino-2-acetylaminoanthraquinone*, m. p. 207° (corr.), long needles. Both of these substances yield 1 : 2-diaminoanthraquinone by hydrolysis, whereby the constitution of the chloroaminoanthraquinone is determined.

By treatment with chlorine in warm glacial acetic acid or with potassium chlorate and concentrated hydrochloric acid in glacial acetic acid at the ordinary temperature, 2-aminoanthraquinone yields 1 : 3-*dichloro-2-aminoanthraquinone*, m. p. 231° (corr.), yellowish-brown needles, which is converted by boiling acetic anhydride into 1 : 3-*dichloro-2-diacetylaminoanthraquinone*, m. p. 199° (corr.), silvery leaflets, and into 1 : 3-*dichloro-2-benzoylaminoanthraquinone*, m. p. 227° (corr.), faintly yellow needles, by benzoyl chloride in boiling nitrobenzene. The constitution of 1 : 3-dichloro-2-aminoanthraquinone is proved by eliminating the amino-group in the usual manner, whereby is obtained the 1 : 3-*dichloroanthraquinone*, m. p. 203° (corr.), which is produced from 1 : 3-dichloro-4-aminoanthraquinone by the same method.

Contrary to statements in the literature, the interaction of equal molecular quantities of 2-aminoanthraquinone and bromine in glacial acetic acid at the ordinary temperature produces 3-*bromo-2-amino-*

anthraquinone hydrobromide, from which the *base*, m. p. 311° (corr.), yellow leaflets, is obtained by boiling with water. 3-Bromo-2-amino-anthraquinone forms an *acetyl* derivative, m. p. 217° (corr.), colourless needles, and a *benzoyl* derivative, m. p. 279° (corr.), colourless needles. Its constitution is proved by deamidation, whereby 2-bromoanthraquinone is produced, and also by the formation of a thiazole derivative (Ullmann and Junghans, below). By prolonged boiling with glacial acetic and concentrated hydrobromic acids, 1 : 3-dibromo-2-amino-anthraquinone loses the halogen atom in position 1 and yields 3-bromo-2-aminoanthraquinone, m. p. 311° (corr.). C. S.

Preparation of β-Bromoaminoanthraquinones Containing a Bromine Atom in the Next Position to an Amino-group. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 261270 and 261271).—3-*Bromo*-2-*aminoanthraquinone*, m. p. 305°, as previously obtained (A., 1904, i, 512) had m. p. 267—270°, and the pure substance has now been prepared as follows: 2-aminoanthraquinone (5·8 parts) and 10 parts of 1 : 3-dibromo-2-aminoanthraquinone (A., 1905, i, 797) dissolved in 160 parts of concentrated sulphuric acid are slowly heated with continual stirring to 160°, when a reaction takes place, and after about fifteen minutes at 170° pure 3-bromo-2-aminoanthraquinone sulphate crystallises out; the same result is obtained if the bases are heated together during ten minutes at 280° in the absence of any solvent.

2-Bromo-1-aminoanthraquinone (A., 1905, i, 910) is obtained in a similar manner from 1-aminoanthraquinone and 2 : 4-dibromo-1-amino-anthraquinone.

1 : 3 : 5 : 7-*Tetrabromo*-2 : 6-*diaminoanthraquinone*, yellowish-brown needles, m. p. above 360°, is prepared by brominating an aqueous suspension of 2 : 6-diaminoanthraquinone, and when molecular proportions of these two bases are heated together at 195° in slightly diluted sulphuric acid during half an hour, they furnish pure 3 : 7-*dibromo*-2 : 6-*diaminoanthraquinone sulphate*; whilst a mixture of 1 : 5-diamino- and 2 : 4 : 6 : 8-tetrabromo-1 : 5-diamino-anthraquinones gives rise to 2 : 6-dibromo-1 : 5-diaminoanthraquinone (A., 1905, i, 88).

II. States that 3-bromo-2-aminoanthraquinone can be prepared in one operation by dissolving 2-aminoanthraquinone in concentrated sulphuric acid, cooling, and treating with bromine (1 mol.); the crude mixture, which contains monobromo-, dibromo-, and unbrominated bases, is then heated at 180—190°, when it furnishes entirely 3-bromo-2-aminoanthraquinone. In a similar manner, 2 : 7-diaminoanthraquinone when treated with bromine (2 mols.) gives rise to 3 : 6-*dibromo*-2 : 7-*diaminoanthraquinone*; this compound closely resembles 3 : 7-dibromo-2 : 6-diaminoanthraquinone, but is more readily soluble in organic liquids. F. M. G. M.

The Anthraquinone Series. II. 1 : 3-Dibromo-2-amino-anthraquinone. FRITZ ULLMANN and WALTER JUNGHANS (*Annalen*, 1913, **399**, 330—345).—The following reactions illustrate the great mobility, in the presence of a copper salt as catalyst, of the halogen

atom in position 1 in 1 : 3-dibromo-2-aminoanthraquinone (compare Ullmann and Medenwald, this vol., i, 735). By boiling with benzoyl chloride and nitrobenzene, or with benzoic anhydride, 1 : 3-dibromo-2-aminoanthraquinone yields 3-*bromoanthraquinonylphenyloxazole*,

$$C_6H_4<\substack{CO\\CO}>C_6HBr<\substack{O\\N}>CPh,$$

m. p. 325° (corr.), yellow leaflets, which is decomposed by boiling 80% sulphuric acid, forming, after the addition of water, 3-*bromo*-2-*amino*-1-*hydroxyanthraquinone*, m. p. 269°, reddish-brown needles. 1 : 3-*Di-bromo*-2-*dibenzoylaminoanthraquinone*, m. p. 233°, yellow needles, is also obtained by the first method of preparing the oxazole derivative.

In a similar manner, 1 : 3 : 5 : 7-tetrabromo-2 : 6-diaminoanthraquinone, by boiling with benzoyl chloride and naphthalene, is converted into the *bisoxazole*,

$$CPh<\substack{N\\O}>C_6HBr<\substack{CO\\CO}>C_6HBr<\substack{N\\O}>CPh,$$

m. p. above 360°, faintly yellow needles.

By boiling with amyl alcohol, anhydrous potassium acetate, a little copper acetate, and *p*-toluenesulphonamide, 1 : 3-dibromo-2-aminoanthraquinone is converted into 3-*bromo*-2-*amino*-1-p-*toluenesulphonylamino-anthraquinone*, $C_{21}H_{15}O_4N_2BrS$, m. p. 237·5° (corr.), yellowish-brown crystals, which yields 3-*bromo*-1 : 2-*diaminoanthraquinone*, m. p. 312° (corr.), dark red crystals, by hydrolysis with sulphuric acid. By boiling 3-bromo-1 : 2-diaminoanthraquinone with benzaldehyde or 3-bromo-2-amino-1-*p*-toluenesulphonylaminoanthraquinone with benzoyl chloride, the *iminoazole*, $C_6H_4<\substack{CO\\CO}>C_6HBr<\substack{N\\NH}>CPh$, m. p. 292° (corr.), yellowish-green needles, is obtained, which forms a *hydrochloride*, colourless needles, and a reddish-brown *sodium* salt.

In the presence of anhydrous sodium acetate and a trace of copper acetate, 1 : 3-dibromo-2-aminoanthraquinone is converted by urethane on the water-bath into *bromohydroxyanthriminazole*,

$$C_6H_4<\substack{CO\\CO}>C_6HBr<\substack{NH\\N}>C\cdot OH,$$

m. p. 370°, yellowish-green needles, and by boiling nitrobenzene into 3 : 3′-*dibromoindanthren*,

$$C_6H_4<\substack{CO\\CO}>C_6HBr<\substack{NH\\NH}>C_6HBr<\substack{CO\\CO}>C_6H_4,$$

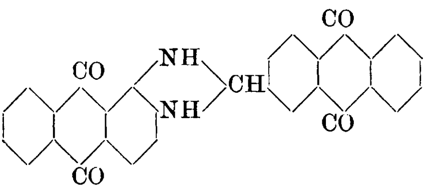
m. p. 515°, indigo-blue needles, and 3-bromo-2-aminoanthraquinone; the dibromoindanthren forms a blue vat which dyes cotton in blue shades.

1 : 3-Dibromo-2-aminoanthraquinone and boiling benzaldehyde yield a *benzylidene* derivative, $C_{21}H_{11}O_2NBr_2$, m. p. 195° (corr.), yellowish-green needles, which is converted by naphthalene and copper powder at 240—245° into 3 : 3′-*dibromo*-2 : 2′-*dibenzylideneamino*-1 : 1′-*dianthra-quinonyl*, $C_{42}H_{22}O_4N_2Br_2$, m. p. 295·5° (corr.), yellow leaflets. By treating the latter in hot nitrobenzene with a little sulphuric acid, or 3-bromo-2-aminoanthraquinone in boiling nitrobenzene with antimony pentachloride, 3 : 3′-*dibromoflavanthren*, $C_{28}H_{10}O_2N_2Br_2$, m. p. 495°, brown needles, is obtained; its hyposulphite vat is deep blue and dyes cotton in the same shades, changing to orange in air. C. S.

[Preparation of a Bromo-derivative of 4-Chloro-1-methylanthraquinone.]—FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 259881).—When a boiling nitrobenzene solution of 4-chloro-1-methylanthraquinone (15 parts) is treated with a similar solution of bromine (8·5 vols.) it furnishes a *compound* which separates in orange crystals as the solution cools; the m. p. is above 300°.

F. M. G. M.

Preparation of Condensation Products in the Anthraquinone Series. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 261737).—The *compound* (annexed formula) is obtained when 1 : 2-diaminoanthraquinone and anthraquinone-2-aldehyde are heated together in pyridine solution at 120°; the aldehyde can be replaced in this reaction by ω-chloro- or ω-dichloromethylanthraquinones, and the diamine by 2 : 3-diaminoanthraquinone.



F. M. G. M.

[Preparation of Anthraquinone Derivatives.] FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 262252).—4-*a-Anthraquinonylaminoanthraquinone*-1 : 2-*acridone* is obtained by condensing 4-aminoanthraquinoneacridone with *a*-chloroanthraquinone in the presence of aluminium chloride, zinc chloride, or sulphuric acid.

F. M. G. M.

Preparation of Condensation Products in the Anthracene Series. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 260662).—The removal of chlorine or bromine by means of potassium iodide and acetone has previously been described (A., 1911, i, 432), and it is now found that when ω-dibromo-2-methylanthraquinone is heated with potassium iodide (2 parts) and acetone (10 parts) at 100° during twelve to fourteen hours, it yields the previously-described compound, $C_{30}H_{14}O_4$ (A., 1908, i, 999).

When ωω′-tetrabromo-2 : 2′-dimethyl-1 : 1′-dianthraquinonyl (A., 1912, i, 361) is treated in a similar manner, it gives rise to a *diphthaloylphenanthren*, an orange-brown powder; the preparation of other derivatives by this reaction is discussed. F. M. G. M.

Synthesis of the Higher Indandiones. II. MARTIN FREUND and KARL FLEISCHER (*Annalen*, 1913, **399**, 182—241).—The reaction whereby diethylmalonyl chloride and benzene or its homologues yield diethylindandiones (A., 1910, i, 490) has been examined in the cases where dimethylmalonyl chloride or dipropylmalonyl chloride is used.

[With MARGARETE DECKERT.]—Dimethylmalonyl chloride, which is identified in small quantities best by conversion into *dimethylmalonanilide*, $CMe_2(CO\cdot NHPh)_2$, m. p. 202·5—203°, reacts abnormally with benzene in the presence of aluminium chloride, yielding ultimately phenyl *iso*propyl ketone and two *substances*, $C_{17}H_{16}O_2$, m. p. 193—194°

and 125° respectively, which are probably ββ-dibenzoylpropane and the lactone of β-hydroxy-ββ-diphenyl-αα-dimethylpropionic acid; the two substances have not been further examined on account of the difficulty of separating them.

Dimethylmalonyl chloride condenses normally with other aromatic hydrocarbons, yielding substituted indandiones. Thus its reaction with *p*-cymene in carbon disulphide in the presence of aluminium chloride leads to the formation of 2 : 2 : 4-*trimethyl*-7-iso*propylindandione*,

$$C_6H_2MePr^{\beta}<^{CO}_{CO}>CMe_2,$$

b. p. 168—169°/14 mm., D^{15} 1·634, which is oxidised to an *acid*, probably $C_6H_2(CO_2H)_2<^{CO}_{CO}>CMe_2$, m. p. 179—180°, by nitric acid at 115—140°.

Under conditions similar to the preceding, dimethylmalonyl chloride and naphthalene ultimately yield three *substances*, $C_{15}H_{12}O_2$, m. p. 101°, 121°, and 137° respectively, which can only be separated by the mechanical sorting of their well-defined crystals. The constitutions of the three substances have been determined by oxidising the products of their decomposition by alkalis. The substance, m. p. 101°, is 2 : 2-*dimethyl*-1 : 8-*naphthindandione*, $C_{10}H_6<^{CO}_{CO}>CMe_2$, since it is converted by boiling 50% potassium hydroxide into 1-iso*butyrylnaphthalene*-8-*carboxylic acid*, $CHMe_2\cdot CO\cdot C_{10}H_6\cdot CO_2H$, m. p. 158·5—159·5°, hexagonal plates and prisms, which is oxidised to naphthalic anhydride by nitric acid at 125°. The substance, m. p. 121°, is 2 : 2-*dimethyl*-1 : 2-*naphthindandione*, $C_{10}H_6<^{CO}_{CO}>CMe_2$; it is converted by 50% potassium hydroxide into 1(or 2)-iso*butyrylnaphthalene*-2(or 1)-*carboxylic acid*, m. p. 153—154°, which is oxidised to naphthalene-1 : 2-dicarboxylic acid and its anhydride by boiling glacial acetic acid and nitric acid, D 1·4. The third substance, m. p. 137°, must be 2 : 2-*dimethyl*-2 : 3-*naphthindandione* by exclusion; it is converted by alkali into 2-iso*butyrylnaphthalene*-3-*carboxylic acid*, m. p. 164—165·5°, which is oxidised to *naphthalene*-2 : 3-*dicarboxylic acid*, m. p. 241° (decomp.), by nitric acid at 120°, or by boiling nitric and glacial acetic acids. Naphthalene-2 : 3-dicarboxylic acid forms an *anhydride*, m. p. 245°, by heating, and yields a fluorescein by the usual method.

By direct treatment with nitric acid at 120—140°, 2 : 2-dimethyl-1 : 8-naphthindandione yields a *nitro*-derivative, $C_{15}H_{11}O_4N$, m. p. 162°, yellow needles; a *dinitro*-derivative, $C_{15}H_{10}O_6N_2$, m. p. 245—248° (decomp.), microscopic, hexagonal plates or prisms, and a colourless *acid*, m. p. 237—239° (decomp.); 2 : 2-dimethyl-1 : 2-naphthindandione yields a yellow *substance* containing nitrogen, and an *acid*, $C_{13}H_{10}O_6$, m. p. 229—233° (decomp.), which is probably 2 : 2-*dimethylindandione*-4 : 5-*dicarboxylic acid*, $CMe_2<^{CO}_{CO}>C_6H_2(CO_2H)_2$, whilst 2 : 2-dimethyl-2 : 3-naphthindandione yields nitrogenous products and a *substance*, m. p. 186—187° (decomp.), colourless needles.

When heated above their m. p.'s, 1-*iso*butyrylnaphthalene-8-carboxylic acid and 2-*iso*butyrylnaphthalene-3-carboxylic acid are converted

into *lactones*, $C_{10}H_6<\genfrac{}{}{0pt}{}{CO\text{———}}{C(:CMe_2)}>O$, m. p. 117·5—118·5° and 174—175° respectively, which are isomeric with the original indandiones; the former lactone is re-converted into 1-*iso*butyrylnaphthalene-8-carboxylic acid by boiling 50% potassium hydroxide, is oxidised to naphthalic anhydride by boiling nitric and glacial acetic acids, and yields a *bromo*-derivative, m. p. 141°, microscopic prisms, by bromination in chloroform. 1(or 2)-*iso*Butyrylnaphthalene-2(or 1)-carboxylic acid remains unchanged by heating above its m. p.

Assuming that the $-CH_2{\cdot}CH_2-$ group is unattacked, acenaphthene could yield three indandiones by reaction with dimethylmalonyl chloride and aluminium chloride in carbon disulphide. Actually only two are obtained, having m. p. 127·5—129° and 176·5—177·5° respectively. The former crystallises in colourless needles, and is 2 : 2-*dimethyl*-3 : 4-*acenaphthindandione*, $CMe_2<\genfrac{}{}{0pt}{}{CO}{CO}>C_{10}H_4<\genfrac{}{}{0pt}{}{CH_2}{CH_2}$, since it is converted by boiling 50% potassium hydroxide into 3-iso*butyrylacenaphthene*-4-*carboxylic acid*, $\genfrac{}{}{0pt}{}{CO_2H\text{———}}{CHMe_2{\cdot}CO}>C_{10}H_4<\genfrac{}{}{0pt}{}{CH_2}{CH_2}$, m. p. 176° (decomp.), colourless, microscopic plates, which is oxidised to naphthalene-1 : 4 : 5 : 8-tetracarboxylic acid by alkaline potassium permanganate. The isomeride, m. p. 176·5—177·5°, crystallises in pale yellow needles, and is named *dimethyl*iso*acenaphthindandione*; its formula has not been definitely determined.

The oxidation of 2 : 2-dimethyl-3 : 4-acenaphthindandione by sodium dichromate and boiling glacial acetic acid yields 2 : 2-*dimethyl*-1 : 8-*naphthindandione*-4 : 5-*dicarboxylic acid*, $CMe_2<\genfrac{}{}{0pt}{}{CO}{CO}>C_{10}H_4(CO_2H)_2$, m. p. 208—209° (*anhydride*, m. p. 207—208°).

When heated above its m. p., 3-*iso*butyrylacenaphthene-4-carboxylic acid is converted into a *lactone*, $\genfrac{}{}{0pt}{}{CH_2}{CH_2}>C_{10}H_4<\genfrac{}{}{0pt}{}{CO\text{———}}{C(:CMe_2)}>O$, m. p. 175—176°, orange needles, which is oxidised by boiling acetic and nitric acids to *acenaphthalic anhydride* (*anhydride* of *acenaphthene*-3 : 4-*dicarboxylic acid*), $\genfrac{}{}{0pt}{}{CH_2}{CH_2}>C_{10}H_4<\genfrac{}{}{0pt}{}{CO}{CO}>O$, m. p. 293—294°, pale brown leaflets. *Acenaphthalic acid* forms an *ammonium* salt, m. p. 283°, yields its anhydride by heating, does not form a fluorescein, and dissolves in concentrated sulphuric acid, yielding a pale yellow solution with a splendid sky-blue fluorescence.

The reaction between anthracene and an excess of dimethylmalonyl chloride in the presence of aluminium chloride leads to the formation of 2 : 2-*dimethylanthraceneindandione*, $C_6H_4<\genfrac{}{}{0pt}{}{CH}{CH}>C_6H_2<\genfrac{}{}{0pt}{}{CO}{CO}>CMe_2$, m. p. 148·5—149·5°, brownish-red needles or plates, which is oxidised by chromic and acetic acids to 2 : 2-*dimethylanthraquinoneindandione*, $C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_2<\genfrac{}{}{0pt}{}{CO}{CO}>CMe_2$, m. p. 231—232°, pale yellow prisms, and is converted by boiling 50% potassium hydroxide into an iso*butyryl*-

anthracene-o-carboxylic acid, $C_6H_4<\overset{CH}{\underset{CH}{|}}>C_6H_2(CO_2H)\cdot COPr^\beta$, m. p. 203—205°, dark brown prisms; the latter, heated above its m. p., is converted into a *lactone*, $C_6H_4<\overset{CH}{\underset{CH}{|}}>C_6H_2<\overset{CO\text{———}}{\underset{C(:CMe_2)}{}}>O$, m. p. 141—142·5°.

Dimethylmalonyl chloride and phenanthrene in carbon disulphide in the presence of aluminium chloride yield ultimately a *dimethylphenanthreneindandione*, m. p. 207—208°, pale yellow needles, which is converted into *dimethylphenanthraquinoneindandione*, $C_{19}H_{12}O_4$, m. p. 246—247°, orange needles, by oxidation, and into a mixture of two isomeric acids by concentrated potassium hydroxide.

[With MAX ROTHSCHILD.]—Dipropylmalonyl chloride is characterised by conversion into the *dianilide*, $CPr^a_2(CO\cdot NHPh)_2$, m. p. 168—168·5°, colourless prisms, and the *bisphenylhydrazide*, $C_{21}H_{28}O_2N_4$, m. p. 216—217°; by warming with carbonyl chloride in toluene at 100°, the latter is converted into the *diazolone*, $\overset{CO-O}{\underset{NPh\cdot N}{|}}>C\cdot CPr^a_2\cdot C<\overset{O-CO}{\underset{N\cdot NPh}{|}}$, m. p. 157—158·5°.

Dipropylmalonyl chloride condenses normally with benzene or other aromatic hydrocarbons in the presence of aluminium chloride. Thus benzene yields, in addition to a small quantity of *δδ-dibenzoylheptane*, m. p. 106—107°, 2 : 2-*dipropylindandione*, $C_6H_4<\overset{CO}{\underset{CO}{}}>CPr^a_2$, b. p. 168—172°/14 mm., D 1·0390, which is converted into phthalic acid by oxidation. *p*-Cymene yields 4-*methyl*-2 : 2-*dipropyl*-7-iso*propylindandione*, $C_6H_2MePr^\beta<\overset{CO}{\underset{CO}{}}>CPr^a_2$, m. p. 94·5°, colourless needles. Diphenyl yields a *phenyldipropylindandione*, $C_{21}H_{22}O_2$, m. p. 221·5°, colourless needles, the constitution of which has not been definitely determined. Naphthalene does not yield definite condensation products, but acenaphthene yields two *isomerides*, m. p. 154—154·5° and 126° respectively. The former crystallises in yellow needles, and is converted by boiling concentrated aqueous alkalis, or, better, by sodium and boiling alcohol into *a-propylvalerylacenaphthenecarboxylic acid*, $\overset{CH_2}{\underset{CH_2}{|}}>C_{10}H_4(CO_2H)\cdot CO\cdot CHPr^a_2$, m. p. 166—167°, yellowish-brown leaflets. The isomeride, m. p. 126°, crystallises in yellow leaflets, and does not yield definite products by decomposition by alkalis.

Dipropylmalonyl chloride yields oily or amorphous products with anthracene, phenanthrene, and retene, but condenses with thiophen in the presence of aluminium chloride and carbon disulphide to form ultimately *dithiophenoyldipropylmethane*, $CPr^a_2(CO\cdot C_4SH_3)_2$ or

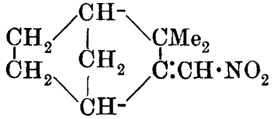
$$CPr^a_2<\overset{C(C_4SH_3)_2}{\underset{CO\text{———}}{}}>O,$$

m. p. 192·5°, yellow needles, and *thiophenoyldipropylmethane*, $C_{12}H_{18}OS$, b. p. 158—163°/25 mm.

A table is given of the colours of the fluorescent solutions of the preceding substances in concentrated sulphuric acid. C. S.

Action of Nitrogen Trioxide on Camphene. Nitrocamphene and Dinitrohydroxycamphane. PETER LIPP (*Annalen*, 1913, **399**, 241—260).—By the oxidation of *iso*camphane by nitric acid the author obtained (A., 1911, i, 731), amongst other products, a substance, $C_{10}H_{15}O_2N$, m. p. 64°, which is identical with so-called camphenile nitrite obtained by Jagelki by the action of nitrogen trioxide on camphene. The author's opinion that the substance is a nitro-compound (*loc. cit.*) has now been confirmed. He has, therefore, re-examined the action of nitrogen trioxide on camphene.

l-Camphene in petroleum (b. p. 30—40°) at −16° is treated with nitrogen trioxide (from arsenious oxide and nitric acid, not from sodium nitrite), whereby a faintly olive-green oil is produced, which decomposes at the ordinary temperature. The solvent is removed and the oily residue, after distillation with steam, is treated with aqueous potassium hydroxide. The deep red alkaline solution is treated as described below, whilst the residue is the desired substance, l-*nitrocamphene* (annexed formula), m. p. 84—85° (corr.), $[\alpha]_D^{20} - 146{\cdot}4°$ in 20% benzene solution, which only differs from *dl*-nitrocamphene, m. p. 64°, in its m. p. and optical activity. The evidence for the presence of a nitro-group is the following: (i) The faintly yellow colour of the substance may be due to the presence of the nitro-group in the neighbourhood of the double linking. (ii) By treatment with alcoholic ammonia at 110—120°, the substance is converted into *l*-camphenilone and nitromethane (identified in the form of methylamine); by the action of boiling, aqueous alcoholic potassium hydroxide, the substance yields *l*-camphenilone and potassium nitroacetate. The nitro-group, therefore, is attached directly to a carbon atom. (iii) By reduction in ethereal solution by aluminium amalgam and water, the substance is converted into, not only ammonia and camphenilanaldehyde (which are the products of reduction in acid or in alkaline solution), but also into *camphenilanaldoxime*,



$$C_8H_{14}{:}CH{\cdot}CH{:}N{\cdot}OH,$$

b. p. 134—135°/12 mm., a colourless, viscous liquid (*hydrochloride*,

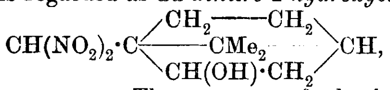
$$C_{10}H_{18}ONCl,$$

m. p. 90—92°, white, crystalline powder). The formation of camphenilanaldoxime is quite analogous to the production of aldoximes by the reduction of nitro-olefines in neutral solution. (iv) The conversion of nitrocamphene into tricyclenic acid by concentrated sulphuric acid is to be described fully in a future communication. The first product is a *sulphate* of camphenylhydroxamic acid, $C_{10}H_{15}O_5NS$, decomp. 127°; this is decomposed by warm water into sulphuric acid and *camphenylhydroxamic acid*, $C_{10}H_{17}O_3N$, decomp. 163°. The latter is decomposed by sulphuric acid into hydroxylamine and camphenylic acid, and from the latter, by loss of water, tricyclenic acid is produced. The whole change is analogous to the conversion of a primary nitro-compound into a carboxylic acid containing the same number of carbon atoms.

A second product of the action of nitrogen trioxide on camphene is the oily substance, $C_{10}H_{16}O_3N_2$, described by Jagelki as camphene

nitrosite. However, the substance, the *potassium* salt, $C_{10}H_{15}O_4N_2K$, garnet prisms or bronze leaflets, decomp. 207—209°, of which is contained in the deep red alkaline solution mentioned above, is, when pure, crystalline, m. p. 158·5° (corr.), and has the formula $C_{10}H_{16}O_5N_2$.

The substance is regarded as *ωω-dinitro-2-hydroxycamphane*,



for the following reasons: The presence of the hydroxyl group is shown by the formation of an *acetyl* derivative, $C_{12}H_{18}O_6N_2$, m. p. 74—75° (corr.), stout plates. The substance, as a secondary alcohol, is oxidised to ketopinic acid by alkaline potassium permanganate at 50—60°. The presence of a *gem*-dinitro-group is suggested by the intense red colour of the potassium salt and by its reconversion into the colourless parent substance by carbon dioxide, and is confirmed by the reduction of an ethereal solution of the substance by aluminium amalgam and water, whereby hydroxylamine and an *oxime*, $C_{10}H_{17}O_2N$, m. p. 127—128·5°, colourless needles, are produced; the oxime is probably *2-hydroxycamphan-ω-aldoxime*, $C_8H_{15}O{:}C{\cdot}CH{:}NOH$, but the aldehyde obtained from it has not been thoroughly examined owing to lack of material.

The formation of a camphane derivative, ωω-dinitro-2-hydroxycamphane, from camphene by the action of nitrogen trioxide is effected possibly by the intermediate production of nitrocamphene. This view, however, is not altogether supported by the fact that nitrocamphene and nitric acid, D 1·514, after being kept for four days yield a substance which dissolves in alkalis with a deep red colour, but cannot be isolated, the chief product of the reaction being ketopinic acid, (p-*bromophenylhydrazone*, $C_{16}H_{19}O_2N_2Br$, m. p. 165—166° (corr.), straw-yellow leaflets). Possibly the nitrocamphene and the nitrous acid in the nitric acid form a nitrolic acid, the camphene ring changing at the same time to the camphane ring; the nitrolic acid is then oxidised to ketopinic acid. Attempts to unite nitrocamphene and nitrous acid directly have been unsuccessful. C. S.

Action of Methyl Iodide and Magnesium on Menthone. ALEXANDER E. ARBUZOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 700).—The author claims priority for Zelinsky (A., 1901, i, 660) and himself (A., 1908, i, 555) over Vanin (A., 1912, i, 788). T. H. P.

Oil of Adansonia Grandidieri. VICTOR THOMAS and F. BOIRY (*Bull. Soc. chim.*, 1913, [iv], **13**, 827—832).—On extraction with ether, the entire seeds of *Adansonia Grandidieri* yield 43% of oil, whilst the decorticated seeds give 64·5%. The oil obtained from the former has m. p. 20—21°; temperature of solidification, 13°; D^{20} 0·9190; n^{40} 1·4585; saponification number, 192·4; iodine number, 65·4—66·1; Reichert-Meissl number, 0·77; Hehner number, 95·5, whilst that obtained from the latter has m. p. 39—40°; temperature of solidification, 33°; D^{40} 0·9135; n^{40} 1·4521; saponification number, 196; iodine number, 36·9. After removal of the fatty acids, the oils from the entire (i) and decorticated seeds (ii) have the following constants:

m. p. (i) 51—52°; (ii) 45—46°; temperature of solidification, (i) 44·5°; acid number, (i) 179; (ii) 204·5; saponification number, (i) 202·5; (ii) 207·6; iodine number, (i) 66·3—66·9; (ii) 34·5—35; iodine number after acetylation, (i) 25·7; (ii) 26·8.

The oil consists of a mixture of esters of solid and unsaturated liquid acids in the proportion of 42% of the former and 58% of the latter. It is further characterised by the presence of a considerable quantity of a lactone, the precise nature of which has not been determined owing to lack of material. It has an iodine number 67·2, and when treated with bromine yields a liquid bromo-derivative.

The mixture of acids contains myristic acid, 7·6%; palmitic acid, 32·5%; oleic acid, 36·5%; linoleic acid, 8·7%, and lactone, 11·41%.

H. W.

Essential Oils. V. Essence of Cypress. GUSTAVE LALOUE (*Bull. Soc. chim.*, 1913, [iv], **13**, 752—754. Compare A., 1911, i, 138; 1912, i, 574, 636).—The author has studied the oils obtained from the branches of *Cupressus sempervirens fastigiata*, L., and *Cupressus lusitanica*, Mill. The latter species yields rather more oil than the former. The oil from the former is brownish, and has D^{15} 0·8744; a_D +12°6′; acid number, 0·7; saponification number, 4·9; it dissolves in 3·5 vols. of alcohol (90%). The acetylated oil has a_D +14°16′; saponification number, 14·7. The oil from the latter is yellow. Its constants are D^{15} 0·8723; a_D +9°10′; soluble in 3 vols. of 90% alcohol; acid number, 1·05; saponification number, 9·8; saponification number after acetylation, 26·6; a_D of acetylated oil, +8°36′.

Practically no oil could be extracted from the seeds of *C. sempervirens*. The strobiles, freed from seeds, yielded 0·415% of an amber-coloured oil, D^{15} 0·8739; a_D +29°52′; soluble in 4 vols. of 90% alcohol; acid number, 1·0; saponification number, 9·8; saponification number after acetylation, 21·0; a_D of acetylated oil, +29°48′. H. W.

Components of the Essence of Seseli bocconi. LUIGI FRANCESCONI and E. SERNAGIOTTO (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 116—121. Compare A., 1912, i, 123).—In addition to *l*-pinene and *β*-phellandrene, previously recorded, this oil contains a dicyclic aldehyde, a second carbonyl compound accompanying the aldehyde, a dicyclic primary alcohol, an unsaturated secondary alcohol, and *d*-*a*-methylbutyric, formic and acetic acids.

Oxidation of the primary alcohol with potassium dichromate and sulphuric acid yields an aldehyde, the *semicarbazone* of which,

$$C_{11}H_{19}ON_3,$$

has m. p. 148—158°. This aldehyde appears to be identical with that of the essential oil mentioned above, so that the aldehyde of the oil probably has the formula $C_{10}H_{16}O$, and the alcohol the composition $C_{10}H_{18}O$. R. V. S.

New Biochemical Syntheses of Glucosides of Alcohols. ÉMILE BOURQUELOT and MARC BRIDEL (*J. Pharm. Chim.*, 1913, [vii], **8**, 109—112).—Positive results indicating the formation of *β*-glucosides have been obtained with the following alcohols. In all cases 100 c.c.

of acetone, containing 20 grams of water per 100 grams of acetone, and 2 grams of dextrose were used, and varying quantities of alcohol and emulsin added. The isolation and characterisation of the glucosides has not yet been effected. The alcohols used were octyl, hexadecyl, benzaldehydecyanohydrin, *cyclo*hexanol, 2-methyl*cyclo*hexanol, α-naphthyl, borneol, morphine, also *tert.*-amyl alcohol and ethylphenylglycollyl ether.

Evidence is also quoted for the synthesis of α-glycerolglucoside. The action of dried yeast on a solution containing 4 grams of salicin and 5 grams of dextrose per 100 c.c. caused an increased dextrorotation. This is considered to indicate the attachment of the alcoholic hydroxyl in salicin to dextrose in the α-position. E. F. A.

Biochemical Synthesis of Glucosides of Multivalent Alcohols: α-Glucosides of Glycerol and Glycol. ÉMILE BOURQUELOT and MARC BRIDEL (*Compt. rend.*, 1913, **157**, 405—408).—α-Glucosidase is capable of exerting a synthesising effect on solutions of glycerol and dextrose in water, the optimum effect being obtained with solutions containing 60 grams of glycerol in 100 c.c. The product is hydrolysed on the addition of water and maceration with more of the α-glucosidase (compare Bayliss, this vol., i, 919). Mixtures of glycol and dextrose are similarly synthesised, the reaction being more rapid than with glycerol. W. G.

Cymarin, the Active Principle of Apocynum cannabinum and Apocynum androsoemifolium. E. IMPENS (*Pflüger's Archiv*, 1913, **153**, 239—275).—Finnemore (P., 1909, **25**, 77) obtained as the active principle of the roots and rhizomes of *A. cannabinum*, "cynotoxin," whilst Moore (T., 1909, **95**, 734) prepared from *A. androsoemifolium*, "apocynamarin." It is now shown that these plants really contain the same bitter principle, *cymarin*, which is so susceptible to the influence even of weak organic acids that the two substances mentioned above may well be decomposition products. Taub and Fickewirth have isolated it by extracting the drug with carbon tetrachloride, dissolving the extract with alcohol, precipitating resins by means of warm water, clarifying the filtrate with basic lead acetate, and, after removing the lead and concentrating under reduced pressure, extracting the residue with chloroform. The cymarin was then precipitated by light petroleum and recrystallised from methyl alcohol. It forms colourless, glistening prisms, m. p. 135—140°, C = 63·6%, H = 8·4%. It is not a glucoside. A series of pharmacological experiments is described which shows that it corresponds in activity with digitalis, being slightly more potent as a diuretic and slightly less so as a cardiac stimulant. J. C. W.

Action of Alkyloxides on Hæmin and its Derivatives. I. Simplification of Hæmin by Potassium Alkoxides and a New Formation of Mesoporphyrin. HANS FISCHER and HEINRICH RÖSE (*Zeitsch. physiol. Chem.*, 1913, **87**, 38—50).—On heating hæmin in an autoclave with potassium methoxide at 220° a considerable quantity of phyllopyrrole is obtained, together with a little trimethylpyrrolepropionic acid.

With potassium ethoxide a mixture of the two dimethyldiethylpyrroles is formed:

$$\text{I. } NH\Big<\begin{matrix} CMe{:}CMe \\ | \quad\; | \\ CEt{=}CEt \end{matrix}, \qquad \text{II. } NH\Big<\begin{matrix} CMe{:}CEt \\ | \quad\; | \\ CEt{=}CMe \end{matrix}$$

in which (I) predominates.

The reaction with alkyloxides is accordingly similar to the reduction effected by hydrogen iodide in the α-position; alkylation follows the simplification of the molecule by reduction.

The hæmin complex remains intact when it is heated with sodium methoxide at 200°. On treatment of the reaction product with hydrogen bromide in acetic acid, the iron is eliminated and mesoporphyrin obtained. E. F. A.

The Difference between the Hæmocyanins according to their Zoological Origin. CHARLES DHÉRÉ (*Compt. rend.*, 1913, **157**, 309—312).—The preliminary results of an investigation into the differences in composition, constitution, and properties of hæmocyanins derived from the blood of different classes of invertebrates. The specimens examined were precipitated more or less completely on dialysis, the oxyhæmocyanin from the snail being obtained in a crystalline form, whilst the others were all amorphous. The behaviour was also varied on applying the biuret test for copper by addition of aqueous sodium hydroxide. Variations were found in the colour of solutions of different samples in $N/10$-acetic acid, but they all exhibited similar ultra-violet absorption spectra. W. G.

Studies on Melanin. V. A Comparison of Certain Nitrogen Ratios in Black and in White Wool from the Same Animal. ROSS AIKEN GORTNER (*J. Amer. Chem. Soc.*, 1913, **35**, 1262—1268. Compare A., 1910, i, 760; 1911, ii, 908; 1912, i, 290). —In order to determine if possible whether the chromogen utilised in the formation of melanin is part of the normal structure of keratin or whether it is secreted solely for pigment formation, the author has made comparative analyses of black and white wool from the same animal. No definite conclusion can be drawn, although the evidence seems somewhat in favour of the latter view.

The distribution of nitrogen in the two wools is very similar, with the exception that the presence of the pigment in black wool causes an excess of 3·54% in the humin nitrogen with a corresponding deficiency of 2·50% in the amino-nitrogen in the filtrate from the bases. The total nitrogen content of the white wool was 16·27%, whilst that of the black wool was 15·11%. D. F. T.

[Carminic Acid.] OTTO DIMROTH (*Annalen*, 1913, **399**, 378).—The author has received information that cochineal, contrary to his recent statement (this vol., i, 977), has been used in dyeing cotton. C. S.

Green Animal Colouring Matters. HANS PRZIBRAM (*Pflüger's Archiv*, 1913, **153**, 385—400).—The green colouring matters in *Bacillus Rossii*, *Dixippus morosus*, grasshoppers, locusts, Egyptian

praying-crickets, the Spanish fly, the skin of frogs, *Bonellia viridis*, and the leaves of the sea-lettuce, fir, syringa, maize, and blackberry have been compared. Ethereal or sometimes alcoholic extracts of equal colour intensity were heated for some time with saturated alcoholic potassium hydroxide, treated with a few drops of concentrated sulphuric or nitric acid, and also examined in the spectroscope. Many authors have doubted that the pigment in these animals is essentially different from chlorophyll, but the present investigations confirm the author in his view that animals develop a different colouring matter. Only in the case of the plant-eating insects could there be any suspicion, from the spectroscopic examination, that a little genuine plant chlorophyll was also present in the extract. In the flesh-eating insects, even in the wing cases of the praying-cricket, there is a different pigment, "animal green." The sea-worm, *Bonellia viridis*, contains a pigment of its own, "bonellein."

The author reviews the literature on the absorption spectra of chlorophyll and animal colouring matters, and finally tabulates the following characteristics. I. Chlorophyll.—Becomes turbid and precipitates black, flocculent masses on heating with alcoholic potassium hydroxide for some time; is only slightly bleached by strong acids, and shows a strong absorption band between 544 and 537 $\mu\mu$. II. Animal green.—Deposits coloured masses and clarifies with alcoholic potassium hydroxide; almost bleached by fuming nitric acid; rendered turbid and brown by sulphuric acid; shows no distinct band between 544 and 537 $\mu\mu$, and no shadow near 630 $\mu\mu$. III. Bonellein. —Coloured violet or blue by strong acids; shows a number of weak bands, and a strong one between 651 and 623 $\mu\mu$. J. C. W.

Azomethine Dyes from β-Furylacraldehyde. WILHELM KÖNIG (*J. pr. Chem.*, 1913, [ii], 88, 193—226).—In the presence of perchloric and hydrobromic acids, β-furylacraldehyde readily reacts with primary aromatic amines and with secondary amines of the tetrahydroquinoline and dihydroindole series in alcoholic solution, yielding blue dyes, related to the furfuraldehyde dyes already described by the author (A., 1906, i, 109) and having the following constitution (X = Br or ClO_4):

(I.) NRR′·CH:CH·CH:C(OH)·CH:CH·CH:NRR′X.

The dyes give violet-blue or greenish-blue alcoholic solutions, which rapidly lose their colour when kept. This disappearance of the blue colour is due to the removal of one of the amine residues and the formation of furfuraldehyde derivatives of the formula:

$$\text{(II.)}\ \begin{matrix}\text{CH·CH}\\ \|\\ \text{CH—O}\end{matrix}\!\!>\!\text{C·CH:CH·CH:NRR′X.}$$

The latter compounds have been isolated in the form of their perchlorates, (i) by heating the perchlorates of the blue dyes, derived from cyclic secondary amines, in glacial acetic acid solution, and (ii) by the direct interaction of molecular amounts of the amines and β-furylacraldehyde in an alcoholic solution of perchloric acid.

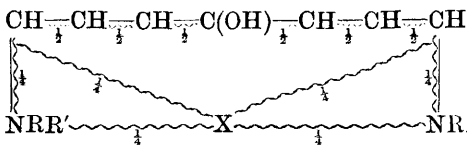
That these compounds have the above constitution (II) and not the open-chain formula, NRR′·CH:CH·CH:C(OH)·CH:CH·CHO, has been

established (i) by the action of phenylhydrazine, which results in the removal of the amino-group and the formation of β-furylacraldehyde-phenylhydrazone (V below), and (ii) by the great similarity in the absorption spectra of the perchlorates of the condensation products, formed by cinnamaldehyde and β-furylacraldehyde with 6-methoxytetrahydroquinoline (thalline); the condensation product from cinnamaldehyde undoubtedly has the constitution represented in formula III, and hence the analogous product from β-furylacraldehyde must be represented by a similar formula (IV).

$$\text{(III.)}\quad CH_2{<}\begin{matrix}C_6H_3(OMe)\\ CH_2\text{—}CH_2\end{matrix}{>}N{<}\begin{matrix}ClO_4\\ CH\cdot CH:CHPh\end{matrix}$$

$$\text{(IV.)}\quad CH_2{<}\begin{matrix}C_6H_3(OMe)\\ CH_2\text{—}CH_2\end{matrix}{>}N{<}\begin{matrix}ClO_4\\ CH\cdot CH:CH\cdot C\end{matrix}\begin{matrix}CH\cdot CH\\ \text{——}O\end{matrix}{>}CH.$$

The author discusses both the mechanism of the formation of the dyes and also the relationship between their absorptive power and constitution from the point of view of Kauffmann's theory of partial valency, and, using Gebhard's method of representing the distribution of the partial valencies, assigns to the dyes the following constitution:



β-Furylacraldehydephenylhydrazone, $C_4H_3O\cdot CH:CH\cdot CH:N\cdot NHPh$ (V), prepared from its components in alcoholic solution, is precipitated from the latter solution in citron-yellow needles, which are transformed by crystallisation from light petroleum into colourless crystals, m. p. 132°.

β-Furylacraldehyde condenses with *m*-nitroaniline in boiling alcoholic solution, yielding the *anil*, $C_4H_3O\cdot CH:CH\cdot CH:N\cdot C_6H_4\cdot NO_2$. This forms citron-yellow needles, m. p. 105°, and yields a *perchlorate*, which crystallises in orange prisms, and is converted by contact with primary or secondary aromatic amines into blue dyes.

The dyes described below were all prepared by the addition of the requisite amine (2 mols.) to a well cooled solution of β-furylacraldehyde (1 mol.) in a small quantity of alcohol, containing either hydrogen bromide (1 mol.) or perchloric acid (1 mol.). They all crystallise with $1H_2O$.

The *bromide* of the dye from the aniline (formula I, R = H, R′ = Ph, X = Br) crystallises in dark bluish-green, microscopic needles, m. p. about 102°; the *perchlorate* in blue needles, m. p. 90°.

The *perchlorate* of the dye from *m*-toluidine forms blue needles, m. p. 108°; that from *p*-anisidine has m. p. about 115°.

The *bromide* of the dye from methylaniline (I, R = Me, R′ = Ph) has m. p. 103°, and on treatment with aniline is converted into the

corresponding dye derived from aniline; the perchlorate forms lustrous, blue needles, m. p. 110°.

Tetrahydroquinoline yields a dye which forms a *bromide*, m. p. about 125°,

$$\begin{matrix}CH_2\cdot C_6H_4\\ | \qquad\\ CH_2-CH_2\end{matrix}>N\cdot CH\!:\!CH\cdot CH\!:\!C(OH)\cdot CH\!:\!CH\cdot CH\!:\!NBr<\begin{matrix}C_6H_4\cdot CH_2\\ \qquad |\\ CH_2-CH_2\end{matrix},$$

and a *perchlorate*, m. p. 118°.

The *perchlorates* of the dyes from 6-methyl- and 5-methyl-tetrahydroquinolines have m. p. 132° and 126° respectively.

The dye from 6-methoxytetrahydroquinoline forms a *bromide*, m. p. 129°, and a *perchlorate*, m. p. 121°.

2-Methyldihydroindole yields a dye, of which the *bromide* has m. p. 138°, and the *perchlorate*, m. p. 131°.

The *bromide* of the dye from α-methylphenomorpholine,

$$\begin{matrix}O\text{———}C_6H_4\\ | \qquad\\ CH_2\cdot CHMe\end{matrix}>N\cdot CH\!:\!CH\cdot CH\!:\!C(OH)\cdot CH\!:\!CH\cdot CH\!:\!NBr<\begin{matrix}C_6H_4-O\\ \qquad |\\ CHMe\cdot CH_2\end{matrix},$$

has m. p. 121°.

When heated in acetic acid solution the perchlorate of the dye from methylaniline yields the *compound*,

$$C_4H_3O\cdot CH\!:\!CH\cdot CH\!:\!NMePh\cdot ClO_4,$$

which forms citron-yellow crystals, m. p. 176°, and is transformed into the original perchlorate on treatment with methylaniline.

In a similar manner the perchlorate of the dye from 6-methyltetrahydroquinoline yields the *compound*

$$C_4H_3O\cdot CH\!:\!CH\cdot CH\!:\!N(ClO_4)<\begin{matrix}C_6H_3Me-\\ CH_2\cdot CH_2\end{matrix}>CH_2.$$

On crystallisation from glacial acetic acid this separates in long red and yellow needles, m. p. 204°, which have the same composition and cannot be separated by crystallisation from solvents; the yellow modification passes into the red form on continued heating at 140—150°.

The *perchlorate* of the condensation product from 6-methoxytetrahydroquinoline and β-furylacraldehyde (formula IV), prepared by mixing the components in molecular proportions in alcoholic solution, forms red crystals, m. p. 188°, resembling chromium trioxide.

The corresponding *perchlorate* from cinnamaldehyde (III) forms orange crystals, m. p. 204°; the *bromide* crystallises in long, orange-red needles, m. p. 185°, containing $1H_2O$.

By the interaction of furfuraldehyde and *m*-nitroaniline in alcoholic solution, Schiff (A., 1880, 391) obtained a substance, which he considered to have the formula: $C_4H_3O\cdot CH(OH)\cdot NH\cdot C_6H_4\cdot NO_2$. The author finds, however, that the substance is not a furfuraldehyde derivative, but a pyrrole derivative of the following constitution: $CH<\begin{matrix}CH\text{———}CH\\ N(C_6H_4\cdot NO_2)\end{matrix}>C\cdot CH\!:\!N\cdot C_6H_4\cdot NO_2$. It separates from ethyl alcohol in orange-yellow crystals, containing the solvent (1 mol.), m. p. 167—168°, and forms a *perchlorate*,

$$C_{17}H_{12}O_4N_4,HClO_4,C_2H_6O,$$

which crystallises in microscopic, brownish-red needles, m. p. 173° (decomp.).

Details of the methods employed in the spectrographic examination of the compounds described in the paper are also given. F. B.

Derivatives of Tetronic Acid. LUDWIG WOLFF (*Annalen*, 1913, **399**, 309—316).—[With H. JUNKER.]—*Bistetronic acid*,

$$\begin{array}{l}CH_2\cdot C(OH)\\ |\\ O\text{———}CO\end{array}\!\!>C\cdot C<\!\!\begin{array}{l}C(OH)\cdot CH_2\\ \qquad\qquad\;\,|\\ CO\text{———}O\end{array},$$

m. p. 235°, colourless, crystalline powder, is obtained by heating *ethyl dibromodiacetylsuccinate* (prepared by the bromination of ethyl diacetylsuccinate in chloroform) at 150—160°, or by treating a boiling aqueous solution of bromotetronic acid with propylidenebistetronic acid and sodium carbonate and subsequently acidifying the solution. Bistetronic acid and ferric chloride develop a blue coloration in aqueous solution and a green in alcohol. The *anilide*, $C_{14}H_{11}O_5N$, m. p. 216°, crystallises in leaflets, and the *dibenzoyl* derivative, $C_{22}H_{14}O_8$, m. p. 215°, in needles.

[With W. HEROLD.]—In general, α-alkyltetronic acids are converted by nitrogen trioxide into nitroso-compounds, $O<\!\!\begin{array}{l}CH_2\cdot CO\\ CO\text{—}CR\cdot NO\end{array}$, in the absence of water, and into oximes, $CO_2H\cdot CH_2\cdot O\cdot CO\cdot CR\colon NOH$, in the presence of water; in the latter case, when the alkyl group R contains more than one carbon atom, it is eliminated in the form of an aldehyde and α-oximinotetronic acid is obtained. Thus 2-ethyltetronic acid and hot aqueous sodium nitrite, in the presence of a little hydrochloric acid, yield acetaldehyde, α-oximinotetronic acid, and *α′-oximinobutyrylglycollic acid*, $CO_2H\cdot CH_2\cdot O\cdot CO\cdot CEt\colon NOH$, m. p. 171°, colourless needles. In a similar manner, 2-benzyltetronic acid yields benzaldehyde, 2-oximinotetronic acid, and *α′-oximino-β′-phenylpropionylglycollic acid*, $CO_2H\cdot CH_2\cdot O\cdot CO\cdot C(\colon NOH)\cdot CH_2Ph$, m. p. 146°, which dissolves in concentrated nitric acid with a blue colour, and is converted into α-oximino-β-phenylpropionic acid by hot aqueous sodium hydroxide, and into the corresponding *amide*, $C_9H_{10}O_2N_2$, m. p. 147°, needles, by aqueous ammonia.

By treatment with 100% nitric acid at 0°, 2-methyltetronic acid or 2-nitroso-2-methyltetronic acid is converted into a neutral *substance*, $C_5H_5O_6N$, m. p. 68°, colourless plates, which probably has the formula $O<\!\!\begin{array}{l}CH_2\cdot C<\!\!\begin{array}{l}O\\ |\\ O\end{array}\\ \qquad\;\;\;|\\ CO\text{—}CMe\cdot NO_2\end{array}$. It does not react with ferric chloride or respond to Liebermann's nitroso-reaction, exhibits powerful oxidising properties, and is decomposed by boiling water into dimethyl diketone, hydrogen cyanide, carbon dioxide, and nitric acid. In a similar manner, 2-nitroso-2-ethyltetronic acid is converted into a *substance*, $C_6H_7O_6N$, m. p. 43°, colourless needles. C. S.

Structural Formula of the Polymeride of the Anhydride of Anethole Glycol. LUIGI BALBIANO (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 93—94. Compare A., 1908, i, 901).—The author now assigns to this polymeride a formula of the type

$$R\cdot C_2H_2Me<\!\!\begin{array}{c}O\\ O\end{array}\!\!>C_2H_2Me\cdot R.$$

R. V. S.

Reactions of the Formamidines. III. Synthesis of *iso*-Oxazolone, *iso*Oxazole, Cyanoacetic and Benzoylacetic Acid Derivatives. FRANK BURNETT DAINS and E. L. GRIFFIN (*J. Amer. Chem. Soc.*, 1913, **35**, 959—970).—In extension of the earlier work (compare A., 1902, i, 602; A., 1909, i, 781) it is found that the methylene group of the *iso*oxazolones of the general formula $\begin{matrix} CH_2\cdot CO \\ CR{=\!=}N \end{matrix}\!>\!O$, like that of phenylmethylpyrazolone is capable of reacting with the arylformamidines.

Diphenylformamidine reacts with an equimolecular quantity of phenyl*iso*oxazolone at 120°, yielding aniline and 3-*phenyl*-4-*anilinomethylene*-5-iso*oxazolone*, $\begin{matrix} O-CO \\ N{:}CPh \end{matrix}\!>\!C{:}CH\cdot NHPh$, yellow, rhombic crystals, m. p. 145°; in a similar manner, di-*o*-tolylformamidine gives 3-*phenyl*-4-o-*toluidinomethylene*-5-iso*oxazolone*, yellow crystals, m. p. 170°; 3-*phenyl*-4-m-*toluidinomethylene*-5-iso*oxazolone*, yellow crystals, m. p. 158°; 3-*phenyl*-4-p-*toluidinomethylene*-5-iso*oxazolone*, slightly red crystals, m. p. 190°; 3-*phenyl*-4-o-*anisidinomethylene*-5-iso*oxazolone*, yellow needles, m. p. 138°; 3-*phenyl*-4-p-*anisidinomethylene*-5-iso*oxazolone*, m. p. 168°; 3-*phenyl*-4-p-*phenetidinomethylene*-5-iso*oxazolone*, m. p. 174°; 3-*phenyl*-4-ψ-*cumidinomethylene*-5-iso*oxazolone*, yellow needles, m. p. 180°; 3-*phenyl*-4-m-*nitroanilinomethylene*-5-iso*oxazolone* yellow needles, m. p. 206°, and 3-*phenyl*-4-p-*bromoanilinomethylene*-5-iso*oxazolone*, a pale yellow substance, m. p. 198°, are all obtainable similarly by applying the suitably substituted formamidine. The last-named product can also be obtained by the action of bromine on an acetic acid solution of phenylanilinomethylene*iso*oxazolone, when an intermediate red monobromo-*compound*, m. p. 148°, is produced, which undergoes rearrangement in solution in pyridine or alcohol with formation of the phenylbromoanilinomethylene*iso*oxazolone.

No derivatives could be obtained from 3-methyl*iso*oxazolone by heating with formamidines as the temperature necessary to induce interaction caused decomposition of the products. Benzylidenemethyl-*iso*oxazolone, however, if heated with an equimolecular proportion of diphenylformamidine at 115—120°, yielded a mixture of benzylideneaniline with 4-*anilinomethylene*-3-*methyl*-5-iso*oxazolone*, pale yellow crystals, m. p. 158°, which dissolves unchanged in cold dilute alkalis, but with a warm solution of potassium hydroxide undergoes decomposition with deposition of aniline and needles of a potassium salt, decomp. 265—270°, of an unidentified *substance*; the above condensation product also reacts with bromine in acetic acid solution with precipitation of a yellow *substance*, which loses hydrogen bromide on drying, and when dissolved in alcohol or boiled with water or pyridine undergoes rearrangement into p-*bromoanilinomethylenemethyl*iso*oxazolone*, yellow needles, m. p. 204°, also obtainable from benzylidenemethyl*iso*oxazolone and di-*p*-bromodiphenylformamidine. A similar rearrangement has been previously noted (A., 1902, i, 602), the substance m. p. 148° having been since recognised as ethyl α-cyano-β-*p*-bromoanilinoacrylate, $C_6H_4Br\cdot NH\cdot CH{:}C(CN)\cdot CO_2Et$, and the explanation of this change appears to be expressed by the following

series of equations: $CHR_2·CH:NPh + Br_2 = CHR_2·CHBr·NBrPh = CR_2:CH·NBrPh + HBr \longrightarrow CR_2:CH·NH·C_6H_4Br$, in the first stage of which the tautomeric form of the anilinomethylene derivative is involved. Diphenylformamidine also combines with bromine, giving a yellow additive *product*, m. p. 262°, which on treatment with potassium hydroxide solution decomposes into *p*-bromoaniline, *p*-bromoformanilide, and aniline.

That the reaction between benzylidenemethyl*iso*oxazolone and formamidines is a general one is evidenced by the following compounds which were also prepared: 4-o-*toluidinomethylene*-3-*methyl*-5-iso*oxazolone*, pale red needles, m. p. 206°; 4-m-*toluidinomethylene*-3-*methyl*-5-iso*oxazolone*, brownish-white needles, m. p. 168°; 4-p-*toluidinomethylene*-3-*methyl*-5-iso*oxazolone*, yellow needles, m. p. 204°, which is decomposed by an alcoholic solution of hydrogen chloride with formation of ammonium chloride and *p*-toluidine hydrochloride, and on treatment with bromine in acetic acid solution gives a yellow additive *product*, m. p. 161—163°; this regenerates the original substance when acted on by alcohol or potassium hydroxide; 4-p-*anisidinomethylene*-3-*methyl*-5-iso*oxazolone*, yellow needles, m. p. 190°; 4-p-*phenetidinomethylene*-3-*methyl*-5-iso*oxazolone*, yellow needles, m. p. 169°; 4-m-*xylidinomethylene*-3-*methyl*-5-iso*oxazolone*, colourless crystals, m. p. 166°; 4-o-*anisidinomethylene*-3-*methyl*-5-iso*oxazolone*, yellow crystals, m. p. 169°.

p-*Methoxybenzylidenemethyl*iso*oxazolone*, deep yellow crystals, m. p. 178°, was prepared by a similar method to the corresponding benzylidene compound, namely, by the action of anisaldehyde and hydrochloric acid on the reaction mixture obtained from ethyl acetoacetate and hydroxylamine hydrochloride in aqueous alcohol containing some pyridine. It reacts with the formamidines in a similar manner to the benzylidene derivative, and on heating with di-ψ-cumylformamidine gave 4-ψ-*cumidinomethylene*-3-*methyl*-5-iso*oxazolone*, a yellow, crystalline substance, m. p. 192°, together with anisylidene-ψ-cumidine, colourless crystals, m. p. 71°.

When a suspension of benzoylanilinomethyleneacetanilide,

$$NHPh·CH:CBz·CO·NHPh,$$

in alcohol is warmed for several hours with rather more than an equimolecular proportion of hydroxylamine hydrochloride and pyridine, there is produced 5-*phenyl*iso*oxazole*-4-*carboxyanilide*,

$$\begin{matrix} N{=}CH \\ | \\ O·CPh \end{matrix}\!\!>\!C·CO·NHPh,$$

colourless needles, m. p. 135°, from the solutions of which in alkali acids precipitate benzoylcyanoacetanilide, CN·CHBz·CO·NHPh, m. p. 203°. In a similar manner, 5-*phenyl*iso*oxazole*-4-*carboxy*-o-*toluidide*, colourless needles, m. p. 114°, can be obtained from *o*-toluidinomethylenebenzoylaceto-*o*-toluidide, and by solution in alkali and reprecipitation by acid is converted into *benzoylcyanoaceto*-o-*toluidide*, colourless needles, m. p. 132°; also 5-*phenyl*iso*oxazole*-4-*carboxy*-p-*toluidide*, colourless needles, m. p. 158°, was prepared, which by successive treatment with alkali and acid yielded *benzoylcyanoaceto*-p-*toluidide*, colourless needles, m. p. 180°; in the preparation of the

p-toluidinomethylenebenzoylaceto-*p*-toluidide required for the last synthesis, a quantity of *ethyl α-benzoyl-*p*-toluidinoacrylate*,

$$C_6H_4Me\cdot NH\cdot CH:CBz\cdot CO_2Et,$$

yellow flakes, m. p. 98°, was obtained. In an analogous manner, p-*anisidinomethylenebenzoylaceto*-p-*anisidide*, yellow crystals, m. p. 196°, obtainable by heating a mixture of ethyl benzoylacetate and di-*p*-anisylformamidine at 140°, could be converted into 5-*phenyl*isoo*xazole*-4-*carboxy*-p-*anisylamide*, colourless needles, m. p. 142°, which under the influence of alkali rearranges to *benzoylcyanoaceto*-p-*anisidide*, colourless needles, m. p. 194°.

Derivatives of 5-methyl*iso*oxazole-4-carboxylic acid can be obtained by taking arylaminomethyleneacetoaceto-arylamides in place of the analogous derivatives of benzoylacetic acid in the immediately preceding general synthetic reaction, and the products under the influence of alkali readily pass into the corresponding amides of cyanoacetoacetic acid; 5-*methyl*isoo*xazole*-4-*carboxy*-o-*toluidide*, colourless needles, m. p. 112°, is converted by alkali into *cyanoacetoaceto*-o-*toluidide*,

$$CN\cdot CHAc\cdot CO\cdot NH\cdot C_6H_4Me,$$

colourless needles, m. p. 110°; 5-*methyl*isoo*xazole*-4-*carboxy*-p-*toluidide*, colourless needles, m. p. 140°, is converted by alkali into *cyanoacetoaceto*-p-*toluidide*, colourless needles, m. p. 176°. 5-*Methyl*isoo*xazole*-4-*carboxyanilide*, a colourless substance, m. p. 136°, which rearranges to cyanoacetoacetanilide, is difficult to isolate on account of its considerable solubility.

During the course of the investigation the following substances were also obtained apparently for the first time: *ethyl* m-*xylidinomethyleneacetoacetate*, $C_6H_3Me_2\cdot NH\cdot CH:CAc\cdot CO_2Et$, colourless crystals, m. p. 122°, by heating ethyl acetoacetate with di-*m*-xylylformamidine at 120°; *cyanoaceto*-m-*toluidide*, colourless crystals, m. p. 138°, by heating together ethyl cyanoacetate and *m*-toluidine for several hours at 160°; *cyanoaceto*-p-*anisidide*, colourless crystals, m. p. 138°, by heating the two components at 160—170°. D. F. T.

Oxindole and Thio-oxindole. CHARLES MARSCHALK (*J. pr. Chem.*, 1913, [ii], 88, 227—250).—A recapitulation and extension of previous work (A., 1912, i, 303, 575).—Thionaphthenquinone reacts with hydrazine hydrate in boiling alcoholic solution, yielding a *substance* (probably a *hydrazone*), which crystallises in yellow leaflets, m. p. 128°, and when heated above its m. p. decomposes into nitrogen and thio-oxindole (2-keto-2:3-dihydro-1-thionaphthen). The latter compound is best prepared by heating *o*-thiolphenylacetic acid with phosphoric oxide in benzene solution. When prepared by this method and submitted to steam distillation, it is generally obtained in stout prisms, m. p. 44—45°, which on distillation under ordinary pressure are transformed into slender needles, m. p. 33—34°. The more fusible modification is also formed by distilling *o*-thiolphenylacetic acid alone, or heating it with acetic anhydride and distilling the product in steam. It differs from the modification of higher m. p. in giving at once a deep-blue coloration with ferric chloride. Only in one instance has it been found possible to transform the modification of m. p. 33—34° into the

less fusible variety, a specimen of the former substance, obtained by heating *o*-thiolphenylacetic acid with phosphoric oxide in benzene solution, being converted into the modification of higher m. p. by acidifying its solution in cold aqueous sodium hydroxide.

On treatment with nitrous acid, thio-oxindole yields thionaphthenquinone-3-oxime, m. p. 181° (Friedländer, A., 1908, i, 200, gives m. p. 186°). It couples with benzenediazonium chloride, yielding a substance, $C_{14}H_{10}ON_2S$, which crystallises in intensely red, lustrous needles, m. p. 159—160°, and is possibly identical with the phenylhydrazone of thionaphthenquinone (m. p. 165—166°) described by Friedländer (*loc. cit.*). With *p*-nitrobenzenediazonium chloride it forms a red *azo-dye*,

$$C_{14}H_9O_3N_3S,$$

m. p. 271—272°.

The *azo-dyes* from α- and β-naphthalenediazonium chlorides crystallise in stout, brown needles, m. p. 192—193° and 154—156° respectively.

When heated with *o*-methoxybenzaldehyde in alcoholic solution in the presence of piperidine, thio-oxindole yields *2-keto-3-o-methoxybenzylidene-2 : 3-dihydro-1-thionaphthen*,

$$OMe\cdot C_6H_4\cdot CH{:}C<\begin{matrix}CO\\C_6H_4\end{matrix}>S,$$

which forms yellow needles, m. p. 96—98°, and is hydrolysed by alcoholic potassium hydroxide to *α-thiolphenyl-o-methoxycinnamic acid*, $OMe\cdot C_6H_4\cdot CH{:}C(C_6H_4\cdot SH)\cdot CO_2H$, crystallising in stout, colourless needles, m. p. 134—136°.

It condenses with thionaphthenquinone-2-*p*-dimethylanil and acenaphthene in hot glacial acetic acid solution containing a little sulphuric acid, yielding 2 : 3′-bisoxythionaphthen (Friedländer, A., 1908, i, 673) and 8-oxy-6-oxythionaphthenylacenaphthene (Bezdzik and Friedländer, *loc. cit.*) respectively.

When heated with isatin in alcoholic solution, thio-oxindole forms an additive *compound*, $S<\begin{matrix}C_6H_4\\CO\end{matrix}>CH\cdot C(OH)<\begin{matrix}C_6H_4\\CO\end{matrix}>NH$, crystallising in colourless needles, which gradually become red at 135°, m. p. 155—160°. The additive compound gives a brown coloration with sulphuric acid, and when heated for a short time with glacial acetic acid containing a few drops of strong hydrochloric acid, is converted into *3′-indoxyl-3-thionaphthen-2′-one*, $S<\begin{matrix}C_6H_4\\CO\end{matrix}>C{:}C<\begin{matrix}C_6H_4\\CO\end{matrix}>NH$, which crystallises in lustrous, silky, brown needles, m. p. 230°, and may also be obtained by the interaction of thio-oxindole or *o*-thiolphenylacetic acid and isatin in the presence of a mixture of glacial acetic and sulphuric acids (1 : 2) at the ordinary temperature.

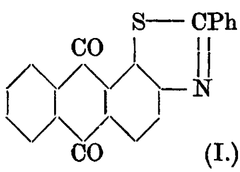
(3′)-5′ : 7′-Dichloroindoxyl-3-thionaphthen-2′-one,

$$S<\begin{matrix}C_6H_4\\CO\end{matrix}>C{:}C<\begin{matrix}C_6H_2Cl_2\\CO\end{matrix}>NH,$$

prepared by maintaining a solution of 5 : 7-dichloroisatin and thio-oxindole in the above acid mixture for three hours at the ordinary temperature, crystallises in dark brown needles, m. p. 330°.

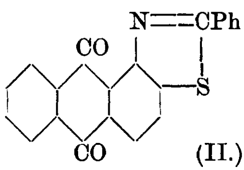
The corresponding *dibromo*-derivative, from 5 : 7-dibromoisatin, forms brown needles, m. p. 331°. F. B.

The Anthraquinone Series. III. Anthraquinonethiazoles. FRITZ ULLMANN and WALTHER JUNGHANS (*Annalen*, 1913, **399**, 345—352).—*2-Phenyl*-4 : 5-(2′ : 1′)-*anthraquinonethiazole* (formula I), m. p. 291° (corr.), yellowish-green needles, is obtained by boiling 2-benzylideneamino-anthraquinone with sulphur and naphthalene, or, better, by heating 1-chloro-2-aminoanthraquinone with potassium thiobenzoate and naphthalene at about 225°.



(I.)

2-Phenyl-4 : 5-(1′ : 2′) - *anthraquinonethiazole* (formula II), m. p. 260° (corr.), brown needles, and *2-phenyl*-4 : 5-(2′ : 3′)-*anthraquinonethiazole*, $C_6H_4<{CO\cdot C{:}CH\cdot C\cdot N \atop CO\cdot C{:}CH\cdot C\cdot S}>CPh$, m. p. 336—337° (corr.), faintly yellow crystals, are prepared by the latter method from 2-bromo-1-aminoanthraquinone and 3-bromo-2-amino-anthraquinone respectively. The last-mentioned thiazole does not possess dyeing properties.



(II.)

1 : 3-Dibromo-2-aminoanthraquinone and potassium thiobenzoate react in boiling amyl alcohol, the initially-formed thiazole being converted into a *thiazole*-3 : 3′-*disulphide*, $C_{42}H_{20}O_4N_2S_4$, m. p. about 385°; by a similar method, 1-chloroanthraquinone is converted into the anthraquinonyl-1 : 1′-disulphide, m. p. 359°, obtained by Gattermann from anthraquinonyl-1-mercaptan. C. S.

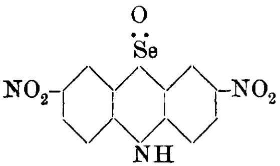
Selenodiarylamines. WILHELM CORNELIUS (*J. pr. Chem.*, 1913, [ii], **88**, 395—408).—The selenium analogues of thiodiphenylamine and its derivatives are readily obtained by heating diarylamines with selenium dichloride in benzene solution (compare Weizmann and Stephen, P., 1913, **29**, 196).

Selenodiphenylamine, $NH<{C_6H_4 \atop C_6H_4}>Se$, prepared from diphenylamine, crystallises in small, lustrous, yellow leaflets, m. p. 195°, which become greenish on exposure to air, owing to slight oxidation. Its constitution has been established by the formation of carbazole on distilling the substance with zinc dust or iron filings. With ferric chloride in alcoholic solution, it yields an emerald-green coloration. When heated with methyl iodide in methyl-alcoholic solution, it forms a *methyl* derivative, which crystallises in white needles, m. p. 138—139°, and is freed from the accompanying green oxidation product by reduction with sulphurous acid in alkaline solution. The methyl derivative resembles the parent substance in yielding various characteristic colorations on treatment with oxidising agents. It forms a yellow *nitro*-compound, which is converted by reduction and subsequent oxidation with ferric chloride into a red dye.

When heated with acetic anhydride, selenodiphenylamine forms an *acetyl* derivative, crystallising in white flakes or stout, lustrous, prismatic crystals, m. p. 176°.

On treatment with concentrated nitric acid at 0°, it yields two isomeric *dinitroselenoxydiphenylamines*, $C_{12}H_7O_5N_3Se$, which are readily

separated by taking advantage of the insolubility of the α-isomeride in alcohol. The α-isomeride crystallises in clusters of small, light brown needles, melts with decomposition, and dissolves in aqueous alkalis and ammonia yielding strawberry-red solutions; the white *silver* and *mercuric* salts are mentioned. On reduction and subsequent oxidation, the α-compound gives rise to the selenium analogue of Lauth's violet, and, therefore must have the annexed constitution.



The β-isomeride forms a reddish-brown, crystalline mass, and is converted by successive reduction and oxidation into a reddish-violet *dye*. When treated with dilute nitric acid, selenodiphenylamine yields a *mononitro*-derivative, which, however, could not be separated from the accompanying dinitro-derivatives. On reducing the mixture of nitro-compounds with tin and hydrochloric acid, *aminoselenodiphenylamine*, $NH{<}{\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_3(NH_2)}}{>}Se$, separates in the form of its *stannichloride*. This crystallises in lustrous needles, and, on treatment with zinc and hydrochloric acid, yields the *zincichloride*, crystallising in small, broad, transparent needles. The free *base* is liberated from the latter compound by aqueous sodium hydroxide and crystallises in small, white, pearly, lustrous leaflets; the *hydrochloride* is precipitated in white needles by passing hydrogen chloride into a benzene solution of the base; the *acetyl* derivative has m. p. above 330° (decomp.).

Oxidation of the hydrochloride or zincichloride by means of ferric chloride in aqueous solution results in the formation of a dye, which is precipitated by the addition of sodium and zinc chlorides in the form of its *zincichloride*, $2\,{\genfrac{}{}{0pt}{}{N{-}C_6H_4}{NH\cdot C_6H_3}}{>}Se,H_2ZnCl_4$. This crystallises in very slender, bronze needles, dyes silk light blue to bluish-violet, and, on the addition of alkalis to its hot alcoholic solution, yields the free *base*, which forms a crystalline red powder, and is converted by hydrogen chloride in ether solution into the *hydrochloride*.

α-Dinitroselenoxydiphenylamine is reduced by stannous chloride and hydrochloric acid to *diaminoselenodiphenylamine stannichloride*,

$$2NH{<}{\genfrac{}{}{0pt}{}{C_6H_3(NH_2)}{C_6H_3(NH_2)}}{>}Se,H_2SnCl_4,H_2O.$$

This crystallises in slender, lustrous, yellowish-brown needles, and is converted by the addition of zinc to its aqueous solution into the *zincichloride*, which is oxidised by ferric chloride to *selenonine*, the selenium analogue of Lauth's violet. The latter compound separates in the form of its *zincichloride*, $2\,{\genfrac{}{}{0pt}{}{N{-}C_6H_3(NH_2)}{NH\cdot C_6H_3}}{>}Se,H_2ZnCl_4$, in very slender, felted, reddish-brown needles, having a bronze lustre. The dye *base*, obtained from the zincichloride by the action of aqueous sodium hydroxide, crystallises in small bronze needles and forms a *hydrochloride*, which crystallises in long, slender, felted needles, having a bronzy-green lustre, and dyes silk turquoise-blue.

The selenium analogue of methylene-blue has been prepared by the action of hydrogen selenide on *p*-nitrosodimethylaniline and subsequent oxidation of the resulting compound with ferric chloride in hydrochloric acid solution.

Selenophenyl-β-naphthylamine, $NH<\substack{C_6H_4\\C_{10}H_6}>Se$, prepared by heating phenyl-β-naphthylamine with selenium dichloride in benzene solution, crystallises in small, yellow needles, m. p. 176°, and gives a greenish-blue coloration with sulphuric acid.

Seleno-α-dinaphthylamine, $NH<\substack{C_{10}H_6\\C_{10}H_6}>Se$, from αα-dinaphthylamine, forms small, yellow needles, m. p. 176—177°.

Seleno-β-dinaphthylamine crystallises from benzene in slender, felted, yellowish-green needles, from nitrobenzene in long, pointed prisms, m. p. 245°, and from alcohol in tabular crystals. On treatment with nitric acid in acetic acid solution, it yields a yellow *nitro*-compound.

Seleno-p-*ditolylamine* crystallises in yellow, lustrous, broad scales, m. p. 240°. F. B.

New Derivatives of Artemisin and of Santonin. II. ENRICO RIMINI and TEMISTOCLE JONA (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 28—32. Compare this vol., i, 748).—When artemisin is reduced with hydrogen in presence of palladium-black, *α-tetrahydroartemisin*, $C_{15}H_{22}O_4$, is obtained. It crystallises in plates, m. p. 192—193°, $[\alpha]_D^{23}$ +49·60° (in 2·671% alcoholic solution). From the mother-liquor a second hydro-derivative, *β-tetrahydroartemisin*, $C_{15}H_{22}O_4$, m. p. 165—167°, can be obtained. This substance has $[\alpha]_D^{23}$ +65·15° (in 2·670% alcoholic solution). Both tetrahydroartemisins are stable towards Baeyer's reagent. *α-Tetrahydroartemisinsemicarbazone*, $C_{15}H_{22}O_3{:}CH_3ON_3$, decomposes at 245°. *β-Tetrahydroartemisinsemicarbazone*, $C_{15}H_{22}O_3{:}CH_3ON_3$, decomposes at 257—258°. *α-Tetrahydroartemisinoxime*, $C_{15}H_{22}O_3{:}NOH$, decomposes at 248°. *β-Tetrahydroartemisinoxime*, $C_{15}H_{22}O_3{:}NOH$, decomposes at 242°. Artemisinoxime yields α-tetrahydroartemisin when hydrogenated in presence of palladium-black. When α-tetrahydroartemisin is dissolved in sodium hydroxide and the solution acidified with sulphuric acid at a low temperature, *α-tetrahydroartemisinic acid* can be extracted with chloroform; it softens and loses water at 55°, decomposing at 118°. Its *sodium* salt crystallises in needles. *β-Tetrahydroartemisinic acid* is similarly prepared, and is much more stable. It forms needles, m. p. 218—220° (decomp.), and on titration with alkali gives figures agreeing with the composition $C_{14}H_{23}O_3{\cdot}CO_2H$. R. V. S.

Action of the Halogens on Artemisin. ENRICO RIMINI and TEMISTOCLE JONA (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 71—74. Compare preceding abstract).—When a solution of artemisin in glacial acetic acid is treated with a solution of hydrogen bromide and bromine in the same solvent, *artemisin dibromide hydrobromide*, $C_{30}H_{37}O_8Br_3$, is

obtained. This unstable oxonium compound, which readily loses bromine, forms lustrous, red crystals which decompose at 94°. Under slightly different experimental conditions, the compound described is accompanied by *monobromoartemisin*, $C_{15}H_{17}O_4Br$, a stable, yellow substance which becomes red at about 70° and decomposes at 95°.

Artemisin di-iodide hydriodide, $C_{30}H_{37}O_8I_3$, similarly prepared, is a brown, crystalline substance, m. p. 118—119° (decomp.).

By the action of chlorine on a chloroform solution of artemisin at 15°, a *chloroartemisin*, $C_{15}H_{15}O_3Cl_3$, is obtained, but the preparation is uncertain; the substance crystallises in needles, which decompose at 212°. When the chlorination is effected at 20°, a crystalline *chloroartemisin*, $C_{15}H_{20}O_4Cl_2$, is obtained; it decomposes at 133°.

R. V. S.

Identity of Lycorine and Narcissine. YASUHIKO ASAHINA and Y. SUGII (*Arch. Pharm.*, 1913, **251**, 357—360).—The authors have examined the base lycorine, which together with a second base sekisanine was isolated by Morishima (A., 1899, i, 93) from the bulbs of *Lycoris radiata*. They are of opinion that lycorine, $C_{16}H_{17}O_4N$, m. p. 275° (decomp.), darkening at about 240°, $[\alpha]_D^{13}$ $-123\cdot7°$ in alcohol and pyridine (*hydrochloride*, colourless needles, m. p. 217°; *picrate*, m. p. 195—202° [decomp.], yellow leaflets), is identical with the alkaloid narcissine, $C_{16}H_{17}O_4N$, m. p. 266—267°, $[\alpha]_D$ $-95\cdot8°$, colourless prisms (hydrochloride, m. p. 198—199°, colourless needles; picrate, m. p. 196—199°, yellow leaflets), obtained by Ewins (T., 1910, **97**, 2406) from the bulbs of *Narcissus pseudonarcissus*.

C. S.

Formula of *apo*Morphine Hydrochloride. VINCENZO PAOLINI (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 121—125).—Estimations of the water of crystallisation in *apo*morphine hydrochloride from various sources all indicate $\frac{3}{4}H_2O$. The amount of chlorine in the salt is that required by the formula $C_{17}H_{17}O_2N,HCl,\frac{3}{4}H_2O$, and the elementary analysis of *apo*morphine gives the composition $C_{17}H_{17}O_2N$. Dibenzoyl-*apo*morphine has, in freezing benzene, the composition required by the formula $C_{17}H_{15}N(OBz)_2$.

R. V. S.

Preparation of Hydrogenised Alkaloids of the Morphine Group. HERMANN OLDENBERG and BABETTE OLDENBERG (D.R.-P. 260233).—Alkaloids of the morphine group are readily hydrogenised by the action of hydrogen in the presence of colloidal palladium, or a metal of the platinum group. *Hydromorphine*, $C_{17}H_{21}O_3N,H_2O$, fine needles, m. p. 155—157°, is obtained when morphine hydrochloride (10 parts) in 250 parts of water is shaken with a mixture of colloidal palladium (1 part) in 10 parts of water which has been saturated with hydrogen; the *hydrochloride* forms microscopic prisms; the *sulphate* is less readily obtained in crystalline form; it gives the colour reactions of Fröhde, Husemann, and Marquis.

Hydrocodeine, rhombic crystals, m. p. 62—63°, has also 1 mol. water of crystallisation and gives Fröhde's and Hesse's colour reactions.

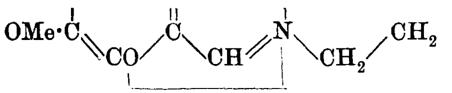
Tetrahydrothebaine, $C_{19}H_{25}O_3N$, is prepared from thebaine and responds to Fröhde's and Erdmann's reagents; the *hydrochloride* forms

prisms; the *hydrogen tartrate* is obtained by the reduction of thebaine hydrogen tartrate.

The therapeutic action of these compounds is also discussed.

F. M. G. M

Berberine. II. Berberrubine. GEORG FRERICHS and P. STOEPEL (*Arch. Pharm.*, 1913, **251**, 321—339).—Berberrubine is best obtained by heating well dried berberine chloride at about 190° in a slow current of carbon dioxide. There can be little doubt that anhydrous berberrubine contains the annexed group.



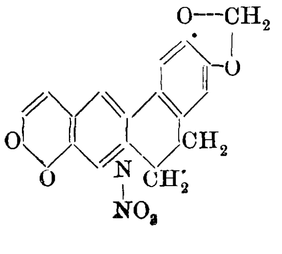
Since it is readily converted into berberine iodide by treatment with methyl iodide, other alkyl haloids may be expected to produce homologous berberines. Thus a large excess of ethyl iodide on the water-bath converts berberrubine into *ethylberberrubine iodide* (*homoberberine iodide*), $C_{21}H_{20}O_4NI$, yellow or yellowish-brown needles, which reacts with boiling alcoholic $N/2$-potassium hydroxide and acetone to form *ethylberberrubineacetone*, $C_{24}H_{25}O_5N$, m. p. 159°, from which the salts of ethylberberrubine are obtained by heating with dilute acids; the *chloride*, $C_{21}H_{20}O_4NCl,2H_2O$, is described.

By boiling with dilute acetic and sulphuric acids and zinc and a little platinum, ethylberberrubine chloride is reduced and yields, after basification with aqueous ammonia, *ethyltetrahydroberberrubine*, $C_{21}H_{23}O_4N$, m. p. 129°, faintly yellow crystals, which resembles tetrahydroberberine throughout.

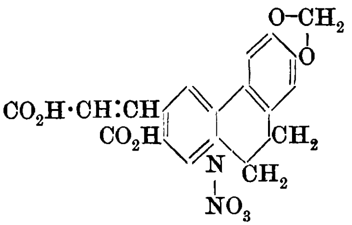
Berberrubine reacts additively, not only with alkyl haloids, but also with other organic halogen compounds. Ethyl bromoacetate and alcohol on the water-bath convert it into the *bromide* of *ethyl berberrubineacetate*, $C_{23}H_{22}O_6NBr$, yellow crystals, which is converted by digestion with silver oxide and hot water into *berberrubineacetic acid*, $C_{21}H_{17}O_6N,5H_2O$; a hot aqueous solution of the latter is converted into the *hydrochloride*, $C_{21}H_{17}O_6N,HCl,2H_2O$, yellow crystals, by N-hydrochloric acid.

In a similar manner, berberrubine and ethyl α-bromopropionate yield the *bromide* of *ethyl berberrubinepropionate*, $C_{24}H_{24}O_6NBr$, yellow needles, from which *berberrubinepropionic acid*, $C_{22}H_{19}O_6N,2H_2O$, yellow needles, is obtained; the *hydrochloride* of the latter also crystallises in yellow needles. Berberrubine does not react with ethyl β-iodopropionate.

Berberrubine, unlike berberine, is attacked by oxidising agents most readily in its methoxylated benzene nucleus. By treatment with hot 25% nitric acid it yields two crystalline substances, berberrubinone and berberrubinic acid, both of which are obtained in the form of nitrates. *Berberrubinone nitrate* (annexed formula) forms dark green, almost black, crystals, which are deep red by transmitted light, is converted into a *sulphate* (or mixture of normal and hydrogen sulphates), dark green crystals, by hot dilute sulphuric acid,



and by treatment with boiling dilute sulphuric acid and 30% sodium hydrogen sulphite is reduced to the sulphate of the corresponding quinol, *berberrubinol sulphate*, a yellow substance. From the hot solution of the latter, saturated sodium hydrogen carbonate liberates *berberrubinol*, $C_{18}H_{13}O_4N,3H_2O$, an amorphous, dark red powder. Anhydrous berberrubinol is a phenol-betaine, and is therefore a completely demethylated berberine; it is not identical with Perkin's berberoline, which has the same composition.



Berberrubinic acid nitrate (annexed formula) and the corresponding *chloride*, $C_{18}H_{14}O_6NCl$, form golden-yellow crystals, and are decomposed by water with the formation of *berberrubinic acid*, an amorphous, yellow substance, which is probably a betaine; it has not been obtained entirely free from the nitrate or chloride.

A hot aqueous solution of berberrubine is converted by sodium hypochlorite into *chloroberberrubine*, $C_{19}H_{14}O_4NCl$, reddish-brown needles, which forms a *chloride*, $C_{19}H_{15}O_4NCl_2,3H_2O$, orange-yellow crystals. Chloroberberrubine certainly contains the chlorine atom in the methoxylated benzene nucleus (probably in the meta-position to the methoxy-group), because by the prolonged action of sodium hypochlorite it is converted into the *lactam chloride*,

$$\begin{array}{l} NCl\cdot CO-C\cdot CH{:}C\cdot O \\ CH_2\cdot CH_2\cdot C\cdot CH{:}C\cdot O \end{array}\!\!>CH_2,$$

m. p. 114°, colourless needles, of ω-aminoethylpiperonylcarboxylic acid; the lactam-chloride, which can also be obtained by the action of sodium hypochlorite on berberine chloride or bromoberberrubine in hot aqueous solution, is converted into Perkin's lactam, m. p. 181°, by treatment with hot aqueous sodium sulphite.

Chloroberberrubine is reduced to *chlorotetrahydroberberrubine*, $C_{19}H_{18}O_4NCl$, m. p. 142°, colourless crystals (*hydrochloride*, white, crystalline powder), by zinc and platinum and hot dilute acetic and sulphuric acids, and reacts with methyl iodide at 100° to form *chloroberberine iodide*, $C_{20}H_{17}O_4NClI$; the latter, which resembles berberine iodide in its behaviour, reacts with alcoholic $N/2$-potassium hydroxide and acetone to form *chloroberberineacetone*, $C_{23}H_{22}O_5NCl$, m. p. 171°, yellow crystals. The following substances are obtained by methods similar to the preceding: *bromoberberrubine*, $C_{19}H_{14}O_4NBr$, reddish-brown needles, and its *chloride*, $C_{19}H_{15}O_4NClBr,3H_2O$, yellow crystals; *bromotetrahydroberberrubine*, $C_{19}H_{18}O_4NBr$, m. p. 145°, colourless crystals; *bromoberberine iodide*, $C_{20}H_{18}O_4NBrI$, golden-yellow leaflets, and *bromoberberine acetone*, $C_{23}H_{22}O_5NBr$, m. p. 153°, yellow crystals.

C. S.

Preparation of Hydrastinine from Berberine. EMMANUEL MERCK (D.R.-P. 259873. Compare Voss, A., 1910, i, 415; Freund, A., 1912, i, 383, 487).—Phenyltetrahydroberberine (m. p. 222°) when digested with methyl iodide furnishes a *methiodide*, m. p. 243°.

Phenyldihydroberberine on electrolytic reduction gives rise to two

stereoisomeric phenyltetrahydroberberines with m. p.'s 222° and 202—204°; these can be separated by fractional crystallisation of their sulphates; the *methiodide* of the isomeride (m. p. 202—204°) has m. p. 247°.

When either of the foregoing phenyltetrahydroberberines is digested with silver chloride, and subsequently reduced with sodium amalgam, it yields a *base*, $C_{27}H_{29}O_4N$, m. p. 112—113° (the *hydriodide* has m. p. 218°), which on oxidation gives rise to hydrastinine. F. M. G. M.

Reactions of the Formamidines. IV. FRANK BURNETT DAINS, O. O. MALLEIS, and J. T. MEYERS (*J. Amer. Chem. Soc.*, 1913, **35**, 970—976. Compare this vol., i, 1086).—The previous investigations have indicated that the general reaction of formamidines with compounds containing methylene hydrogen may be formulated:

$$CH_2XY + NR\colon CH\cdot NHR = CXY\colon CH\cdot NHR + NH_2R.$$

If Y is a carbethoxy-group the amine produced can react with it to give an amide and an alcohol. The occurrence of the second reaction is more marked the higher the temperature.

p-Aminophenylbenzyl ether (hydrochloride, m p. 222—223°; *benzoyl* derivative, m. p. 226—227°; *benzylidene* derivative, colourless leaflets, m. p. 118°; *anisylidene* derivative, m. p. 150°) when warmed with ethyl orthoformate readily enters into reaction, producing *di*-p-*benzyloxydiphenylformamidine*, $C_7H_7O\cdot C_6H_4N\colon CH\cdot NH\cdot C_6H_4\cdot OC_7H_7$, colourless crystals, m. p. 153°; *hydrochloride*, m. p. 261°; *picrate*, m. p. 209°. When heated with ethyl cyanoacetate at 120—130°, the formamidine reacts, producing aminophenylbenzyl ether and *ethyl α-cyano-β*-p-*benzyloxyanilinoacrylate*, $CH_2Ph\cdot O\cdot C_6H_4\cdot NH\cdot CH\colon C(CN)\cdot CO_2Et$, brown crystals, m. p. 120°. The formamidine reacts in the usual manner with ethyl malonate, giving *ethyl* p-*benzyloxyanilinomethylenemalonate*-p-*benzyloxyanilide*, colourless crystals, m. p. 131°, as with ethyl malonate the molecule of amine produced in the first stage of the reaction is always found to enter into amide formation. Ethyl acetoacetate with the formamidine yields products of both the first and second stages of the reaction, giving *ethyl* p-*benzyloxyanilinomethyleneacetoacetate*, $CH_2Ph\cdot O\cdot C_6H_4\cdot NH\cdot CH\colon CAc\cdot CO_2Et$, a pale yellow substance, m. p. 95°, together with *p*-benzyloxyanilinomethyleneacetoaceto-*p*-benzyloxyanilide, fine, yellow needles, m. p. 164°.

As was to be expected from experiments with other formamidines, phenylmethylpyrazolone readily reacts with di-*p*-benzyloxydiphenylformamidine, giving 1-*phenyl*-4-p-*benzyloxyanilinomethylene*-3-*methyl*-5-*pyrazolone*, red needles, m. p. 181°.

When ethyl orthoformate is heated with *p*-aminodimethylaniline at 125° for two hours, *di*-p-*dimethylaminodiphenylformamidine*, m. p. 157°, is obtained, which gives a yellow *monohydrochloride*, m. p. 233°, a *dihydrochloride* and a colourless *trihydrochloride*, m. p. 193°; *picrate*, m. p. 172°. The formamidine reacts with ethyl malonate, yielding *ethyl* p-*dimethylaminoanilinomethylenemalonate-dimethylaminoanilide*, $NMe_2\cdot C_6H_4\cdot NH\cdot CH\colon C(CO_2Et)\cdot CO\cdot NH\cdot C_6H_4\cdot NMe_2$, m. p. 142°, and with ethyl cyanoacetate giving *ethyl α-cyano-β*-p-*dimethylaminoanilinoacrylate*, $NMe_2\cdot C_6H_4\cdot NH\cdot CH\colon C(CN)\cdot CO_2Et$, colourless needles, m. p. 134°. When heated with ethyl acetoacetate the amidine produced phenylene-

dimethyldiamine and p-*dimethylaminoanilinomethyleneacetoaceto*-p-*dimethylaminoanilide*, $NMe_2{\cdot}C_6H_4{\cdot}NH{\cdot}CH{:}CAc{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}NMe_2$, m. p. 178°, together with a little *ethyl dimethylaminoanilinomethyleneacetoacetate*, m. p. 88°.

Di-p-*iododiphenylformamidine*, $C_6H_4I{\cdot}N{:}CH{\cdot}NH{\cdot}C_6H_4I$, colourless needles, m. p. 175°, is easily obtained by the combination of *p*-iodoaniline and ethyl orthoformate at water-bath temperature; *hydrochloride*, m. p. 249°; picrate, dark yellow crystals, m. p. 226°. With ethyl cyanoacetate at 125°, it produces *ethyl α-cyano-β*-p-*iodoanilinoacrylate*, brown needles, m. p. 154°, whilst with ethyl malonate *ethyl* p-*iodoanilinomethylenemalonate*-p-*iodoanilide*,

$$C_6H_4I{\cdot}NH{\cdot}CH{:}C(CO_2Et){\cdot}CO{\cdot}NH{\cdot}C_6H_4I,$$

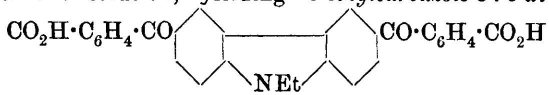
colourless crystals, m. p. 176°, is obtained. With ethyl acetoacetate the products are iodoaniline, *ethyl* p-*iodoanilinomethyleneacetoacetate*,, $C_6H_4I{\cdot}NH{\cdot}CH{:}CAc{\cdot}CO_2Et$, colourless crystals, m. p. 96°, and p-*iodoanilinomethyleneacetoaceto*-p-*iodoanilide*, m. p. 184°. The formamidine also reacts with acetylacetone, producing p-*iodoanilinomethyleneacetylacetone*, $CAc_2{:}CH{\cdot}NH{\cdot}C_6H_4I$, pale yellow needles, m. p. 180°, whilst with benzylidenemethyl*iso*oxazolone at 140°, 3-*methyl*-4-p-*iodoanilinomethylene*-5-iso*oxazolone*, $\begin{matrix}N{:}CMe\\ | \\ O{-}CO\end{matrix}{>}C{:}CH{\cdot}NH{\cdot}C_6H_4I$, yellow crystals, m. p. 208°, is obtained. The *benzylidene* derivative, m. p. 85°, and *anisylidene* derivative, colourless needles, m. p. 151°, of *p*-iodoaniline were also prepared.

5-Iodo-*o*-toluidine (acetyl derivative, m. p. 176°, reacts quantitatively with bromine in chloroform solution producing 5-bromoaceto-*o*-toluidide, m. p. 158—159°; *benzylidene* derivative, colourless needles, m. p 55°) also reacts with ethyl orthoformate, giving *di*-5-*iododi*-o-*tolylformamidine*, $C_6H_3MeI{\cdot}N{:}CH{\cdot}NH{\cdot}C_6H_3MeI$, needles, m. p. 169°; *hydrochloride*, m. p. 254°. This formamidine shows the usual behaviour towards compounds containing the methylene group, for example, with ethyl acetoacetate it forms *ethyl* 5-*iodo*-o-*toluidinomethyleneacetoacetate*, m. p. 137—138°, and 5-*iodo*-o-*toluidinomethyleneacetoaceto*-5-*iodo*-o-*toluidide*, silky needles, m. p. 238°. With ethyl cyanoacetate and malonate the reaction products are *ethyl* 5-*iodo*-*α*-*cyano*-o-*toluidinoacrylate*, m. p. 207°, and *ethyl* 5-*iodo*-o-*toluidinomethylenemalonate*-5-*iodo*-o-*toluidide*, m. p. 201°. At 120° with benzylidenemethyl*iso*oxazolone the formamidine gives rise to 3-*methyl*-4-*iodotoluidinomethylene*-5-iso*oxazolone*, needles, m. p. 209°. D. F. T.

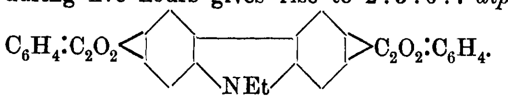
Preparation of Carbazolemonosulphonic Acids and their 9-Alkyl Derivatives. LEOPOLD CASSELLA & Co. (D.R.-P. 260898. Compare this vol., i, 516).—When carbazole (17 parts) is dissolved in 10—15 parts of hot nitrobenzene and cooled to 0° (when part of the carbazole separates), treated with chlorosulphonic acid (12 parts), and the temperature subsequently allowed to rise to 20°, it furnishes *carbazolesulphonic acid*, which is isolated in the form of its sodium salt, colourless, glistening leaflets; the *barium* salt, glistening scales, is more sparingly soluble. This compound condenses with *p*-nitrosophenol in concentrated sulphuric acid solution to furnish soluble blue dyes containing sulphur.

9-*Ethylcarbazolesulphonic acid* can also be prepared in quantitative yield by this method. F. M. G. M.

[Preparation of 9-Ethylcarbazole-3 : 6-diphthaloylic Acid.] LEOPOLD CASSELLA & Co. (D.R.-P. 261495. Compare A., 1911, i, 567). —9-Ethylcarbazole reacts with phthalic anhydride and aluminium chloride in nitrobenzene solution, yielding 9-*ethylcarbazole*-3 : 6-*diphthaloylic acid*,



and this when heated with concentrated sulphuric acid at 100—105° during five hours gives rise to 2 : 3 : 6 : 7-*diphthaloyl*-9-*ethylcarbazole*,



F. M. G. M.

Catalytic Decomposition of Acetonylacetonephenylhydrazone. ALEXANDER E. ARBUZOV and N. E. CHRUCKI (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 699).—Catalytic decomposition of acetonylacetonephenylhydrazone at 180—190° in presence of cuprous chloride yields ammonia, dimethylaminophenylpyrrole, benzene and aniline, the last two products probably arising from the decomposition of a little admixed phenylhydrazine. T. H. P.

Catalytic Decomposition of Methyl Propyl Ketonephenylhydrazone. ALEXANDER E. ARBUZOV and A. P. FRIAUF (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 694—696).—Catalytic decomposition of methyl propyl ketonephenylhydrazone at 185—210° in presence of cuprous chloride yields, as principal product, *propylindole*, $C_{11}H_{13}N$, which is an almost odourless, pale yellow liquid, b. p. 155—156°/9 mm., and forms a *picrate*, $C_{17}H_{16}O_7N_4$, m. p. 148—149°. Small proportions of secondary gaseous and liquid products also result from the decomposition. T. H. P.

Catalytic Decomposition of Dipropyl Ketonephenylhydrazone. ALEXANDER E. ARBUZOV and R. E. VAGNER (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 697—699).—Catalytic decomposition of dipropyl ketonephenylhydrazone at 175—235° in presence of cuprous chloride yields principally 3-*ethyl*-2-*propylindole*, $C_{13}H_{17}N$, which crystallises in unstable, colourless plates, m. p. 45·5°, and forms a *picrate*, $C_{13}H_{17}N,C_6H_3O_7N_3$, m. p. 117·5°. Other products, including aniline, are formed in small proportions. T. H. P.

Syntheses in the Indole Group. V. Syntheses of *N*- and *C*-Substituted Derivatives of Scatole and Methylketole. BERNARDO ODDO (*Gazzetta*, 1913, **43**, ii, 190—211. Compare A., 1912, i, 649 ; this vol., i, 755).—3-Acetyl-2-methylindole can be obtained in 86% yield by the action of acetyl chloride on the magnesium derivative of 2-methylindole (*loc. cit.*). Its *hydrochloride*,

$C_{11}H_{11}ON,HCl$,

was also prepared. The *aurichloride*, $C_{11}H_{11}ON,HCl,AuCl_3$, becomes brown at about 135°, melting at 158° (decomp.). The *platinichloride*, $(C_{11}H_{11}ON,HCl)_2PtCl_4$, blackens above 170°, melting at 195° (decomp.). The hydrochloric acid solution of the ketone gives precipitates with phosphotungstic acid, potassium cadmium iodide, potassium bismuth iodide, and potassium dichromate.

1-*Acetylscatole*, $C_6H_4\left\langle\begin{array}{l}CMe\\ \\ NAc\end{array}\right\rangle CH$, is obtained by the action of acetyl chloride on the magnesium derivative of scatole, a low temperature being maintained with ice. It forms colourless needles, m. p. 68°, and has about the normal molecular weight in freezing benzene. Its constitution is shown by its yielding scatole when treated with alcoholic potassium hydroxide, and by the fact that it gives no precipitate with silver nitrate. In the preparation of 1-acetylscatole, a *substance* crystallising in needles of m. p. 146° is also obtained.

2-Acetylscatole is obtained when the above reaction is effected at the temperature of the water-bath. Its *hydrochloride* has the composition $(C_{11}H_{11}ON)_2,HCl$, and its solution gives precipitates with phosphotungstic acid, potassium bismuth iodide, potassium dichromate, and gold chloride. The *platinichloride* has the composition

$$(C_{11}H_{11}ON,HCl)_2PtCl_4,$$

The action of propionyl chloride on the magnesium derivative of scatole yields both propionylmethylindoles, which can be separated by distillation with steam. 1-*Propionylscatole*, $C_{12}H_{13}ON$, has m. p. 45°. 2-*Propionylscatole*, $C_{12}H_{13}ON$, has m. p. 161°, and when fused with potassium hydroxide yields indole-3-carboxylic acid. 3-*Propionyl*-2-*methylindole*, $C_{12}H_{13}ON$, is obtained from propionyl chloride and the magnesium derivative of methylketole; it forms colourless crystals, m. p. 194°, and has about half the calculated molecular weight in freezing phenylhydrazine (*K* for phenylhydrazine is 58·59). Oxidation of the substance with potassium permanganate yields acetyl-*o*-aminobenzoic acid.

3-*Butyryl*-2-*methylindole*, $C_{13}H_{15}ON$, is prepared by the action of butyryl chloride on the magnesium derivative of methylketole; it is a white, crystalline substance, m. p. 157—158°, and tends to become yellow when exposed to the air.

3-Benzoyl-2-methylindole, $C_{16}H_{13}ON$ (from benzoyl chloride and the magnesium derivative of methylketole), forms colourless needles, m. p. 181°. When the reaction is effected at a low temperature, traces of a *substance* of m. p. 81° are produced, which is probably the 1-derivative.

R. V. S.

Condensation of Aldehydes with *N*-Mono-substituted *p*-Diamines. RICHARD SCHLÖGL (*J. pr. Chem.*, 1913, [ii], 88, 251—256).—An account of the preparation of a number of anils by the condensation of acetyl-*p*-phenylenediamine, *p*-amino-oxanilic acid, and *p*-aminophenylglycine with aromatic aldehydes.

The *salicylidene*, *cinnamylidene* (m. p. 120°), 3:4-*dihydroxybenzylidene*, *vanillidene*, and *furfurylidene* (m. p. 135°) derivatives of *p*-amino-

phenylglycine are prepared by warming the glycine with an alcoholic solution of the corresponding aldehyde.

The *benzylidene* derivative of *p*-aminophenyloxamic acid is obtained in the form of its *hydrochloride*, $C_{15}H_{13}O_3N_2Cl$, m. p. 180°, by heating an alcoholic suspension of the oxamic acid with benzaldehyde and hydrochloric acid.

The following compounds were prepared in a similar manner: the *hydrochlorides* of the *vanillidene* (m. p. 170°), *cinnamylidene* (m. p. 125°), and *furfurylidene* (m. p. 130°) derivatives of *p*-aminophenyloxamic acid, and the *hydrochlorides* of the *benzylidene* (m. p. 165°), *vanillidene* (m. p. 208°), and *cinnamylidene* (m. p. 195°) derivatives of acetyl-*p*-phenylenediamine.

The condensation *product* from acetaldehyde and *p*-aminophenylglycine forms a dark brown powder (decomp. 280°), insoluble in the ordinary solvents; attempts to effect a condensation of acetyl-*p*-phenylenediamine and *p*-aminophenylglycine with formaldehyde and acetaldehyde were unsuccessful.

All the derivatives mentioned above are readily resolved by boiling with water or alkali hydroxides into their components, and on account of the presence of the azomethine group, are coloured, those of *p*-aminophenylglycine being red. F. B.

Hydrazones. LUIGI VECCHIOTTI (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 75—76).—Many nitrohydrazones exist in red and in yellow modifications. The present paper gives a list of these compounds and the forms observed in each instance. R. V. S.

Extractives of Muscle. XIV. Carnosine and Carnosine Nitrate. WLADIMIR GULEWITSCH (*Zeitsch. physiol. Chem.*, 1913, **87**, 1—11. Compare A., 1900, i, 516; 1905, i, 726; 1906, i, 627; 1907, i, 264, 436).—The purification of carnosine nitrate and carnosine is described. The nitrate crystallises in large, stellate aggregates of needles, m. p. 219° (decomp.), $[\alpha]_D + 23.3°$ in 5% solution. The rotatory power increases slightly on dilution; it falls to about half its value in presence of nitric acid.

Carnosine crystallises in large, colourless needles, which unite to rosettes and cauliflower-like aggregates, m. p. 246—250° (decomp.). It has an insipid taste, and is strongly alkaline. It has $[\alpha]_D + 21°$, independently of the concentration. No racemisation takes place in preparing it from the nitrate. E. F. A.

Preparation of Chloro- and Bromo-substitution Products of Indophenols and Indophenolic Substances or their Leuco-derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 260328 and 260329).—The action of *p*-nitrosophenol on carbazoles has previously been studied (A., 1906, i, 890; 1911, i, 1025), and halogen derivatives of these compounds have now been prepared.

When 4-dimethylamino-4′-hydroxydiphenylamine (230 parts) dissolved in concentrated hydrochloric acid (1700 parts) is treated at 10—15° with 150 parts of chlorine, it furnishes a *dichloro-4-dimethylamino-4′-hydroxydiphenylamine hydrochloride* in quantitative yield

which on oxidation gives rise to the corresponding *indophenol*. *Compounds* obtained by the action of chlorine on an *o*-dichlorobenzene solution of the following substances, and their oxidation products are described: from *p*-nitrosophenol with carbazole and the leuco-compound of the same; from *p*-nitrosophenol with *N*-methyl- or *N*-ethyl-carbazole and their leuco-compounds.

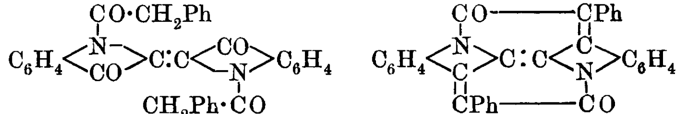
II. describes the preparation of the corresponding bromo-derivatives; in this case the reaction is carried out in *o*-dichlorobenzene solution.

F. M. G. M.

Constitution of Anilopyrine. LINO METELLO ZAMPOLLI (*Boll. chim. farm.*, 1913, **52**, 502—504).—Polemical. A reply to Comanducci (this vol., i, 903).

R. V. S.

Preparation of Red Condensation Products from Indigotin, its Homologues, and Substitution Products. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 260243. Compare this vol., i, 763).—The action of phenylacetyl chloride on indigotin yields the red, crystalline *compounds* I or II, according to the conditions of the experiment:



(I.) (II.)

Analogous *compounds* prepared from tetrabromoindigotin are also described, which are of a somewhat bluer shade.

F. M. G. M.

Benzoylation of Benziminazoles. LUDWIG WOLFF (*Annalen*, 1913, **399**, 297—309).—The reaction described by Bamberger and Berlé, in which secondary benziminazoles yield dibenzoyl-*o*-phenylenediamine and a fatty acid by treatment with benzoyl chloride and aqueous sodium hydroxide, is explained by the author's experiments on the benzoylation of secondary or tertiary benziminazoles. He finds that secondary benziminazoles yield a benzoyl derivative. This benzoyl derivative or, in the case of a tertiary compound, the benziminazole itself forms an additive compound with benzoic acid, which probably has the constitution $C_6H_4<\begin{matrix}NR\cdot COR'\\ NHBz\end{matrix}$, and is decomposed by the alkali, yielding benzoylated *o*-phenylenediamines and a fatty acid.

[With R. GRÜN and F. KOLASIUS.]—The benziminazoles are treated with benzoyl chloride (2 or 4 mols.) and 10% sodium hydroxide (4 or 6 mols.). The precipitate is treated with ether, whereby the benzoyl derivative and oily products are dissolved; the residue is separated by chloroform into the acylphenylenediamine and dibenzoyl-*o*-phenylenediamine.

Benziminazole yields 1-benzoylbenziminazole (in very small amount), dibenzoyl-*o*-phenylenediamine, and *dibenzoylformyl*-o-*phenylenediamine*, $NHBz\cdot C_6H_4\cdot NBz\cdot CHO$, m. p. 155—156°, needles, which is converted into formic acid and dibenzoyl-*o*-phenylenediamine by boiling

with alcohol, hydrochloric acid, or sodium hydroxide, and yields, by heating at 180—200°, carbon monoxide, benzoic acid, dibenzoyl-*o*-phenylenediamine, and 1-benzoylbenziminazole.

2-Methylbenziminazole yields 1-*benzoyl*-2-*methylbenziminazole*

$$C_6H_4<\genfrac{}{}{0pt}{}{NBz}{N}>CMe,$$

m. p. 86°, long needles, dibenzoyl-*o*-phenylenediamine, and *dibenzoylacetyl*-o-*phenylenediamine*, $NHBz\cdot C_6H_4\cdot NBzAc$, m. p. 154°, prisms, which is converted into acetic acid and dibenzoyl-*o*-phenylenediamine by alcoholic hydrochloric acid or sodium hydroxide. 2-Ethylbenziminazole yields similar products; 1-*benzoyl*-2-*ethylbenziminazole*, colourless plates, has m. p. 89°, whilst *dibenzoylpropionyl*-o-*phenylenediamine*, m. p. 124°, yields propionic acid and dibenzoyl-*o*-phenylenediamine by treatment with sodium hydroxide or hydrochloric acid.

1-*Phenyl* 2-*ethylbenziminazole*, $C_6H_4<\genfrac{}{}{0pt}{}{NPh}{N}>CEt$, m. p. 45°, colourless plates (*hydrochloride*, $C_{15}H_{14}N_2,HCl,H_2O$, prisms), is prepared by warming *o*-aminodiphenylamine with propionic anhydride and treating the resulting o-*propionylaminodiphenylamine*, $C_{15}H_{16}ON_2$, m. p. 144°, needles, with 10% hydrochloric acid; by treating the solution with sodium carbonate the benziminazole is precipitated. By the action of benzoyl chloride and 10% sodium hydroxide at 50°, it yields an oil and *propionyl*-o-*benzoylaminodiphenylamine*, $NHBz\cdot C_6H_4\cdot NPh\cdot COEt$, m. p. 157°, plates, which is converted by warm alcoholic potassium hydroxide into propionic acid and *o*-benzoylaminodiphenylamine.

By treatment with benzoyl chloride and 10% sodium hydroxide at 50—60°, 1-phenyl-2-methylbenziminazole yields *acetyl*-o-*benzoylaminodiphenylamine*, $NHBz\cdot C_6H_4\cdot NPhAc$, m. p. 122° (which is decomposed into acetic acid and *o*-benzoylaminodiphenylamine by hot alcoholic sodium hydroxide), a *substance*, $C_{28}H_{20}O_2N_2$, m. p. 165°, needles, and an oil which yields the substance, m. p. 165°, by further benzoylation. The substance, m. p. 165°, is possibly $C_6H_4<\genfrac{}{}{0pt}{}{NPh}{N}>C\cdot CH\colon CPh\cdot OBz$, since it does not develop a coloration with ferric chloride, and is converted in hot alcoholic solution, by elimination of a benzoyl group, into 1-*phenyl*-2-*phenacylbenziminazole*,

$$C_6H_4<\genfrac{}{}{0pt}{}{NPh}{N}>C\cdot CH_2\cdot COPh,$$

m. p. 119°, large plates or prisms. The latter develops a green coloration with ferric chloride, yields the substance, m. p. 165°, by benzoylation, and forms a *hydrochloride*, m. p. 240—245° (decomp.), *semicarbazone*, m. p. 202°, colourless prisms, and *phenylhydrazone*, m. p. 164°, colourless prisms. C. S.

Pyrimidines. LXIII. A New Method of Synthesising Uramils and Thiouramils. TREAT B. JOHNSON and NORMAN A. SHEPHARD (*J. Amer. Chem. Soc.*, 1913, **35**, 994—1007).—Ethyl phthaliminomalonate reacts with thiocarbamide in warm alcoholic solution containing sodium ethoxide, the product being 2-thiouramil, $CS<\genfrac{}{}{0pt}{}{NH\cdot CO}{NH\cdot CO}>CH\cdot NH_2$, which is probably formed by the hydrolysis of a previous condensation product; thiouramil when warmed with

sodium hydroxide solution undergoes hydrolysis, giving a substance, possibly *aminothiomalonuric acid*, $NH_2\cdot CS\cdot NH\cdot CO\cdot CH(NH_2)\cdot CO_2H$.

Ethyl β-phthaliminoethylmalonate also condenses with thiocarbamide in the presence of sodium ethoxide in hot alcoholic solution, forming 2-*thio*-5-β-*phthaliminoethylbarbituric acid*,

$$CS<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>CH\cdot CH_2\cdot CH_2\cdot N<\begin{matrix}CO\\CO\end{matrix}>C_6H_4,$$

prisms, decomp. 265—270° (*sodium* salt, bright yellow), which on hydrolysis yields 2-*thio*-5-β-*aminoethylbarbituric acid*,

$$CS<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>CH\cdot CH_2\cdot CH_2\cdot NH_2,$$

prisms, decomp. 298—300°, together with phthalic acid. If the condensation is effected with carbamide in place of thiocarbamide, phthalimide and 2 : 4 : 6-triketo-5-β-hydroxyethylpyrimidine (5-hydroxyethylbarbituric acid), $CO<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>CH\cdot CH_2\cdot CH_2\cdot OH$, a pale yellow powder which did not melt below 300°, were obtained.

Ethyl anilinomalonate also readily reacts with thiocarbamide in the presence of sodium ethoxide, giving rise to 2-*thio*-7-*phenyluramil*, $CS<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>CH\cdot NHPh$, orange-coloured prisms, decomp. 250—260°. With carbamide, however, a new type of compound was obtained, namely, *anilinomalonuric acid*, $NH_2\cdot CO\cdot NH\cdot CO\cdot CH(NHPh)\cdot CO_2H$, prismatic crystals, which do not melt below 300°. This substance when digested with acetic acid undergoes dehydration to γ-*phenyluramil*, $CO<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>CH\cdot NHPh$, an insoluble, crystalline powder. Allylthiocarbamide resembles thiocarbamide in behaving normally with ethyl anilinomalonate, and gives 2-*thio*-7-*phenyl*-1-*allyluramil*,

$$CO<\begin{matrix}CH(NHPh)\cdot CO\\NH\text{———————}CS\end{matrix}>N\cdot CH_2\cdot CH{:}CH_2,$$

an insoluble powder, m. p. 185—187° (decomp.); *sodium* salt, brown powder.

When ethyl anilinomalonate is added to an alcoholic solution of sodium ethoxide, it gives a sodium derivative, which on the further addition of *p*-nitrobenzyl chloride reacts with the formation of two substances, one of which is insoluble in ether; the insoluble substance, needles or prisms, m. p. 180—182°, is probably 2-p-*nitrobenzylindoxyl*, $C_6H_4<\begin{matrix}CO\\NH\end{matrix}>CH\cdot CH_2\cdot C_6H_4\cdot NO_2$, whilst the soluble substance is *ethyl* p-*nitrobenzylanilinomalonate*, $NO_2\cdot C_6H_4\cdot CH_2\cdot C(NHPh)(CO_2Et)_2$, an oil, which on hydrolysis yields p-*nitrobenzylanilinomalonic acid*, prisms or leaflets, m. p. 205—210° (decomp.). D. F. T.

Pyrimidines. LXIV. Synthesis of 4-Methyl-5-ethylcytosine. TREAT B. JOHNSON and GEORGE C. BAILEY (*J. Amer. Chem. Soc.*, 1913, **35**, 1007—1014).—The paper commences with a summary of the alkyl derivatives of cytosine, $NH<\begin{matrix}CO—N\\CH{:}CH\end{matrix}>C\cdot NH_2$, which have been prepared in the same laboratory.

When warmed together in sodium ethoxide solution, ethyl ethylacetoacetate and thiocarbamide react normally, giving the colourless

sodium salt of 2-*thio*-4-*methyl*-5-*ethyl*-1 : 2 : 3 : 6-*tetrahydro*-6-*pyrimidone*, $CS<\substack{NH-CO \\ NH\cdot CMe}>CEt$, the free substance forming colourless prisms, m. p. 212°; alkylation is effected when the alcoholic solution of the sodium salt is treated with an alkyl haloid, for example, benzyl chloride gives rise to 2-*benzylthiol*-4-*methyl*-5-*ethyl*-1 : 6-*dihydro*-6-*pyrimidone*, blocks, m. p. 160°, whilst ethyl bromide yields 2-*ethylthiol*-4-*methyl*-5-*ethyl*-1 : 6-*dihydro*-6-*pyrimidone*, colourless crystals, m. p. 138°. The last-named derivative is converted by a molecular proportion of phosphorus pentachloride at 100° into 6-*chloro*-2-*ethylthiol*-4-*methyl*-5-*ethylpyrimidine*, b. p. 177—180°/21—23 mm., which is stable in contact with water, but is decomposed by warm alcohol, and also reacts with strong alcoholic ammonia at 140—150°, yielding 6-*amino*-2-*ethylthiol*-4-*methyl*-5-*ethylpyrimidine*, $CEt<\substack{C(NH_2):N \\ CMe——N}>C\cdot SEt$, stout blocks, m. p. 89—91°. Both the benzylthiol- and the ethylthiol-substituted pyrimidines described above are converted by hydrolysis with acids into 4-methyl-5-ethyluracil, $CO<\substack{NH-CO \\ NH\cdot CMe}>CEt$, the yield being quantitative when the ethylthiol compound is heated with a boiling aqueous solution of chloroacetic acid. The same uracil derivative is obtained in the action of chloroacetic acid on the parent substance, 2-thio-4-methyl-5-ethyl-1 : 2 : 3 : 6-tetrahydro-6-pyrimidone.

2-Ethylthiol-4-methyl-5-ethyl-1 : 6-dihydro-6-pyrimidone, when heated with aniline at 100° and with alcoholic ammonia at 150—160°, eliminates the thiol group with formation respectively of 2-*anilino*-4-*methyl*-5-*ethyl* 1 : 6-*dihydro*-6-*pyrimidone*, $CNHPh<\substack{NH\cdot CO \\ N-CMe}>CEt$, m. p. 195°, and 2-*amino*-4-*methyl*-5-*ethyl*-1 : 6-*dihydro*-6-*pyrimidone*, prisms, m. p. 281—282° (decomp.); *hydrobromide*, needles, m. p. 160—175°, according to rate of heating; *hydrochloride*, m. p. 115°, crystallises with one H_2O.

Boiling hydrochloric acid converts 6-amino-2-ethylthiol-4-methyl-5-ethylpyrimidine into 6-*amino*-4-*methyl*-5-*ethyl*-2 : 3-*dihydro*-2-*pyrimidone* (*methylethylcytosine*), $CO<\substack{N:C(NH_2) \\ NH—CMe}>CEt$, blocks or rectangular prisms, m. p. 295° (decomp.), which is obtained first as the *hydrochloride*, a colourless powder, decomp. at 125°; the *hydrobromide*, blocks, decomp. near 260°; the *picrate*, needles, *mercurichloride*, *phosphotungstate*, and *potassio-bismutho-iodide* were also prepared.

The sodium salt of 2-thio-4-methyluracil reacts with diphenylmethyl bromide in alcoholic solution with formation of 2-*diphenylmethylthiol*-4-*methyl*-1 : 6-*dihydro*-6-*pyrimidone*, $CH<\substack{CO\cdot NH \\ CMe-N}>C\cdot S\cdot CHPh_2$, m. p. 214°, in small yield.

D. F. T.

Hydantoins. XXIII. Synthesis of 2-Thiohydantoins from Acyl Derivatives of α-Amino-acids. TREAT B. JOHNSON and WALTER M. SCOTT (*J. Amer. Chem. Soc.*, 1913, **35**, 1130—1136. Compare Johnson, A., 1912, i, 390; Johnson and Nicolet, A., 1912, i, 53, etc.).—The reaction between ammonium thiocyanate and an acyl derivative

of an α-amino-acid in acetic anhydride solution appears to be a general one, but the only β-amino-acid examined merely underwent acetylation without any subsequent reaction with the thiocyanate.

o-Carboxybenzoylaminoacetic acid, $CO_2H\cdot C_6H_4\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, obtained by the hydrolysis of ethyl phthalylaminoacetate, when heated by steam for twenty minutes with a $1\frac{1}{4}$ molecular proportion of ammonium thiocyanate in 5—7 parts by weight of acetic anhydride, gave 2-thiohydantoin, m. p. 225—227°, phthalylaminoacetic acid, m. p. 192—193°, and phthalic acid. This was the only case in which the acylhydantoin could not be isolated, although the results indicate that it must have been an intermediate product of the reaction.

p-Methoxyhippuric acid with ammonium thiocyanate in acetic anhydride solution gave 3-p-*methoxybenzoyl*-2-*thiohydantoin*,

$$\begin{matrix} CO\cdot CH_2 \\ | \\ NH\text{—}CS \end{matrix}\!\!>N\cdot CO\cdot C_6H_4\cdot OMe,$$

pale yellow prisms, m. p. 166°, whilst *m*-nitrohippuric acid yielded 3-m-*nitrobenzoyl*-2-*thiohydantoin*, m. p. 198—199°.

Benzenesulphonylaminoacetic acid in an analogous manner gave rise to 3-*benzenesulphonyl*-2-*thiohydantoin*, $\begin{matrix} CO\cdot CH_2 \\ | \\ NH\text{—}CS \end{matrix}\!\!>N\cdot SO_2Ph$, colourless needles, m. p. 210—211° (decomp.).

The product obtained by a similar process with carbethoxyaminoacetic acid was ethyl 2-thiohydantoin-3-carboxylate, $\begin{matrix} CO\cdot CH_2 \\ | \\ NH\text{—}CS \end{matrix}\!\!>N\cdot CO_2Et$, plates, m. p. 168°.

The application of dibromophenylalanine and benzoylalanine to this reaction resulted in the formation of 2-*thio*-3-*acetyl*-4-*dibromobenzylhydantoin*, $\begin{matrix} NH\text{—}CO \\ | \\ CS\cdot NAc \end{matrix}\!\!>CH\cdot CH_2\cdot C_6H_3Br_2$, plates, m. p. 171° (which on hydrolysis gave 2-*thio*-4-*dibromobenzylhydantoin*, colourless needles, m. p. 243°), and 2-*thio*-3-*benzoyl*-4-*methylhydantoin*, m. p. 158° respectively.

Anthranilic acid under similar treatment merely became converted into acetylanthranilic acid. D. F. T.

Hydantoins. XXIV. Action of Ammonium Thiocyanate on Lactone Anhydrides of Acylamino-acids. TREAT B. JOHNSON and WALTER M. SCOTT (*J. Amer. Chem. Soc.*, 1913, **35**, 1136—1143. Compare preceding abstract).—The provisional interpretation of the mechanism of the reaction between thiocyanic acid (as ammonium thiocyanate) and the acyl derivative of a monobasic α-amino-acid in acetic anhydride (Johnson and Nicolet, A., 1912, i, 53) is withdrawn in favour of the scheme:

$$RCO\cdot NH\cdot CH_2\cdot CO_2H \xrightarrow{Ac_2O} \begin{matrix} CR{:}N \\ | \\ O\cdot CO \end{matrix}\!\!>CH_2 \xrightarrow{HSCN}$$
$$RCO\cdot NH\cdot CH_2\cdot CO\cdot NCS \longrightarrow \begin{matrix} NH\text{—}CS \\ | \\ CO\cdot CH_2 \end{matrix}\!\!>N\cdot COR.$$

Among the reasons for this new view are the facts that acetic anhydride is the only solvent which has been found suitable, and that

the first ring formation is a normal change when acylamino-acids are heated with acetic anhydride; it has already been shown that the lactonoid anhydrides undergo scission by hydrogen chloride, producing acid chlorides in a manner analogous to the second change above (compare Mohr and Kohler, A., 1910, i, 116).

In agreement with the above explanation it is found that with hippuric acid or benzoylalanine, acylthiohydantoins are not produced in acetic acid with ammonium thiocyanate, although if the amino-acid is previously heated with acetic anhydride the resulting lactonoid anhydride readily gives rise to the corresponding acylthiohydantoin in acetic acid solution.

Acetylphenylglycine and ethyl hippurate are not affected by ammonium thiocyanate in acetic anhydride, thus indicating the necessity for the presence of unsubstituted hydrogen at the nitrogen atom and at the carboxyl group. With benzamide, no evidence of the formation of benzoylthiocarbamide was obtained; this is a further reason for discarding the old theory of formation in favour of that now suggested.

Contrary to expectation, the lactim of α-benzoylamino-β-phenylacrylic acid failed to react with thiocyanic acid in acetic anhydride, whilst the free acid under such treatment only yielded the lactim.

D. F. T.

Rings Containing a Triple Linking. II. Optimum Number of Atoms in the Ring. PAUL RUGGLI (*Annalen*, 1913, **399**, 174—182).—The following substances of the type

$$C_6H_4 <\begin{matrix} NH\cdot CO\cdot[CH_2]_x\cdot CO\cdot NH \\ \text{———}C{:}C\text{———} \end{matrix}> C_6H_4$$

have been prepared from *oo'*-diaminotolan and the requisite acid chloride in the same manner as *cyclo*succinyldiaminotolan (A., 1912, i, 914); cyclo*glutaryldiaminotolan*, $C_{19}H_{16}O_2N_2$, m. p. 300—302° (decomp.), colourless crystals, cyclo*adipyldiaminotolan*, $C_{20}H_{18}O_2N_2$, m. p. 252° (decomp.), colourless needles, cyclo*pimelyldiaminotolan*, $C_{21}H_{20}O_2N_2$, m. p. 248° (decomp.), colourless needles, cyclo*suberyldiaminotolan*, $C_{22}H_{22}O_2N_2$, m. p. 223—224·5°, colourless needles, and cyclo*lepargyldiaminotolan*, $C_{23}H_{24}O_2N_2$, m. p. about 240° (decomp.), colourless needles.

A comparison of the yields obtained under similar conditions shows *cyclo*adipyldiaminotolan, containing a 14-membered ring, is obtained in the largest amount, namely, 50% of that theoretically possible. Cyclic compounds containing a nuclear triple linking have not been obtained from *pp'*-diaminotolan or from *trans-oo'*-diaminostilbene.

pp'-Dinitrotolan, which is best prepared by boiling *pp'*-dinitrostilbene dibromide with pyridine, is readily reduced to *pp'*-diaminotolan by stannous chloride and hydrochloric and acetic acids in the cold.

C. S.

Benzylcreatinine. WILLY HENNIG (*Arch. Pharm.*, 1913, **251**, 396—400).—Creatinine and benzyl chloride at 136—140° yield *benzylcreatinine hydrochloride*, $C_{11}H_{13}ON_3,HCl$, faintly yellow needles, blackening at about 230° (*aurichloride*, $C_{11}H_{13}ON_3,HAuCl_4$, m. p. 158°, yellow needles; *platinichloride*, $2C_{11}H_{13}ON_3,H_2PtCl_6$, m. p.

177—178°, red crystals), from an aqueous solution of which lead hydroxide liberates *benzylcreatinine*, m. p. 225°, faintly yellow crystals. The action, therefore, of benzyl chloride, similarly to that of alkyl iodides, on creatinine is substitutive, not additive. The oxidation of benzylcreatinine hydrochloride by alkaline 5% potassium permanganate at 30—40° yields *benzylmethylguanidine* (*platinichloride*,

$$2C_9H_{10}N_3,H_2PtCl_6,$$

m. p. 148°; *aurichloride*, m. p. 190—191°). C. S.

Addition of Phenylazoimide to Quinones. II. LUDWIG WOLFF (*Annalen*, 1913, **399**, 274—297).—[With R. HERCHER.]—α-Naphthaquinone and phenylazoimide react to form a dihydrotriazole derivative, $C_6H_4<\begin{matrix}CO\cdot CH\cdot NPh\\ | \\ CO\cdot CH\text{——}N\end{matrix}>N$, which cannot be isolated, but decomposes, yielding mainly 1-*phenylazoimino-α-naphthaquinone* [4 : 9-*diketo*-1-*phenyldihydro*-ββ-*naphtha*iso*triazole*],

$$C_6H_4<\begin{matrix}CO\cdot C\cdot NPh\\ \| \\ CO\cdot C\text{——}N\end{matrix}>N,$$

m. p. 241°, pale yellow leaflets, at 60—65°, and mainly *indandione*-2-*aldehydeanil*, $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>CH\cdot CH{:}NPh$, m. p. 191°, yellow prisms or plates, on the water-bath.

Phenylazoiminonaphthaquinone forms an *oxime*,

$$C_6H_4<\begin{matrix}C({:}NOH)\cdot C\cdot NPh\\ \| \\ CO\text{————}C\text{——}N\end{matrix}>N,$$

m. p. 232° (decomp.), almost colourless needles, which probably contains the oximino-group in the position shown, because, unlike the parent substance, it is not ruptured by sodium hydroxide. Phenylazoiminonaphthaquinone itself is decomposed by boiling aqueous alcoholic sodium hydroxide, yielding after acidification 4-o-*carboxybenzoyl*-1-*phenyl*-1 : 2 : 3-*triazole*, $CO_2H\cdot C_6H_4\cdot CO\cdot C<\begin{matrix}CH\cdot NPh\\ | \\ N{=}N\end{matrix}$, m. p. 177—178° (anhydrous), colourless needles containing $\frac{1}{2}H_2O$. This acid is decomposed into phthalic acid, aniline, and probably acetic acid by aqueous sodium hydroxide at 150°, and in alkaline solution yields with hydroxylamine hydrochloride and subsequent acidification the oxime of the acid, which, however, slowly changes to an *anhydride*, $C_{16}H_{10}O_2N_4$, m. p. 220°, colourless needles, insoluble in sodium carbonate.

Indandione-2-aldehydeanil does not develop a coloration with ferric chloride, forms a *sodium* salt, red needles, with alcoholic sodium hydroxide, and is decomposed by boiling aqueous sodium hydroxide, yielding aniline and indandione-2-aldehyde in the form of its *sodium* salt, $C_{10}H_5O_3Na$, yellow needles. Indandione-2-aldehyde crystallises in colourless needles containing H_2O, m. p. 125° (decomp.) (141°, anhydrous), develops a red coloration with ferric chloride, and behaves like a strong, monobasic acid, decomposing carbonates; the *calcium* salt crystallises in sparingly soluble prisms. The aldehyde or its salt in cold aqueous solution reacts with aniline, phenylhydrazine, hydroxylamine, and semicarbazide to form respectively the preceding anil;

phenylhydrazone, $C_{16}H_{12}O_2N_2$, m. p. 220° (decomp.), yellow prisms; *oxime*, $C_{10}H_7O_3N,H_2O$, m. p. 205° (decomp.), orange needles, and *semicarbazone*, $C_{11}H_9O_3N_3$, m. p. 233° (decomp.), yellow needles.

By boiling with 20% hydrochloric acid, the sodium salt of indandione-2-aldehyde is decomposed into formic acid, bindone, indandione, and a *substance*, $C_{19}H_{10}O_4$, m. p. about 308° (decomp.), red needles, which is probably $C_6H_4{<}{}^{CO}_{CO}{>}C{:}CH{\cdot}CH{<}{}^{CO}_{CO}{>}C_6H_4$, since it can also be produced by heating equal molecular quantities of indandione and its aldehyde at 120° or in boiling alcohol, and can be converted into these two substances by aqueous sodium hydroxide.

[With M. KÖRBS.]—Three of the four substances produced by the interaction of phenylazoimide and *p*-benzoquinone have been previously described (A., 1912, i, 1034). The fourth is a *substance*, $C_{18}H_{14}O_2N_4$, m. p. 157—160° (decomp.), yellow leaflets, the constitution of which has not yet been entirely established. The author recommends the formula $N{<}{}^{NPh\cdot CH\cdot CO}_{N\text{——}CH\cdot CO}{>}CH{\cdot}CH{:}NPh$, according to which the substance is the *anil* of *phenylazoiminopentionaldehyde*. The absence of an imino-group and the presence of a triazole ring are respectively proved by the inactivity of the substance towards phenylcarbimide and by the oxidation of the sodium salt of phenylazoiminopentionaldehyde to 1-phenyl-1 : 2 : 3-triazole-4-carboxylic acid and 1-phenyl-1 : 2 : 3-triazole-5-carboxylic acid by 2% sodium hypobromite at 0°. The presence of the C_5-ring in the anil has not been proved, but is rendered very probable by the great similarity of the substance to the anil of indandione-2-aldehyde in its method of formation and behaviour.

By treatment with 10% potassium hydroxide and a little alcohol at 30—40°, the anil is converted into the *potassinm* salt of phenylazoiminopentionaldehyde, $C_{12}H_8O_3N_3K,\frac{1}{2}H_2O$, colourless prisms which become yellow in light; the *sodium* salt, $C_{12}H_8O_3N_3Na,H_2O$, crystallises in colourless leaflets, and forms a *semicarbazone*, $C_{13}H_{11}O_3N_6Na,2\frac{1}{2}H_2O$, faintly yellow needles. These salts and also the semicarbazone are extensively decomposed by treatment with even weak acids.

By fusion or by boiling with xylene or aniline, the anil of phenylazoiminopentionaldehyde loses nitrogen and yields a *substance*,

$$C_{18}H_{14}O_2N_2,$$

m. p. 185°, colourless needles, which behaves very similarly to the original anil and is, therefore, probably the *anil* of *phenyliminopentionaldehyde*, $NPh{<}{}^{CH\cdot CO}_{CH\cdot CO}{>}CH{\cdot}CH{:}NPh$. It does not react with phenylcarbimide or with ferric chloride, and is converted by boiling sodium hydroxide into aniline and the *sodium* salt of *phenyliminopentionaldehyde*, $C_{12}H_8O_3NNa,2H_2O$, white needles.

By keeping phenylazoiminopentionaldehydeanil in glacial acetic acid until the evolution of nitrogen ceases, a *substance*, $C_{18}H_{16}O_3N_2$, m. p. about 186° (decomp.), yellow, crystalline powder, is obtained, which is converted by hot aqueous alcoholic sodium hydroxide into aniline and the *sodium* salt of an *acid*, $C_{12}H_9O_3N$, m. p. 234°, colourless needles.

C. S.

3 : 6-Diamino-1 : 2 : 4 : 5-tetrazine. I. GIACOMO PONZIO and G. GASTALDI (*Gazzetta*, 1913, **43**, ii, 129—137).—3 : 6-*Diamino*-1 : 2 : 4 : 5-*tetrazine*, $H_2N \cdot C \lessdot_{N \cdot N}^{N:N} \gtrdot C \cdot NH_2, H_2O$, begins to crystallise in a few days when a mixture of concentrated solutions of aminoguanidine hydrochloride and potassium hydroxide are kept over concentrated sulphuric acid and solid potassium hydroxide. The substance crystallises in reddish-violet, monoclinic needles, which have a metallic lustre, or in amethyst-coloured laminæ. On heating, it loses water at about 100°, and melts at 204—205° (decomp.), or 206—207° (decomp.), according to the mode of heating; cyanogen and ammonia are evolved. When boiled with sulphuric acid, it yields nitrogen, carbon dioxide, and hydrazine sulphate, whilst heating with potassium hydroxide furnishes ammonia. It is readily reduced to 3 : 6-diamino-1 : 2-dihydro-1 : 2 : 4 : 5-tetrazine. 3 : 6-*Diamino*-1 : 2 : 4 : 5 - *tetrazine hydrochloride*, $C_2H_4N_6$,HCl, forms orange-yellow laminæ, and decomposes about 200°; the *nitrate*, $C_2H_4N_6, HNO_3, \frac{1}{2}H_2O$, crystallises similarly, and has m. p. 180—182° (decomp.). The *oxalate*,

$$(C_2H_4N_6)_2, H_2C_2O_4,$$

forms orange prisms, which decompose at about 205°. R. V. S.

Action of Dichlorocarbamide on Amines. Synthesis of 3-Hydroxy-6-keto-3-phenyl-2 : 4-dibenzyl-1 : 2 : 4 : 5-tetrazine. RASIK LAL DATTA and SATYARANJAN DAS GUPTA (*J. Amer. Chem. Soc.*, 1913, **35**, 1183—1185).—By modifying the conditions for the interaction of dichlorocarbamide and amines, which has already been shown to yield chloroamines (Datta, T., 1912, **101**, 166; A., 1912, i, 962), it is found that other substances can be isolated from the reaction product.

When a cooled saturated solution of dichlorocarbamide is added to a cooled fairly strong aqueous solution of allylamine, a small amount of *p*-urazine separates.

On applying benzylamine in a similar reaction the crystalline product which deposits is a mixture of *p*-urazine with 3-hydroxy-6-keto-3-phenyl-2 : 4-dibenzyl-1 : 2 : 4 : 5-tetrazine. The latter, which can be separated by its greater solubility in acetone, probably owes its formation to the primary formation of benzylchloroamine, two molecules of which then condense with one of free benzylamine and one of dichlorocarbamide. D. F. T.

The Solubility of Uric Acid in Acetic Acid. FRANCESCO ROSSI (*Biochem. Zeitsch.*, 1913, **54**, 297—304).—The solubility of uric acid in varying strengths of acetic acid from $N/100$ to $16N$ (glacial acetic acid) and at temperatures varying from 15° to 100° was determined. Between the concentrations $N/100$ and $N/10$ the solubility is less than in water; above the latter concentration it increases and reaches a maximum somewhere about the concentration of $4N$ to $6N$; in higher concentrations, the solubility again declines, especially at higher temperatures. The latter phenomenon is probably due to an action of acetic acid on the uric acid. S. B. S.

Some New Derivatives of Azoxybenzene. BRUNO VALORI (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 125—133. Compare Angeli and Valori, A., 1913, i, 533).—When Zinin's *p*-nitroazoxybenzene is treated with nitric acid (D 1·48) on the water-bath, 2 : 4-*dinitroazoxybenzene*, $C_6H_3(NO_2)_2\cdot N\colon NPh\colon O$, is produced; it forms pale yellow needles, m. p. 141°.

When Zinin's *p*-nitroazoxybenzene is heated with bromine in presence of iron for one hour at 130° in a sealed tube, 2-*bromo*-4-*nitroazoxybenzene*, $NO_2\cdot C_6H_3Br\cdot N\colon NPh\colon O$, is formed; it is a yellow powder, m. p. 127°.

o-Nitroazoxybenzene is acted on by nitric acid (D 1·48) on the water-bath, yielding 2 : 6-*dinitroazoxybenzene*, $C_{12}H_8O_5N_4$, which forms colourless scales, m. p. 172°.

If *o*-*p*-bromoazoxybenzene is heated with bromine in presence of iron in a sealed tube for two hours at 115—120°, 2 : 4-*dibromoazoxybenzene*, $C_{12}H_8ON_2Br_2$, is formed; it crystallises in yellow needles, m. p. 97°. In its preparation a small quantity of 2 : 4 : 6-tribromoaniline is produced. Reduction of 2 : 4-dibromoazoxybenzene with tin and hydrochloric acid yields aniline and 2 : 4-dibromoaniline. 2 : 4-Dibromoazoxybenzene yields 2 : 4-*dibromoazobenzene*, $C_{12}H_8N_2Br_2$, when treated with concentrated sulphuric acid, or when reduced with aluminium amalgam and subsequently oxidised with yellow mercury oxide. 2 : 4-Dibromoazobenzene forms orange-red prisms, m. p. 96°. It regenerates the azoxy-compound when treated with hydrogen peroxide in glacial acetic acid solution. 2 : 4 : 4′-*Tribromoazobenzene*,

$$C_{12}H_7N_2Br_3,$$

can be obtained by warming dibromoazobenzene with bromine and iron for a few minutes on the water-bath; it is a pale red substance, m. p. 146°. On oxidation with hydrogen peroxide in glacial acetic acid solution, this compound yields the corresponding 2 : 4 : 4′-*tribromoazoxybenzene*, which on reduction with aluminium amalgam and subsequent oxidation with yellow mercury oxide yields the tribromoazo-compound again. 2 : 4 : 4′-Tribromoazoxybenzene, $C_{12}H_7ON_2Br_3$, crystallises in yellow needles, m. p. 154°.

When 4-bromo-2-nitroazoxybenzene (m. p. 99°) is heated on the water-bath with nitric acid (D 1·50) two products are obtained: (1) 4-*bromo*-2 : 6-*dinitroazoxybenzene*, which forms very pale yellow needles, m. p. 163°, and on treatment with concentrated sulphuric acid yields the isomeric *hydroxyazo*-compound,

$$C_6H_2Br(NO_2)_2\cdot N\colon N\cdot C_6H_4\cdot OH$$

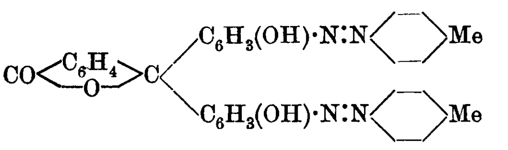
(m. p. 224°); (2) 4-*bromo*-2 : 6 : 3′-*trinitroazoxybenzene*,

$$C_6H_2Br(NO_2)_2\cdot N\colon NO\cdot C_6H_4\cdot NO_2,$$

which is a yellowish-green, crystalline powder, m. p. 209° (decomp.). The latter compound is exclusively formed if stronger acid (D 1·52) is used in the reaction. R. V. S.

Phthaleins. II. Some Nitrogenous Derivatives of Phenolphthalein and the Constitution of its Salts. BERNARDO ODDO (*Gazzetta*, 1913, **43**, ii, 175—190. Compare Oddo and Vassallo, A., 1912, i, 792).—*Bis*-p-*tolueneazophenolphthalein* (formula overleaf) is obtained when a diazotised solution of *p*-toluidine (1 mol.) is poured

into a cold solution of phenolphthalein ($\frac{1}{2}$ mol.) in potassium hydroxide



(3 mols.). It is an orange-yellow, crystalline substance, m. p. 249—253°. When the mother-liquor is acidified, a bright red substance, m. p. 207—210°, is precipitated; the *acetyl* derivative of this compound forms pale yellow scales, m. p. 148—150°. The *diacetyl* derivative of bis-*p*-tolueneazophenolphthalein, $C_{38}H_{30}O_6N_4$, has m. p. 125—131°.

Bis-o-*nitrobenzeneazophenolphthalein*, $C_{32}H_{20}O_8N_6$, is an orange-yellow substance, m. p. 277°. Its *diacetyl* derivative has m. p. 124—129°. In the preparation of bis-*o*-nitrobenzeneazophenolphthalein, a *substance* of similar appearance but different solubility is formed; its *acetyl* derivative has m. p. 169°.

When bis-*p*-tolueneazophenolphthalein is heated to 110° with phenylhydrazine, a reaction occurs, which is accompanied by rise of temperature and yields diaminophenolphthalein,

$$CO<\!\!{}^{C_6H_4}_{-O-}\!\!>C:[C_6H_3(NH_2)\cdot OH]_2,$$

which forms pale coffee-coloured crystals, m. p. 245° (decomp.). The substance dissolves in alkalis, alkali carbonates and ammonia, giving a Prussian-blue coloration which disappears on acidification. The substance gives the same coloration with aqueous solutions of pyridine, but not with alcoholic solutions. Diaminophenolphthalein can also be obtained by reduction of dinitrophenolphthalein with stannous chloride (compare Errera and Bertè, A., 1896, i, 564; Gattermann and Bamberg, A., 1899, i, 514).

Dinitrophenolphthalein yields a *monoacetyl* derivative, $C_{24}H_{16}O_{10}N_2$, which has m. p. 94—100°, and occurs in a white and in a yellow form.

R. V. S.

Mechanism of Formation and Scission of the Hydroxyazo-compounds. G. Charrier and G. Ferreri (*Gazzetta*, 1913, **43**, ii, 148—162. Compare this vol., i, 535).—When an ethereal solution of nitric acid (prepared by adding about 20% of nitric acid [D 1·48] to ether cooled in ice) is added to an ethereal solution of 1-benzeneazo-2-naphthyl methyl ether, the *nitrate* of the ether, $C_{17}H_{14}ON_2,2HNO_3$, separates in red, silky needles, m. p. 67° (decomposing with evolution of gas at 69—70°). The salt has about the normal molecular weight in boiling chloroform. It is hydrolysed by water. The salt readily decomposes into benzenediazonium nitrate and 1-nitro-2-naphthyl methyl ether.

The *nitrate* of 1-benzeneazo-2-naphthyl ethyl ether,

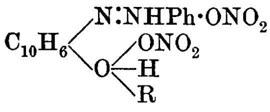
$$C_{18}H_{16}ON_2,2HNO_3,$$

forms quadrangular tablets, which are green by reflected and red by transmitted light, and have m. p. 80—81° (decomp.). It readily decomposes in an analogous manner to the methyl ether nitrate.

When 1-nitro-2-naphthyl ethyl ether is warmed with nitric acid

(D 1·40), it is converted quantitatively into 1 : 6-dinitro-2-naphthyl ethyl ether.

A dark red, crystalline crust, consisting probably of 1-benzeneazo-2-naphthol nitrate, is obtained after mixing ethereal nitric acid with an ethereal solution of 1-benzeneazo-2-naphthol. The substance is very unstable.



The probable structure of these salts is indicated by the annexed formula, and their mode of decomposition mentioned above suggests an analogous mechanism of formation and scission of the hydroxyazo-compounds.

R. V. S.

Etherification of *o*-Hydroxyazo-compounds. III. G. CHARRIER and G. FERRERI (*Gazzetta*, 1913, **43**, ii, 211—227. Compare A., 1912, i, 812; this vol., i, 535, and preceding abstract).—In this paper further nitrates of ethers of arylazo-β-naphthols are described. Their chemical and physical properties resemble those of the members already described (*loc. cit.*).

1-o-*Tolueneazo-2-naphthyl methyl ether nitrate*, $C_{18}H_{16}ON_2,2HNO_3$, forms cantharides-green, acicular crystals, m. p. 71° (decomp.).

1-o-*Tolueneazo-2-naphthyl ethyl ether nitrate*, $C_{19}H_{18}ON_2,2HNO_3$, crystallises in cantharides-green leaflets, m. p. 62—63° (decomp.).

1-m-*Tolueneazo-2-naphthyl methyl ether nitrate*, $C_{18}H_{16}ON_2,2HNO_3$, crystallises similarly, and has m. p. 72° (decomp.).

1-m-*Tolueneazo-2-naphthyl ethyl ether nitrate*, $C_{19}H_{18}ON_2,2HNO_3$, forms cantharides-green leaflets, m. p. 84° (decomp.).

1-p-*Tolueneazo-2-naphthyl methyl ether hydrochloride* forms red needles which have a golden lustre. The *hydrobromide* crystallises in metallic-looking, green leaflets. The *nitrate*, $C_{18}H_{16}ON_2,2HNO_3$, forms dark red needles with a green lustre, and has m. p. 77° (decomp.).

1-p-*Tolueneazo-2-naphthyl ethyl ether nitrate*, $C_{19}H_{18}ON_2,2HNO_3$, crystallises in garnet-red leaflets of golden lustre, and has m. p. 94° (decomp.).

1-o-4-*Xyleneazo-2-naphthol*, $C_{18}H_{16}ON_2$, crystallises in cherry-red needles of golden lustre, m. p. 146°; it dissolves in concentrated sulphuric acid, producing an intense red coloration. The *methyl ether*, $C_{19}H_{18}ON_2$, crystallises in red, prismatic leaflets, m. p. 106°. The *methyl ether hydrochloride* forms red needles with golden lustre; the *hydrobromide*, garnet-red needles. The *nitrate*, $C_{19}H_{18}ON_2,2HNO_3$, forms coffee-coloured scales of golden lustre, m. p. 87—88° (decomp.). The *ethyl ether*, $C_{20}H_{20}ON_2$, forms red needles of golden lustre, m. p. 94—95°. The *ethyl ether hydrochloride* forms metallic-looking, coffee-coloured needles; the *hydrobromide*, red needles.

1-m-4-*Xyleneazo-2-naphthyl methyl ether*, $C_{19}H_{18}ON_2$, forms garnet-red leaflets of violet lustre, m. p. 72—73°. The *hydrochloride* and *hydrobromide* form garnet-red, acicular crystals. The *nitrate*,

$$C_{19}H_{18}ON_2,2HNO_3,$$

crystallises in cantharides-green needles, m. p. 83° (decomp.).

m-4-Xylenediazonium nitrate and 2-naphthylamine yield 1-m-4-*xylene-*

azo-2-naphthylamine, $C_{18}H_{17}N_3$, which crystallises in orange-red leaflets, m. p. 128°. The substance dissolves in concentrated sulphuric acid, producing a reddish-violet coloration.

1-m-4-*Xyleneazo-2-naphthyl ethyl ether*, $C_{20}H_{20}ON_2$, forms garnet-red needles, m. p. 47°. The *hydrochloride* forms coffee-coloured needles, and the hydrobromide, garnet-red needles. The *nitrate*,

$$C_{20}H_{20}ON_2,2HNO_3,$$

crystallises in cantharides-green needles, m. p. 82° (decomp.).

1-p-*Xyleneazo-2-naphthyl methyl ether*, $C_{19}H_{18}ON_2$, forms garnet-red, prismatic tablets, m. p. 91—92°. The *hydrochloride* crystallises in garnet-red needles; the *hydrobromide* in coffee-coloured needles. The *nitrate*, $C_{19}H_{18}ON_2,2HNO_3$, crystallises in cantharides-green laminæ, m. p. 75° (decomp.). The *ethyl ether*, $C_{20}H_{20}ON_2$, crystallises in tufts of red needles or laminæ, m. p. 61—62°. The *hydrochloride* forms a crust of copper-coloured needles, and the *hydrobromide* crystallises similarly. The *nitrate*, $C_{20}H_{20}ON_2,2HNO_3$, forms dark copper-coloured laminæ of golden lustre, m. p. 71° (decomp.).

1-α-*Naphthaleneazo-2-naphthyl methyl ether hydrobromide* crystallises in iridescent, brownish-green needles. R. V. S.

Etherification of *o*-Hydroxyazo-compounds. IV. G. Charrier and G. Ferreri (*Gazzetta*, 1913, **43**, ii, 227—244. Compare preceding abstracts).—1-*Anisoleazo-2-naphthyl methyl ether hydrobromide* forms reddish-brown needles. The *nitrate*, $C_{18}H_{16}O_2N_2,2HNO_3$, forms dark green needles, m. p. 90—91° (decomp.). 1-*Anisoleazo-2-naphthylamine*, $C_{17}H_{15}ON_3$, crystallises in garnet-red prisms, m. p. 133—134°; it is soluble in concentrated sulphuric acid with production of a reddish-violet coloration.

1-*Anisoleazo-2-naphthyl ethyl ether hydrobromide* forms brownish-red needles. The *nitrate*, $C_{19}H_{18}O_2N_2,2HNO_3$, is a dark green, crystalline substance, m. p. 85° (decomposing at 86—87°).

1-p-*Methoxybenzeneazo-2-naphthyl methyl ether hydrobromide* forms cantharides-green needles. The *nitrate*, $C_{18}H_{16}O_2N_2,2HNO_3$, forms green, acicular crystals, m. p. 55—56° (decomp.). 1-p-*Methoxybenzeneazo-2-naphthylamine*, $C_{17}H_{15}ON_3$, crystallises in garnet-red leaflets, m. p. 127°. It dissolves in concentrated sulphuric acid, giving a violet-red coloration.

1-p-*Methoxybenzeneazo-2-naphthyl ethyl ether hydrobromide* forms coffee-coloured needles. The *nitrate*, $C_{19}H_{18}O_2N_2,2HNO_3$, crystallises in cantharides-green leaflets, m. p. 67° (decomp.).

1-o-*Ethoxybenzeneazo-2-naphthyl methyl ether hydrochloride* forms garnet-red crystals; the *hydrobromide*, coffee-coloured needles. The *nitrate*, $C_{19}H_{18}O_2N_2,2HNO_3$, crystallises in dark red leaflets of metallic lustre.

1-o-*Ethoxybenzeneazo-2-naphthyl ethyl ether hydrobromide* forms brown needles; the *nitrate*, $C_{20}H_{20}O_2N_2,2HNO_3$, crystallises in green needles, m. p. 86° (decomp.). 1-o-*Ethoxybenzeneazo-2-naphthylamine*, $C_{18}H_{17}ON_3$, forms bright red leaflets, m. p. 117°. It dissolves in concentrated sulphuric acid, giving a reddish-violet coloration.

1-p-*Ethoxybenzeneazo-2-naphthyl methyl ether hydrobromide* forms

coffee-coloured needles. The *nitrate*, $C_{19}H_{18}O_2N_2,2HNO_3$, forms green needles, m. p. 71° (decomp.). 1-p-*Ethoxybenzeneazo-2-naphthylamine*, $C_{18}H_{17}ON_3$, crystallises in orange-yellow laminæ of golden lustre, m. p. 133—134°.

1-p-*Ethoxybenzeneazo-2-naphthyl ethyl ether hydrobromide* forms golden leaflets. The *nitrate*, $C_{20}H_{20}O_2N_2,2HNO_3$, forms orange-yellow plates of golden lustre, m. p. 73—74° (decomp.).

1-o-*Nitrobenzeneazo-2-naphthyl methyl ether*, $C_{17}H_{13}O_3N_3$, crystallises in garnet-red leaflets, m. p. 136—137°. It dissolves in concentrated sulphuric acid, giving an intense red coloration. The *hydrochloride* forms coffee-coloured needles, and the *hydrobromide* is a pale coffee-coloured, crystalline substance. The *nitrate*, $C_{17}H_{13}O_3N_3,2HNO_3$, forms red crystals, m. p. 103°.

1-o-*Nitrobenzeneazo-2-naphthyl ethyl ether*, $C_{18}H_{15}O_3N_3$, crystallises in thin, dark red tablets, m. p. 111°. The *hydrochloride* and the *hydrobromide* are red, crystalline substances. The *nitrate*,

$$C_{18}H_{15}O_3N_3,2HNO_3,$$

forms dark red leaflets of metallic lustre, m. p. 105° (decomp.).

1-m-*Nitrobenzeneazo-2-naphthyl methyl ether nitrate*,

$$C_{17}H_{13}O_3N_3,2HNO_3,$$

consists of golden leaflets, m. p. 66—68° (decomp.).

1-m-*Nitrobenzeneazo-2-naphthyl ethyl ether hydrobromide* is a red, crystalline substance. The *nitrate*, $C_{18}H_{15}O_3N_3,2HNO_3$, crystallises in golden leaflets, m. p. 70° (decomp.).

1-p-*Nitrobenzeneazo-2-naphthyl methyl ether*, $C_{17}H_{13}O_3N_3$, forms dark red, iridescent leaflets, m. p. 128—129°. The *hydrochloride* is a red, and the *hydrobromide* a coffee-coloured, crystalline substance. The *nitrate*, $C_{17}H_{13}O_3N_3,2HNO_3$, forms cantharides-green leaflets, m. p. 75° (decomp.).

1-p-*Nitrobenzeneazo-2-naphthyl ethyl ether*, $C_{18}H_{15}O_3N_3$, crystallises in dark red leaflets, m. p. about 186°. The *hydrochloride* and the *hydrobromide* are red, crystalline substances. The *nitrate*,

$$C_{18}H_{15}O_3N_3,2HNO_3,$$

forms cantharides-green leaflets, m. p. 95—97° (decomp.).

1-α-*Naphthaleneazo-2-naphthyl ethyl ether hydrobromide* crystallises in cantharides-green needles. The *nitrate*, $C_{22}H_{18}ON_2,2HNO_3$, crystallises in copper-red, flat needles of metallic lustre, m. p. 62° (decomp.).

1-β-*Naphthaleneazo-2-naphthyl methyl ether hydrobromide* crystallises in coffee-coloured needles. The *nitrate*, $C_{21}H_{16}ON_2,2HNO_3$, forms deep green, lustrous needles, m. p. 80—81° (decomp.).

Diphenyl-4 : 4'-bisazo-2-naphthol,

$$HO\cdot C_{10}H_6\cdot N{:}N\cdot C_6H_4\cdot C_6H_4\cdot N{:}N\cdot C_{10}H_6\cdot OH,$$

is a dark green, microcrystalline powder, m. p. about 275°; it dissolves in concentrated sulphuric acid with production of a violet-blue coloration. Its *diethyl ether*, $C_{36}H_{30}O_2N_4$, is a red, microcrystalline powder, m. p. about 98—100°. It is soluble in concentrated (and to some extent also in dilute) acids with production of a bluish-violet coloration. The *hydrochloride* and the *hydrobromide* are dark green, crystalline substances. The *nitrate*, $C_{36}H_{30}O_2N_4,4HNO_3$, forms dark green needles of metallic lustre, m. p. 60—61°. R. V. S.

The Conjugation of the Products of Protein Hydrolysis to Colloidal Carbohydrates. H. FRIEDENTHAL (*Biochem. Zeitsch.*, 1913, **54**, 174—181).—Attention is called to the fact that by the condensation of hydroxyl groups in polysaccharides of colloidal character with the amino-groups of amino-acids, it is theoretically possible to obtain derivatives which have the same empirical composition as proteins, and should yield the same reactions. Although it is not claimed that the majority of the proteins is constituted in this way, it is suggested that substances of this character may exist in the organism. S. B. S.

Coagulation of Proteins by Ultra-violet Light. W. T. BOVIE (*Science*, 1913, **37**, 24—25).—Exposure of certain proteins in quartz tubes to the rays of a quartz mercury-vapour lamp causes them to coagulate. Usually no coagulum forms in glass tubes, but dialysed crystallised egg-albumin is sensitive to longer wave-lengths than the fresh egg-white, since it coagulates in a glass tube. The coagulum has the same properties as that produced by heat without exposure to ultra-violet light. E. F. A.

Temperature-coefficient of the Coagulum Caused by Ultra-violet Light. W. T. BOVIE (*Science*, 1913, **37**, 373—375).—Two reactions are involved in the coagulation of proteins by light: the chemical change caused by the light, and the production of a visible coagulum. The light reaction, resembling other photochemical changes, has a very low temperature-coefficient. The chemical change producing the visible coagulum has a temperature-coefficient as high as two. Probably similar relations exist in other physiological processes which result from the action of light. E. F. A.

The Precipitation of Colloids. II. KARL SPIRO (*Biochem. Zeitsch.*, 1913, **54**, 155—158. Compare A., 1904, i, 124).—A table is given showing that salts, of which the hydrogen-ion concentration in solution is highest, have the greatest action in inhibiting the precipitation of proteins. The hydrogen-ion concentration of the mixtures of the salt and protein solutions is not the mean of the two, but in the case of the sodium, potassium, and lithium salts it is nearly the same as that of the original protein solutions, and in the case of the ammonium salts a little greater. The acetates form an exception, in that the hydrogen-ion concentration of the mixture of protein–salt solutions approaches very nearly the [H$^{\cdot}$]-concentration of the salt solution. The results seem to indicate the formation of a salt-protein compound, and the influence of salts on the precipitation of proteins is briefly discussed. S. B. S.

The Content of the Blood-Plasma Proteins in Basic Constituents. KARL LOCK and KARL THOMAS (*Zeitsch. physiol. Chem.*, 1913, **87**, 74—81).—The amounts of ammonia, arginine, histidine, and lysine in serum-albumin, serum-globulin, and fibrin were estimated and the table of results shows considerable discrepancies between

different preparations of the same protein, and according to the method used. W. D. H.

The Soluble Protein Substances of Milk. Léon Lindet (*Compt. rend.*, 1913, **157**, 307—309).—The so-called albumin of milk possesses all the properties of caseinogen itself, with the exception of its rotatory power, where it has $[\alpha]_D$ $-30°$ instead of $-116°$. The author suggests for it the name β-caseinogen, the α-caseinogen being the one, which is the chief constituent of the protein matter of milk. These two substances resemble one another closely in their solubility in milk serum, in their capillary adherence to the casein in suspension, in their precipitation by phenol, and in their partial coagulation at 75°. W. G.

Influence of Calcium Chloride on the Curdling of Milk. Léon Lindet (*Compt. rend.*, 1913, **157**, 381—384. Compare preceding abstract).—Boiled milk is not clotted by rennet, but clots if a small amount of calcium chloride is added. This the author suggests is due to the interaction of the calcium chloride with the alkali phosphate and citrate in the milk serum, thus reducing the quantity of these, and rendering the two caseinogens less soluble. Further, the dicalcium phosphate by dissociation gives rise to phosphoric acid, which removes the calcium oxide from the caseinogens, rendering them still further insoluble. W. G.

The Action of Rennin on Caseinogen. Alfred W. Bosworth (*J. Biol. Chem.*, 1913, **15**, 231—236).—Calcium caseinogenate which is neutral to litmus is not curdled by rennin; but solutions which are acid and contain two equivalents of base for each molecule of caseinogen are curdled by rennin. Ammonium, sodium and potassium caseinogenates are not curdled by rennin. No other protein is formed except casein (2 molecules to one of caseinogen) during rennin curdling. Coagulation is the result of a change in solubility, and is the first stage in hydrolytic cleavage. W. D. H.

Nucleohistone. I. Hermann Steudel (*Zeitsch. physiol. Chem.*, 1913, **87**, 207—213).—Nucleohistone prepared by the method given by Lilienfeld (A., 1894, ii, 146) had exactly the composition given previously. The whole of the nucleic acid present is proved to be true nucleic acid, no other substance containing phosphorus being present in nucleohistone. E. F. A.

Processes Operative in Solutions, XXX, and Enzyme Action, XX. The Nature of Enzymes and of their Action as Hydrolytic Agents. E. Frankland Armstrong and Henry E. Armstrong (*Proc. Roy. Soc.*, 1913, *B*, **86**, 561—586).—A discussion of the problems of hydrolysis based on the experience gained in the course of two convergent series of enquiries.

The catalyst is defined as the agent which brings about the inclusion of the interacting substance in the circuit within which change takes place as soon as the circuit is established, the electrolyte being the

actual agent by which change is effected. Action between two non-electrolytes is impossible.

Enzymes are regarded as having a double function, namely, that of attracting or holding the hydrolyte and that of determining its hydrolysis. This twofold action is attributed to the presence in the enzyme of an acceptor together with an agent. The acceptor is a radicle very closely allied to a dominant group in the hydrolyte. The agent is an acid radicle in immediate or compatible proximity, so that a conducting path is formed between agent and acceptor by their association with the solvent. The efficiency of an enzyme depends also on its colloidal character. Each enzyme particle tends to absorb the hydrolyte, so that the solution at its surface is relatively concentrated; in addition it is hydrolated, the activity of the water molecules at the surface being greater than the average activity of the water. As a consequence the colloid surface remains highly charged with the hydrolyte probably up to the point at which the supply in the solution is exhausted.

The change is, therefore, not a simple mass action effect; in fact, in each successive interval of time the enzyme determines the hydrolysis of the same amount of hydrolyte. The observed departures from this rule are shown to be due to the influence of the products of change.

The relationship of the acceptor section of the enzyme to the hydrolyte is that of a superposable and, therefore, practically identical radicle.

The enzymes which hydrolyse the glucosides may be compounds of the glucoprotein class containing either α- or β-glucosidic radicles and therefore capable of hydrolysing either α- or β-glucosides, because their configuration harmonises with that of the one or of the other type of compound. Urease is an enzyme in which the urea residue in arginine is in suitable relationship with the carboxyl group. These conceptions are illustrated by photographs of solid models.

The resting enzyme is not an acid proper, but an internal salt of the glycine type. A substance of superior acidic power must be added to render the zymogen active. The action of acids and alkalis is considered from this point of view.

As the products of change accumulate in the solution, they affect the enzyme in various ways. The product immediately allied to the acceptor enters directly into competition with the hydrolyte. Other products act on the enzyme by neutralising it, by converting it into a derivative different in structure and no longer compatible with hydrolyte, or by changing the osmotic conditions in the solution, and altering the state of hydrolation at the colloid surface. These influences have been studied experimentally. E. F. A.

The Velocity of the Appearance of Protective Enzymes after Repeated Introduction of the Foreign Substrate. I. EMIL ABDERHALDEN and ERWIN SCHIFF (*Zeitsch. physiol. Chem.*, 1913, **87**, 225—230).—Whereas it takes some little time for the protective enzymes to appear on the first injection of a foreign peptone into the blood-serum, if a second injection is made, after the serum has become inactive again, the protective enzymes appear in a much

shorter time. The organism reacts much more rapidly to the second invasion. Experiments made on rabbits with silk peptone and gelatin peptone are described. The injection was preferably intravenous.

E. F. A.

Studies on the Specific Nature of the Intracellular Enzymes by means of the Optical Method. I. EMIL ABDERHALDEN and ANDOR FODOR (*Zeitsch. physiol. Chem.*, 1913, **87**, 220—224).—The behaviour of the juices obtained from various macerated tissues after they had been completely deprived of blood was tested towards the peptones from each of the tissues. Whereas liver juice hydrolysed liver peptone, it had no action on kidney or thyroid peptone. Thyroid juice only attacked thyroid peptone. Kidney juice hydrolysed both kidney and liver peptones, and also, in one experiment out of three, it acted on thyroid peptone. The liver and thyroid cells contain enzymes adapted to their specific components only; the kidney cells have a wider function, and their enzymes are adapted to peptones from other sources.

E. F. A.

Enzymes of Fresh Foods. T. TADOKORO (*J. Coll. Agric. Sapporo, Japan*, 1913, **5**, 57—72).—The fresh sap of Udo twigs, yams, cabbage and lettuce leaves, onions, ginger and radish roots of Japanese origin has been investigated for enzymes. Peptolytic action was only found in ginger and the onion. All the juices contained trypsin and a weak diastase, also oxydase and catalase, but they differed greatly in activity. Lipase was present only in the cabbage. E. F. A.

Specific Nature of the Intracellular Enzymes by means of the Optical Method. II. EMIL ABDERHALDEN and ERWIN SCHIFF (*Zeitsch. physiol. Chem.*, 1913, **87**, 231—232).—The enzymes in muscle juice (from the horse) hydrolyse muscle peptone, but not liver or brain peptone.

Testicle peptone is hydrolysed only by the enzymes in testicle and kidney juice. Brain peptone is hydrolysed only by brain and kidney juices. E. F. A.

Some Conditions Affecting the Activity and Stability of Certain Ferments. JOHN H. LONG and WILLIAM A. JOHNSON (*J. Amer. Chem. Soc.*, 1913, **35**, 1188—1201).—An extension of the earlier investigation on amylopsin (this vol., i, 919) to trypsin. Raw egg-albumin is found to be unsuited to the measurement of proteolytic action, and where egg-albumin is necessary, the authors make use of a Chinese dried albumin; but fibrin and casein are the best materials for comparative studies.

It is found that trypsin is not appreciably injured by the action of 0·3% hydrochloric acid for thirty minutes at 40°, for, although no digestion will occur in the presence of the acid, fibrin can be digested in considerable quantity after neutralisation.

Aqueous solutions of trypsin become weaker on long keeping at the ordinary temperature, the deterioration being more rapid the purer the product; in this respect it is more sensitive than pepsin. In the

presence of sodium carbonate between the concentrations 0·2% and 1% at 40°, the activity of trypsin in fibrin digestion is not affected.

D. F. T.

Purification of Invertase Preparations by Treatment with Acids. JAKOB MEISENHEIMER, STEFAN GAMBARJAN, and L. SEMPER (*Biochem. Zeitsch.*, 1913, **54**, 108—121).—It is found that the content of invertase in a preparation can be increased by preliminary treatment of the expressed juices with acids. Not only acetic, but also hydrochloric, and more especially the dibasic sulphuric and oxalic acids effect this purpose. The addition of acids produces a precipitate of proteins, which carries down with it practically none of the ferment. The addition of too much acid acts deleteriously on the ferment, and for every preparation it is necessary, by means of preliminary experiments, to ascertain the amount of acid which yields the optimal result. For this purpose, the ferment is precipitated by means of acetone, and obtained in a dry form, and its reaction constant is determined polarimetrically with the employment of the equation $K = 1/t \log . a/a - x$. The above-stated facts are illustrated by numerous examples.

S. B. S.

Inhibition of Enzyme Action by Lime-softened Waters. OLAF BERGEIM and PHILIP BOUVIER HAWK (*J. Amer. Chem. Soc.*, 1913, **35**, 1049—1056).—It is found that lime-softened waters exert a pronounced inhibitory effect on the action of salivary and pancreatic amylases. Of the mineral constituents of the water, magnesium hydroxide exerts by far the greatest effect, whilst sodium carbonate and calcium carbonate have a less considerable effect. Investigation shows that the influence of the magnesium hydroxide is due to its existence in a colloidal form which adsorbs the enzyme. In contrast to the action of amylolytic ferments, peptic digestion is but little affected by magnesium hydroxide solution or by lime-softened water.

From the difference in effect of calcium carbonate solution on salivary amylase and pancreatic amylase, it appears that these enzymes are not identical.

D. F. T.

Action of Ammonia on Diastase Rendered Inactive by Heating. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1913, **86**, 401—406).—Ammonia gas has the same effect on diastase whether it has been rendered inactive by heating or not. It cannot therefore have any action on those groupings in the molecule which are altered by heat, that is, on the groupings to which the activity of the enzyme is due.

E. F. A.

Action of Hydrogen Chloride and Ammonia on Diastase Rendered Inactive by Heating. XI. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1913, **87**, 115—121).—Diastase which has been rendered inactive by heating, regains some feeble activity when treated first with dry hydrogen chloride and then with dry ammonia.

E. F. A.

The Enzymes of the Tobacco Plant. J. DU P. OOSTHUIZEN and OLIVER MARCH SHEDD (*J. Amer. Chem. Soc.*, 1913, **35**, 1289—1309). —An investigation of the enzymes in two types of Kentucky tobacco, the White Burley variety of the Burley region, and the Yellow Pryor variety of Western Kentucky.

The results indicate the presence of appreciable amounts of invertase, diastase, emulsin, and reductases both in the seed and in the leaf at all stages of its growth and after curing. Small amounts of lipase, inulase, and a proteolytic enzyme also appear to be present. Oxydases were present in the green leaf, but the quantity decreased towards maturity, and was too small for definite detection in the cured leaf. Generally enzymes were found to be absent from the soil.

The probable rôles of the various enzymes are discussed.

D. F. T.

Enzymes in the Leaves of Salix caprea. IWAN BOLIN (*Zeitsch. physiol. Chem.*, 1913, **87**, 182—187. Compare Armstrong, A., 1912, i, 816).—The leaves of *Salix caprea* may contain a salicase, an amygdalin-splitting and a glucoside-splitting enzyme. Salicase is specific for salicin, and has no action on β-methylglucoside. The enzyme acting on β-methylglucoside was present in the leaves in 1911, but absent from the leaves of the same tree in 1912. E. F. A.

Enzyme Action. XXI. Lipase. III. HENRY E. ARMSTRONG and H. W. GOSNEY (*Proc. Roy. Soc*, 1913, *B*, **86**, 586—600. Compare A., 1906, i, 126; 1907, i, 103; Tanaka, A., 1910, i, 800).—Methods of preparing active lipase preparations from castor oil seeds in the form of a dry powder and of testing their hydrolytic activity are described. Dilute acetic acid is used to activate the zymogen, which is probably a salt. Lipase is very sensitive to the action of acids, and easily rendered inert by excess of acid. The inferiority as a hydrolyst of esters other than fats is due to the fact that the acids liberated from fats are scarcely soluble in water and very weak.

Lipase is specially fitted to hydrolyse the oily glycerides, and is not suited to act in aqueous solutions. Interaction takes place at and between surfaces separated only by a thin film of water. The interaction of enzyme and oil is inhibited by both the fatty acid and the glycerol, especially the former. As in other cases of enzyme action, the law of mass action does not apply, and the influence of the products of change and the destruction of the enzyme combine to cause departures from the simple law of enzyme action (compare this vol., i, 116).

Lipase is considered to contain a glycerol nucleus attached to a carboxylic centre in proximity to an acidic group, which can determine the hydrolysis of a fatty molecule that becomes attached to the glycerol acceptor. E. F. A.

Some New Properties of Peroxydase. The Comparison of its Action with that of Nitrites. JULES WOLFF (*Ann. Inst. Pasteur*, 1913, **27**, 554—567. Compare A., 1912, i, 928).—Plant sap is sufficiently acid to liberate nitrous acid from nitrites. The nitrous

acid thus set free is able to bring about oxidation phenomena similar to those caused by the combination of a peroxydase with hydrogen peroxide. Nitrites are decomposed by monopotassium phosphate.

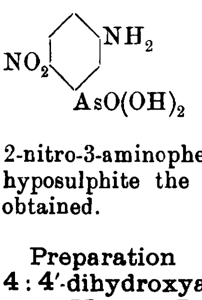
Peroxydase can be kept for some time in contact with ammonia without being changed. At first the oxidising activity diminishes somewhat, but then it increases, reaching the original value in four to five hours and attaining a maximum activity in forty hours, nearly double the original. This high activity persists for a time and then decreases slowly to the original value.

Orcinol absorbs oxygen from the air in presence of alkali hydroxides, carbonates, etc. The rate of absorption is greatly increased on adding a vegetable peroxydase—it may amount to five times the original value.

When the surface exposed to the air is large, orcinol absorbs oxygen, but does not form any quantity of coloured oxidation product (orcein). The addition of peroxydase increases the oxygen absorption, but not the amount of colour formed. On the contrary when the surface exposed to the air is small, only about one-seventh of the amount of oxygen is absorbed, but orcein is formed. Peroxydase accelerates the formation of the orcein and not the absorption of oxygen under these conditions.

E. F. A.

Preparation of a Nitro-3-aminophenyl-1-arsinic Acid. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 261643. Compare Bertheim, A., 1911, i, 1055).—When 3-*oxalylaminophenyl*-1-*arsinic acid*, $C_6H_4(AsO_3H_2)\cdot NH\cdot CO\cdot CO_2H$, needles, is dissolved in sulphuric acid, treated at 0—5° with 26% nitric acid, and the oxalyl group subsequently eliminated, it gives rise to the hitherto undescribed 6-*nitro*-3-*aminophenyl*-1-*arsinic acid*, pale yellow needles; this when heated with concentrated alkalis yields 6-nitro-3-hydroxyphenylarsinic acid, whilst the mother liquor furnishes 2-nitro-3-aminophenylarsinic acid; and on reduction with sodium hyposulphite the corresponding diaminodihydroxyarsenobenzenes are obtained.



F. M. G. M.

Preparation of Neutral Derivatives of 3 : 3′-Diamino-4 : 4′-dihydroxyarsenobenzene, Soluble in Water. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 260235).—The preparation of compounds by the action of formaldehyde sulphoxylate on 3 : 3′-diamino-4 : 4′-dihydroxyarsenobenzene have previously been described (A., 1912, i, 595), and the reaction has now been modified by dissolving the hydroxy-base in ethylene glycol before treating with formaldehyde sulphoxylate and subsequently isolating the product by the addition of alcohol and ether.

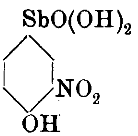
F. M. G. M.

Preparation of Aromatic Stibinic Acids. CHEMISCHE FABRIK VON F. HEYDEN (D.R.-P. 261825. Compare this vol., i, 416).—p-*Chlorophenylstibinic acid*, a colourless powder, is obtained when a solution of *p*-chlorobenzenediazonium chloride is treated with antimony trichloride and the yellow precipitate of the additive compound (compare

May, T., 1912, **101**, 1037) collected and decomposed with warm sodium hydroxide; it is purified by methods previously described (*loc. cit.*).

Phenylstibinic acid can also be obtained when aniline is diazotised in the presence of a mixture of antimony trichloride and hydrochloric acid, and the cooled solution slowly added to a solution of sodium hydroxide, when elimination of nitrogen occurs with the formation of the required product. F. M. G. M.

Preparation of an Aromatic Nitrohydroxystibinic Acid. Chemische Fabrik von F. Heyden (D.R.-P. 259875. Compare A. 1886, 884; 1899, i, 209; 1910, i, 803; 1911, i, 594, 1056).—3-*Nitro-4-hydroxyphenylstibinic acid* (annexed formula) is prepared by the following series of reactions. Anhydrous sodium *p*-acetylaminophenylstibinic acid (this vol., i, 416) dissolved in acetic acid (3 parts) is added drop by drop to 8 parts of concentrated sulphuric acid at a temperature below $-2°$; above this, elimination of the acetyl group occurs; nitric acid (D 1·51) mixed with concentrated sulphuric acid at 0° is then added, and the mixture maintained at this temperature for several hours with continual agitation; on dilution, 3-*nitro*-4-*acetylaminophenyl*-1-*stibinic* acid is obtained as a yellowish-brown powder; this when heated with a solution of potassium hydroxide (D 1·30) loses ammonia and gives rise to the foregoing 3-nitro-4-hydroxyphenyl-1-stibinic acid, a brown powder, which when heated decomposes without fusion.



F. M. G. M.

Physiological Chemistry.

A Respiration Apparatus for Small Animals in which the Oxygen Consumption is Automatically Registered. L. S. FRIDERICIA (*Biochem. Zeitsch.*, 1913, **54**, 92—167).—This apparatus combines the Haldane principle, according to which the animal with all excreta are weighed before and after the experiment, the water and carbon dioxide given out by the animal being collected in the ordinary absorption apparatus, with the Regnault-Reiset principle, modified more or less according to Benedict, in which the oxygen which is used up in respiration is automatically replaced from a gasometer, the amount added to the respiration apparatus being automatically registered. For these purposes a circulation is kept up through a closed system by means of a specially designed rotatory blower, which is figured in the text, and the air after leaving the cage containing the animal passes over weighed sulphuric acid and soda-lime tubes. In conjunction with this system is the oxygen holder, the lid of which is counterpoised by a

weight over a pulley, and the whole circuit is so arranged, by the interposition of wash-bottles serving as manometers, that it is constantly under atmospheric pressure. There is a double check, therefore, on the oxygen consumption, namely, the diminution of the oxygen in the gasometer, which is automatically registered, and the gain of weight in the animal holder and absorption apparatus. Both determinations yielded results concordant with one another.

S. B. S.

The Part Played by the Lungs in the Oxidative Processes of the Body. C. LOVATT EVANS and ERNEST H. STARLING (*J. Physiol.*, 1913, **46**, 413—434).—The gaseous metabolism of the lung in the perfused heart-lung preparation is best measured in reference to the heart-weight as the lungs soon become œdematous. It is 1 c.c. of oxygen and 0·94 c.c. carbon dioxide per gram of heart per hour. The lungs do not exercise any general or specific activity in completing oxidations partly carried out in other tissues. W. D. H.

The Influence of the Carbon Dioxide Tension of the Blood on the Ventilation by the Lungs. OTTO PORGES and A. L. SAMPLE (*Biochem. Zeitsch.*, 1913, **54**, 182—185).—In investigations on the influence of the acidity of the blood on the respiration, many authors have attempted to ascertain the stimulability of the breathing centre. Lindhard, more especially, has determined this factor, by allowing the subject of the research to inhale ordinary atmospheric air, and estimating the alveolar ventilation and carbon dioxide tension, and then determining the same factors after inhalation of air to which has been added varying amounts of carbon dioxide. Attention is now called to the fact that in these and similar experiments no account is taken of the fact that the effect on inhaling increased amounts of carbon dioxide will vary according to the pre-existing stimulus. As this pre-existing stimulus depends on the acidity of the blood, it is necessary to take into account, not only the carbon dioxide tension, but also the amount of non-volatile acids, which, according to Porges and his co-workers, are present accompanied by a diminished carbon dioxide tension in acidosis. The influence of the amounts of acid on the action of lungs is illustrated by some experiments on a pregnant patient, and patients with diabetes, and the conclusion is drawn that the method employed by Lindhard and others is not adapted to the determination of the true stimulability of the respiratory centre. S. B. S.

Influence of Alcohol on the Respiratory Exchange During Rest and During Muscular Exercise. C. J. C. VAN HOOGENHUYZE and J. NIEUWENHUYSE (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 164—172).—The authors have subjected themselves to experiments on the influence of alcohol on the respiratory exchange. While resting, they measured the oxygen-intake and carbon dioxide-output by means of the Zuntz-Geppert apparatus, and found that the respiratory quotient, CO_2/O_2, remained lower for a few hours after

the consumption of alcohol. The experiments involving muscular exercise were performed on a bicycle with adjustable and registrable resistance. The brake-band was tightened until the subject was fatigued, and then, whilst he was pedalling against a constant resistance, without or after a dose of 60 c.c. of 96% alcohol, the respiratory exchange was examined as above. The experiments were performed at 8—15° and at 28°. The respiratory quotient was again found to be lowered for a time after the consumption of alcohol, even at the higher temperature, at which muscular work was less economically performed. Alcohol, therefore, can produce energy for muscular exercise, and this is more economically performed for an hour or two after taking the stimulant. This favourable influence, however, gradually decreases, and tends towards the opposite in time. J. C. W.

The Influence of Muscular Rigidity on the Oxygen-intake in Decerebrate Cats. HERBERT E. ROAF (*Quart. J. expt. Physiol.*, 1913, **6**, 393—402).—During decerebrate rigidity the oxygen intake is only slightly greater than when the muscles are flaccid. W. D. H.

Rate of Reproduction of the Blood Constituents in an Immunised Horse After a Large Bleeding. R. A. O'BRIEN (*J. Path. Bact.*, 1913, **18**, 89—98).—After the withdrawal of ten litres of blood from an immunised horse, the fluid first appearing in the circulatory system contains an amount of protein far above the normal; hæmolysin and diphtheria antitoxin are reproduced at different rates, and the rate of reproduction of the various blood-proteins is probably associated therewith. Details regarding salts and corpuscles are also given. W. D. H.

The Effect of Certain Drugs, Toxic Substances, and Micro-organisms on the Fragility of the Red Corpuscles of Man and Animals. W. W. C. TOPLEY (*J. Hygiene*, 1913, **13**, 191—236).—Arsenious acid and atoxyl in toxic doses increase the fragility of red corpuscles *in vivo*. Bile and bile salts cause no change. Various pathogenic hæmolytic micro-organisms cause a rise in fragility, so also do specific hæmolytic sera; the ambocepter alone does not. Experiments *in vitro* were not satisfactory, but, so far as they went, the results confirmed the findings *in vivo*. W. D. H.

The Formation of Indophenol at the Nuclear and Plasma Membranes of Frog's Blood Corpuscles, and its Acceleration by Induction Shocks. RALPH S. LILLIE (*J. Biol. Chem.*, 1913, **15**, 237—247).—The formation of indophenol by the intracellular oxidation of *α*-naphthol and dimethyl-*p*-phenylenediamine takes place most rapidly in the neighbourhood of the nuclear and plasma membranes. This is accelerated by passing induction shocks through the suspension of blood corpuscles. W. D. H.

Rapid Method of Preparing Thrombin. WILLIAM H. HOWELL (*Amer. J. Physiol.*, 1913, **32**, 264—265).—Pig's fibrin is well washed,

and then extracted with 8% solution of sodium chloride; the extract is heated with an equal volume of acetone; the bulky precipitate of protein contains thrombin; this is filtered off and rapidly dried, then extracted with water, and filtered; the filtrate contains the thrombin, traces of salt, and a heat-coagulable protein; the latter is removed by shaking with chloroform, and the final fluid is evaporated to dryness in a current of cold air. The dried material can be left indefinitely in a desiccator. It is easily and completely soluble in water. W. D. H.

The Relation of Metathrombin to Thrombin. F. W. WEYMOUTH (*Amer. J. Physiol.*, 1913, **32**, 266—285).—The thrombin content of serum is determined by its clotting power on solutions of fibrinogen, and the metathrombin content by the clotting power after activation by alkali and subsequent neutralisation. In dog's serum the activity of both disappears after three to four days; five to eighteen days later there is almost complete return, and then it disappears completely. If kept sterile the initial loss of power is slower, and there is no reappearance of activity. Bacterial growth is responsible for both phases. Thrombin prepared by Howell's method retains its power for long periods (at least eighteen days); its power is destroyed by a substance in serum and in oxalate plasma, which is antithrombin. After the action of antithrombin the presence of metathrombin can still be shown in certain cases. Metathrombin is regarded as a thrombin-antithrombin compound; it is absent in oxalate and fluoride plasma. W. D. H.

The Nitrogen of Blood-serum Freed from Protein. RUDOLF PHILIPP (*Zeitsch. physiol. Chem.*, 1913, **86**, 494—502).—The residual nitrogen after serum has been freed from protein by heat-coagulation is about twice as great as when phosphotungstic acid, uranyl acetate, or ferrum oxydatum dialysatum are employed. The two last-named reagents entirely free the serum from protein. In cases of uræmia the residual nitrogen is increased. W. D. H.

Alterations Produced in Complement-containing Sera by the Introduction of "Lecithin." JOHN CRUICKSHANK and THOMAS J. MACKIE (*J. Path. Bact.*, 1913, **18**, 99—113).—"Lecithins" differ markedly with regard to their power to produce the alterations in complement activity, hæmolysis, etc., with which the paper deals. A large number of preparations are quite inefficient. W. D. H.

Fibrin in Sol and Gel State. The Blood-coagulation Problem. EBEL HEKMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 172—185).—The author has investigated the relation between fibrinogen and fibrin. Pure fibrin, free from blood corpuscles, was found to dissolve quite readily in very dilute sodium hydroxide or sodium carbonate, but a fibrous coagulum could be reproduced by the cautious addition of dilute acids, such as phosphoric or carbonic, or by sodium dihydrogen phosphate or calcium chloride.

Fibrin also dissolved in a slight excess of acid, but could be reprecipitated on neutralisation. Coagulation was also effected in solutions which had been boiled, from which the conclusion is drawn that ferments play no part in the process. Fibrin is therefore a reversible gel.

Further experiments showed that centrifugated, fluid plasma, or ascites fluid (that is, a natural fibrinogen solution), like alkaline fibrin solutions, could be coagulated by traces of acids. Moreover, alkaline fibrin solutions could be coagulated by serums or organic extracts which are known to coagulate fibrinogen, and also, like fluid plasma or ascites fluid, by means of saturated solutions of sodium chloride or fluoride. A great similarity was thus established between fibrinogen as found in blood and body fluids, and a solution of fibrin in very dilute alkali.

Dried fibrils, the single threads of fibrin, swell out again very quickly in alkaline solutions, and, if the volume of liquid is small, raw fibrin will imbibe the whole of it and become jelly-like. A swollen fibril, however, contracts to its original size in dilute acids, 1% calcium chloride or any saturated salt solution, or even in excess of water. The swelling process is therefore of a superficial kind, and it is assumed that it consists in the formation of an alkali adsorption-compound, which eventually, by the continuation of the imbibition, passes into colloidal solution. Fibrinogen is thus considered to be an alkali-hydrosol of fibrin, and its conversion into the gel, fibrin, and therefore the coagulation of blood, is merely due to the withdrawal of hydroxyl ions from the adsorption compound by means of one or other of the factors mentioned above.

J. C. W.

The Inhibition of Hæmolysis by Cholesterol and Oxycholesterol. E. Schreiber and Lénard (*Biochem. Zeitsch.*, 1913, **54**, 291—296).—A method is described for preparing oxycholesterol from cholesterol, and of obtaining emulsions of the same. Although, by itself, the former substance has a much weaker power of inhibiting hæmolysis than cholesterol, it increases this power of the latter substance when added to it in quite small quantities. Oxycholesterol acts also more weakly than cholesterol in inhibiting hæmolysis by cobra poison. S. B. S.

The Influence of Nutrition on the Gaseous Metabolism of Cold-blooded Animals. Bernhard Elsas (*Zeitsch. Biol.*, 1913, **62**, 1—31).—The experiments were made on groups of frogs in a modified Regnault-Reiset apparatus. The inanition metabolism is first found; but as this is influenced by the temperature, all the observations must be carried out at a constant temperature. Food may then be given in amounts equivalent to the inanition metabolism (isopeinic), or the quantities may be below or above this (hypo- and hyper-peinic respectively). Iso- and hyper-peinic administration of dextrose increases the metabolism by from 6 to 20%. Isopeinic feeding with fat does not raise the metabolism. The increase of metabolism after isopeinic feeding on protein is

very pronounced, 17—40%. These results are compared with some previously published by Weiss. The observations lend no support to the view that the increase of activity is due to alimentary work, but confirm Rubner's views on the specific dynamic values of foods.

W. D. H.

Metabolism of Ammonium Salts. I. The Estimation of Ingested Ammonium Salts in the Dog on an Adequate Mixed Diet. FRANK P. UNDERHILL (*J. Biol. Chem.*, 1913, **15**, 321—335).—Ammonium salts of organic acids were given to dogs on a fixed diet, but failed to increase the ammonia nitrogen of the urine. Ammonium salts and inorganic acids caused a varying degree of increase in the ammonia nitrogen of the urine. The experiments afford no adequate explanation for the temporary retention of the ammonium salts. All the inorganic ammonium salts used, and some of the organic salts, cause a distinct excess of total urinary nitrogen, and they apparently stimulate nitrogenous katabolism. Sodium chloride under the same conditions lowers the output of urinary ammonia nitrogen. W. D. H.

Metabolism of Ammonium Salts. II. Elimination of Ammonium Salts During a Period of Prolonged Inanition. FRANK P. UNDERHILL (*J. Biol. Chem.*, 1913, **15**, 337—339).—During inanition in the dog, ingestion of ammonium carbonate fails to produce an increase of urinary ammonia nitrogen. Ammonium chloride causes, however, a marked increase, and also an increase in total nitrogen. At this stage a second ingestion of ammonium carbonate may also bring about an increase of total urinary nitrogen. W. D. H.

Metabolism of Ammonium Salts. III. The Utilisation of Ammonium Salts with a Non-nitrogenous Diet. FRANK P. UNDERHILL and SAMUEL GOLDSCHMIDT (*J. Biol. Chem.*, 1913, **15**, 341—355).—Ammonium chloride added to a non-nitrogenous diet caused no retention of nitrogen, as Grafe states. It exercises a toxic action, and increases the output of urinary ammonia. Ammonium acetate and citrate decrease the nitrogen loss, and lead to retention of nitrogen. The ability of the body to deal with the organic and inorganic salts of ammonium is radically different. W. D. H.

Excretion of Creatine. R. A. KRAUSE (*Quart. J. expt. Physiol.*, 1913, **7**, 87—101).—The metabolism of children differs from that of the adult. In boys, creatinuria occurs until the age of five or six; in girls it persists longer, and may last until the intermittent creatinuria occurs which characterises the female sexual cycle. The power to assimilate creatine given with the food is much weaker in children than in the adult. The excretion or non-excretion of creatine depends on the balance between formation and destruction, two processes which are always at work. This view will render it necessary to revise current theories on creatinuria as a pathological condition. W. D. H.

Nitrogen Retention in Feeding on Urea. EDUARD GRAFE (*Zeitsch. physiol. Chem.*, 1913, **86**, 347—355).—These experiments are given to support the author's contention (compare A., 1912, ii, 659; 1913, i, 216) that urea in the food leads to retention of nitrogen. The experiments lasted over a long period. W. D. H.

The Relation of Growth to the Chemical Constituents of the Diet. THOMAS B. OSBORNE, LAFAYETTE B. MENDELL, EDNA L. FERRY and ALFRED J. WAKEMANN (*J. Biol. Chem.*, 1913, **15**, 311—326).—It has been previously shown that growth and maintenance are different things. The best food to promote growth is milk, even if only small quantities are occasionally given, mixed with an artificial diet of protein, fat, carbohydrates, and salts. Protein-free milk is not adequate for growth, but the addition of butter to the protein-free milk restores growth. Evidently some substance is removed from the protein-free milk which is essential, and this is present mixed with the butter-fats. What the substance is, is as yet unknown. W. D. H.

Sugar Absorption. KORNÉL VON KÖRÖSY (*Zeitsch. physiol. Chem.*, 1913, **86**, 356—367).—By interference with the circulation through the intestines, lungs, and heart, absorbed sugar does not occur as such in the blood. The absorption of sugar is not a simple process, and the effect of internal secretions, such as that of the adrenal gland, has to be taken into account. Phosphates may also play an imporant rôle in sugar absorption, as they do in alcoholic fermentation. W. D. H.

The Distribution of Creatine in the Animal Organism J. C. BEKER (*Zeitsch. physiol. Chem.*, 1913, **87**, 21—37).—A large number of organs and tissues in different animals were found to contain creatine in amounts which are greater than that in the blood. These results are given in tables. Experiments are also given which confirm the view that the liver is able to convert creatine into creatinine. W. D. H.

The Lecithin Content of Different Tissues. JOHN CRUICKSHANK (*J. Path. Bact.*, 1913, 134—136).—The amount of lecithin in various tissues was estimated by the author's method. In 100 grams of moist tissue, ox red corpuscles yielded 2·5, sheep's liver 1·6, human brain 0·6, ox pancreas 0·68, testicles 0·62 gram, and other tissues amounts varying from 0·14 to 0·48 gram. W. D. H.

Gases Evolved During the Autolysis of Some Organs and Tissues. FILIPPO TRAETTA-MOSCA (*Gazzetta*, 1913, **43**, ii, 144—148).—The liver, kidney, brain, and suprarenal capsules yield carbon dioxide, nitrogen, and hydrogen; the intestine evolves carbon monoxide and oxygen in addition to these gases, whilst the pancreas, spleen, lungs, and heart yield only nitrogen. R. V. S.

Calcium and Magnesium in the Brain Under Different Physiological and Pharmacological Conditions. IVO NOVI *Eighth Inter. Cong. App. Chem.*, 1912, **19**, 261).—The proportion of

calcium in the brain of the dog varies from 0·0143 to 0·031, and that of magnesium from 0·0143 to 0·0167% of the fresh material. Age has a marked influence on the calcium-content of the brain. With dogs this content is at its maximum before and just after birth, the minimum is reached prior to weaning, and in old age the initial value is again attained; a similar course is followed in the case of the human brain. With guinea-pigs, the proportion of calcium is minimal in the fœtus, becomes almost doubled a few days after birth, and continues to increase for a month; subsequently it remains constant until old age is reached, when it again increases, sometimes as much as tenfold. Introduction, either subcutaneously or into the stomach, veins, or carotids, of sodium chloride in isotonic or hypertonic solution results in the diminution of the calcium-content of the brain, in some cases by one-half.

The proportion of magnesium in the brain remains constant at all ages and under all the experimental conditions employed.

T. H. P.

Cerebrosides of Brain Tissue. PHOEBUS A. LEVENE (*J. Biol. Chem.*, 1913, **15**, 359—364).—The conclusion that the cerebrosides are optically different isomerides is confirmed by further work, but more data are still wanting to render this certain. W. D. H.

Autolysis of, and Presence of, Proteolytic Ferments in the Brain of the Calf. FILIPPO TRAETTA-MOSCA (*Gazzetta*, 1913, **43**, ii, 138—143).—When the brain of the calf is subjected to autolysis (incubation with water in presence of chloroform for a month), lysine, choline, xanthine, and adenine can be subsequently obtained from it. This indicates the presence in the brain of ferments capable of attacking albumin, nucleins, and lecithin. R. V. S.

The Effect of Alcohol on the Excitation, Conduction, and Recovery Processes in Nerves. KEITH LUCAS (*J. Physiol.*, 1913, **46**, 470—505).—After exposure to 5% alcohol, a nerve recovers its properties when replaced in Ringer's solution. The impairment of conduction in the nerve produced by alcohol, and the increase in threshold current strength follow a parallel course. The rate of conduction is much slowed, however, at a stage when the rate of recovery is not slowed. This suggests that the recovery process, which is responsible for the refractory period, is a process different from the disturbance which is the basis of propagation of the nervous impulse. W. D. H.

The Influence of Anoxybiosis on the Disappearance of Glycogen from the Autonomous Organs of the Frog. ERNST J. LESSER (*Biochem. Zeitsch.*, 1913, **54**, 236—251).—As autonomous organs are designated those tissues, such as liver and muscles, in which action takes place when they are separated from the nervous systems, and the hormones contained in the blood supply. The author has already shown that the rate of glycogen disappearance from the liver after removal from the animal is greater in summer

frogs than in winter frogs, and he now compares this rate when the organs are well supplied with oxygen (oxybiosis) and when they are kept in a current of nitrogen (anoxybiosis). These experiments were of interest, as it has been found that under the influence of anoxybiosis of the whole animal the rate of glycogen disappearance could be increased, and it was thought possible that by this means the behaviour of the livers from winter frogs could be made to approximate to that of summer frogs. It was found that in the months of the year in which the glycogen of the liver is stable, the rate of disappearance is not influenced by anoxybiosis, whereas in the months when the glycogen is labile, anoxybiosis increases the rate. The experiments were carried out at the temperature of 22—24°, and did not extend beyond five hours. Similar results were obtained with muscular tissues. S. B. S.

Chemical and Bio-chemical Properties of the Lipoids Extracted from Pig's Liver and Egg-yolk. FREDERICK P. WILSON (*J. Path. Bact.*, 1913, **18**, 60—63).—The lipoids extracted from pig's liver and from egg-yolk differ greatly in their chemical (iodine value, etc.) and biochemical (anti-complementary, hæmolytic powers, etc.) properties. W. D. H.

The Thyroid Gland. XI. WALTER EDMUNDS (*J. Path. Bact.*, 1913, **18**, 52—59).—The thyroid gland in dogs hinders the assimilation of sugar; the parathyroid glands favour it. W. D. H.

Carbohydrate Metabolism in its Relation to the Thyroid Gland. The Effect of Thyroid Feeding on the Glycogen-content of the Liver and on the Nitrogen Distribution in the Urine. W. CRAMER and R. A. KRAUSE (*Proc. Roy. Soc.*, 1913, *B*, **86**, 550—560).—When rats or cats are fed on a carbohydrate-rich diet plus small amounts of fresh thyroid gland for two or three days, the liver only contains traces of glycogen. This is due to an inhibition of the glycogenic function of the liver, and not to increased utilisation of carbohydrates. There is no glycosuria. The distribution of the nitrogenous constituents in the urine is similar to that observed after withdrawal of carbohydrates from the diet. W. D. H.

Changes in the Metabolism of Animals After Extirpation of the Thyroids and Parathyroids. J. GREENWALD (*Biochem. Zeitsch.*, 1913, **54**, 159—160).—The author controverts the statement of Paladino (this vol., i, 675) that there is an increased phosphorus output after extirpation of the thyroids. He contends that there is rather a diminution, and the discrepancy between Paladino's results and those of other authors is due to the fact that the former did not investigate the metabolism immediately after the operation, but only after a prolonged period at the onset of tetany, which, it is admitted, may produce increased phosphorus output. S. B. S.

The Enzymes of the Pituitary Body. LUCIE BUETOW (*Biochem. Zeitsch.*, 1913, **54**, 40—52).—The following ferments were found to be present: Catalase, diastase, pepsin, trypsin, peroxydase, tributyrinase, and urease. The following enzymes could not be detected: Invertase, lactase, a glycolytic ferment, and deamidase. S. B. S.

The Chemistry of the Mammary Gland. J. ARGYLL CAMPBELL (*Quart. J. expt. Physiol.*, 1913, **7**, 53—56).—Considerable differences exist in the mammary gland of different animals, and even between different parts of the gland in the same animal. Lactose is found only when the gland contains milk, and the amount present is thus a measure of the quantity of milk in the gland. The fat, on the other hand, is present, not only in milk, but in the secreting cells, and in the adipose tissue between the alveoli. W. D. H.

The Phosphatides of Human Placenta. III. C. SAKAKI (*Biochem. Zeitsch.*, 1913, **54**, 1—4).—From the alcohol-ether obtained in the purification of the so-called jecorin by Drechsel's method, a precipitate was obtained on addition of alcoholic cadmium chloride, part of which was soluble in ether and the other part insoluble. Both these products were analysed, but the results do not accord with any definite chemical formula. S. B. S.

The Distribution of Phosphorus in the Placenta. C. SAKAKI (*Biochem. Zeitsch.*, 1913, **54**, 5—10).—From the determination of the phosphorus soluble in organic solvents (light petroleum or benzene) the amount of lecithin was calculated as 6·8% of the dried substance. S. B. S.

The Absorption of Water by the Skin of the Frog. S. S. MAXWELL (*Amer. J. Physiol.*, 1913, **32**, 286—294).—An empty frog's skin immersed in water takes up an enormous amount; this depends on the permeability of the skin to water, and its relative impermeability to salts. The assumption of "vital activity" in this process is regarded as unnecessary. W. D. H.

The Absolute Mechanical Efficiency of the Contraction of an Isolated Muscle. ARCHIBALD V. HILL (*J. Physiol.*, 1913, **46**, 435—469).—Fick's results on the mechanical efficiency of muscular contraction are inaccurate; for instance, they do not take into account the heat-production which occurs in the period of recovery. The subject was re-investigated by the author's new methods; his apparatus, however, requires calibration for each experiment and each muscle used. In the sartorius, the initial process of contraction consists mainly of the liberation of free potential energy, which is manifested as tension energy in the excited muscle; this can be used indifferently for the production of work or of heat; the efficiency of the whole process may be almost as high as 50%. The chemical substance possessing the free energy is the lactic acid precursor. W. D. H.

Extractives of Muscle. XV. Presence of Carnosine, Methylguanidine, and Carnitine in Horse Flesh. J. SMORODINZEV (*Zeitsch. physiol. Chem.*, 1913, **87**, 12—20).—Horse flesh is shown to contain about 0·58 gram of creatine, 0·08 gram of purine substances, 1·82 gram of carnosine, 0·18 gram of carnitine, and from 0·11 to 0·83 gram of methylguanidine per kilogram of fresh muscle. These proportions are those observed in the muscles of other animals. E. F. A.

The Influence of Starvation on the Creatine Content of Muscle. VICTOR C. MYERS and MORRIS S. FINE (*J. Biol. Chem.*, 1913, **15**, 283—304).—The creatine of rabbit's muscle is relatively increased in the early part of starvation, but decreased at the close, owing to its loss by the urine. That creatine and creatinine are independent in metabolism is dissented from; the old view that the creatinine is derived from muscular creatine is favoured, though the proof is not yet complete. W. D. H.

Influence of Carbohydrate Feeding on the Creatine Content of Muscle. VICTOR C. MYERS and MORRIS S. FINE (*J. Biol. Chem.*, 1913, **15**, 305—310).—The effect of carbohydrate feeding on the creatine of rabbit's muscles is similar to that seen in starvation. The decreased elimination of creatine under these conditions is primarily dependent on the sparing action of carbohydrate on the muscle proteins. W. D. H.

The Derivatives of Ethyl Alcohol Contained in Muscle. ALONZO L. TAYLOR (*J. Biol. Chem.*, 1913, **15**, 217—220).—In dogs which had been without food for one day, and in which the entire alimentary canal had been extirpated, the muscles still yielded alcohol in small amounts. It could not have been derived from food, and the theory is advanced that alcohol is an intermediate stage in the metabolism of dextrose. W. D. H.

Chemical and Physico-chemical Properties of Liquids Expressed from Striated and Plain Muscle. II. Amount of Protein in the Juice and Relations between the Granules (Myosin) Suspended and the Myoprotein Dissolved. FILIPPO BOTTAZZI and G. QUAGLIARIELLO (*Atti R. Accad. Lincei.*, 1913, [v], **22**, ii, 52—59. Compare Bottazzi, A, 1912, ii, 1192).—The granular substance amounts to 33—61% of the total protein of the juice. The total protein amounts to 5·32—9·54%. Data regarding the yield, density, viscosity, total nitrogen, and ash of the juice obtained in different experiments and with muscle from different animals are also recorded. R. V. S.

Presence of Succinic Acid in Meat Extract and in Fresh Meats. HANS EINBECK (*Zeitsch. physiol. Chem.*, 1913, **87**, 145—158). —Succinic acid in some quantity is obtained, both from Liebig's meat extract and from fresh ox and dog flesh. It is present in the carniferrin fraction, and particularly in the mother liquors from

this. It is not derived from the decomposition of Siegfried's phosphorcarnic acid. E. F. A.

Does Milk Contain Phosphatides? VLADIMIR NJEGORAN (*Biochem. Zeitsch.*, 1913, **54**, 78—82).—Milk was treated with anhydrous sodium sulphate, and the mixture was kept in a vacuum until free from water. The residual powder was then extracted with various organic solvents. No phosphorus could be detected in these solutions, and the author draws the conclusion that phosphatides are not present in milk. S. B. S.

The Effect of Pituitary Extract on the Secretion of Milk. JOHN HAMMOND (*Quart. J. expt. Physiol.*, 1913, **6**, 311—338).—Injection of pituitary extract produces an immediate action on the flow of milk, which is followed by a period of decreased flow. The effect, however, is not muscular, nor is it effected through the rise of blood-pressure. Microscopic evidence points to a direct action on the epithelium cells which set free the milk constituents. The milk formed is rich in fat. The daily yield of milk is only slightly increased as the result of the injection. W. D. H.

Hydrocephalus Fluid. E. SIEBURG (*Zeitsch. physiol. Chem.*, 1913, **86**, 503—510).—An analysis of fluid from a case of hydrocephalus is given. The noteworthy points are: (1) the absence of protein; a faint reaction with Millon's reagent indicates the presence of certain hydrolytic products of protein; and (2) the presence of certain enzymes, namely, diastase, invertase, lipase, and enzymes capable of splitting glucosides and esters. W. D. H.

The Nature of the Depressor Substance in Dog's Urine and Tissues. ALONZO A. TAYLOR and RICHARD M. PEARCE (*J. Biol. Chem.*, 1913, **15**, 213—216).—Attempts to isolate the substance failed. W. D. H.

The Excretion of Formic Acid in Human Urine Under Normal and Pathological Conditions. RUDOLF STRISOWER (*Biochem. Zeitsch.*, 1913, **54**, 189—211).—The formic acid was estimated by distilling urine acidified with phosphoric acid under diminished pressure, collecting the distillate in excess of alkali, and determining the acid in this distillate after concentration by heating with mercuric chloride in the presence of sodium acetate. The mercurous chloride produced by the reduction was weighed. The yield of formic acid thus found is about 90% of the theoretical. Formic acid is found under normal conditions in the urine to the extent of about 13·5 milligrams daily; and the amount is not increased by moderate muscular activity. It does not appear to be influenced by the character of the diet. In many diseases the amount excreted is normal, as in compensated heart affections, carcinoma, gastric ulcer, colelithiasis, constipation, and various febrile conditions. It is increased, however, in uncompensated heart affections, in asphyxia due to work in heart affections in man,

and in animals. It is also increased in diabetes as the result of changes in the fat metabolism. In a single case investigated of muscular dystrophy there was also found an increased output of the acid, due apparently to changes in the muscular metabolism. Reasons are given for supposing that formic acid is a metabolism product of fats, carbohydrates, and proteins. S. B. S.

Excretion of Formic Acid in Disease. I. GREENWALD and N. W. JANNEY (*Zeitsch. physiol. Chem.*, 1913, **86**, 511—512).—By the use of the method of Dakin, Janney, and Wakeman, it is shown that the excretion of formic acid in the urine is increased in pneumonia, especially during the stage of resolution. Figures are also given in isolated cases of other diseases, but no generalisations are possible from these. W. D. H.

Substances in Urine Giving Rise to Indigotin. I. ROBERT V. STANFORD (*Zeitsch. physiol. Chem.*, 1913, **87**, 188—206).—The substances in human urine which give rise to indigotin are very unstable. Their amount has greatly diminished in one to three hours, and they have disappeared in three to six hours. The cause of the decomposition is not understood; it is perhaps due to autoxidation. The indigotin-forming substances were obtained by salting-out and extraction with a mixture of ether and alcohol. Even under these conditions they decompose too rapidly for their isolation to be effected. It is considered improbable that they are identical with potassium indoxylsulphate. E. F. A.

Excretion of Morphine in the Urine. WILHELM RITTER VON KAUFMANN-ASSER (*Biochem. Zeitsch.*, 1913, **54**, 161—173).—The author finds that neither the biological method of Hermann and Straub (action on white mice) nor the chemical method described by van Ryn are suitable for the quantitative estimation of morphine in the urine. He describes a method devised by himself, in which the morphine is finally extracted with chloroform, and estimated by means of iodoeosin. By this method it is found that larger quantities of the alkaloid are excreted by the kidneys than was formerly supposed, the amount eliminated by this channel reaching 39% during a course of constant administration of the drug. Seventy-two hours after the last injection in this series of experiments sufficient alkaloid could be found in the liver, kidneys, and stomach for quantitative estimation. S. B. S.

The Antagonism Between Adrenaline and Anæsthetics on the Heart. JAMES A. GUNN (*Quart. J. expt. Physiol.*, 1913, **7**, 75—86).—Using the perfusion method on the heart of cat or rabbit it was found that adrenaline can antagonise a concentration of chloroform which enfeebles the beat, but not such a concentration as arrests it. In the case of chloral the antagonism of adrenaline is greater, and the latter drug will set a heart going which is completely arrested by chloral. Adrenaline is also antagonistic to many other substances which weaken cardiac activity. The

rhythmic contractions which adrenaline arouses in a quiescent heart are independent of intrinsic motor ganglia. W. D. H.

Pharmacological Testing of Sulphuric Acid. Esters of Atropine and Scopolamine. PAUL TRENDELENBURG (*Arch. expt. Path. Pharm.*, 1913, **73**, 118—138).—By the esterification of the alcoholic hydroxyl of alkaloids of the atropine group with sulphuric acid, the intramolecular salt formation with the nitrogen of the tropine or scopolamine causes a marked weakening of their affinity for the endings of the vagus nerve. In most cases the stimulating action on the nervous system is increased. The toxicity is not altered as a rule. The esters of the atropine group stimulate the respiratory centre very strongly; this may be useful therapeutically. The scopolamine ester does not possess this property. W. D. H.

Creatine Formation in the Animal Kingdom. Creatine Formation from Betaine and Choline. OTTO RIESER (*Zeitsch. physiol. Chem.*, 1913, **86**, 415—453).—This paper contains a very useful résumé of recent work on the subject. The experiments recorded deal with the effect of the administration of betaine and choline (by mouth or hypodermically) on the amount of creatine in the muscles, and creatinine in the urine. In some cases the material was mixed with surviving muscle. Although in a certain number of cases creatine or creatinine, as the case may be, was increased, the conclusion is drawn that there is no certain proof that betaine or choline leads to creatine formation. W. D. H.

The Fate of Cocaine and Ecgonine in the Organism. SULEIMAN RIFÀTWACHDANI (*Biochem. Zeitsch.*, 1913, **54**, 83—91).—Cocaine is excreted, after administration to rabbits, in the urine, in amounts which can be quantitatively estimated. For this purpose the urine is extracted by benzene or ether, and the amount of alkaloid thus obtained is estimated by Gordin's method. By long-continued administration of the drug, the amount excreted each day in the urine gradually increases. No destruction of cocaine, when kept in contact with living tissue, could be detected. Ecgonine is also excreted in the urine; for the purposes of detection the urine was evaporated to dryness and treated with methyl alcohol and hydrochloric acid; the alkaloid after conversion into its methyl ester can be extracted by ether. S. B. S.

The Influence of Lecithin on the Action of Drugs. DAVID M. LAVROV (*Biochem. Zeitsch.*, 1913, **54**, 16—26. Compare Hanschmidt, this vol., i, 796).—A summary is given of earlier experiments on the combined action of lecithin and various drugs on frogs, in which it is shown that within certain limits the lecithin diminishes the action of the drug, whereas within higher limits it increases it. In the cases of phosphorus and phenol poisoning, an increase only of the toxic effect was observed. In doses of 0·0015 to 0·003 gram lecithin markedly increases the toxic action of ricin on frogs. Doses of other magnitudes cause a two-fold action. During the first ten

or eleven days they increase the toxic action, but afterwards the ricin effects begin to weaken. The general condition of the animals employed is not without effect. S. B. S.

Is the Pressor Effect of Pituitrin Due to Adrenal Stimulation? R. G. Hoskins and Clayton McPeek (*Amer. J. Physiol.*, 1913, **32**, 241—244).—The experiments recorded show that the answer to the question is in the negative. W. D. H.

Pharmacological Notice Concerning Two New Derivatives of Santonin, α- and β-Santonan (α- and β-Tetrahydrosantonin). E. Sieburg (*Chem. Zeit.*, 1913, **37**, 945—946).—Pharmacological experiments with α- and β-sodium tetrahydrosantonate (Wienhaus and von Oettingen, this vol., i, 474) show that they are not cramp poisons, neither do they act as vermicides. The reduction of the ethylene linking in santonin thus destroys its specific properties. T. S. P.

***p*-Hydroxy-β-phenylethylamine, the Poison in the Salivary Gland of Cephalopods.** Martin Henze (*Zeitsch. physiol. Chem.*, 1913, **87**, 51—58).—*p*-Hydroxy-β-phenylethylamine is shown to be the only poisonous constituent of the saliva of the octopus. This base, which had previously been obtained by Barger and Dale from ergot (A., 1909, ii, 689), is thus, like adrenaline, the product of metabolism in a gland. E. F. A.

Chemistry of Vegetable Physiology and Agriculture.

The Resistance of Spores to Heating in Anhydrous Fluids such as Glycerol and Similar Substances. HOWARD BULLOCK (*J. Hygiene*, 1913, **13**, 168—177).—The method at present in use for the sterilisation of glycerol or oil are quite inadequate; the heating of these fluids has no greater effect than the same temperature in the air. To sterilise these fluids, a temperature of 170° for half an hour or 180° for ten to fifteen minutes is necessary. W. D. H.

Bacterial Metabolism. XI. Estimation of Urea Nitrogen in Cultures of Certain Bacteria. ARTHUR I. KENDALL and ARTHUR W. WALKER (*J. Biol. Chem.*, 1913, **15**, 277—282).—Urea nitrogen estimated by Folin's method is probably not all due to urea. In bacteria the main nitrogenous end-product of metabolism is ammonia. The urea nitrogen in the culture fluid does not alter. W. D. H.

Bacterial Metabolism. XIII—XXX. ARTHUR I. KENDALL, ALEXANDER A. DAY, and ARTHUR W. WALKER (*J. Amer. Chem. Soc.*, 1913, **35**, 1201—1249).—An investigation of the effect

of utilisable carbohydrate on the metabolism of protein and protein derivatives by bacteria. The media used consisted of a prepared broth containing meat juice and peptone, and a mixture of the same broth with 1% of dextrose. Four flasks of the sugar-free and of the sugar-containing broths were inoculated with the desired organism and incubated at 37°, the progress of the action being followed by examination of the contents of the flasks over a period of nine days. Determinations were made of the free ammonia, the total nitrogen, the acidity resulting on the addition of formaldehyde, and the acidity or alkalinity of the liquid, using alizarin, neutral red, and phenolphthalein as indicators.

Seventeen groups of bacteria were submitted to examination, and the results are tabulated in the original. D. F. T.

Disinfecting Value of Mercuric Oxycyanide and of Mercuric Oxycyanide Containing Mercuric Cyanide. H. KÜHL (*Arch. Pharm.*, 1913, **251**, 340—349).—In general, a solution of a poison at extreme dilution promotes the growth of lower vegetable organisms; at a definite, greater concentration of the poison, the multiplication of the organisms is retarded, whilst at still greater concentrations the poison exerts its lethal action. The author has examined the action on *Bacillus coli* of two samples of mercuric oxycyanide, one practically pure (99%), the other containing 33·3% of oxycyanide and 66·6% of mercuric cyanide. At concentrations of 1 in 200,000 to 1 in 400,000 it is found that solutions of both samples approximately double the rate of growth of the bacilli.

The retarding action of the two disinfectants on the growth of organisms is shown in two ways. Milk coagulates when it contains 0·0005% of either of the two samples, but does not do so when the amount of the poison is increased to 0·005%. In the second set of experiments, urine containing 0·01—0·2% of either of the poisons remains unchanged under the conditions in which the urine alone becomes turbid and evolves ammonia.

Experiments on pure cultures of *Staphylococcus pyogenes*, on raw milk, on tuberculous milk, and on the contents of the stomach and of the intestines and on the brains of a decomposed corpse lead to the astonishing result that there is no appreciable difference in the bactericidal value of the two samples under examination. Another series of comparative experiments shows that the disinfecting value of mercuric oxycyanide is almost equalled by that of a mixture of the oxycyanide and sodium chloride containing 33·3% of the latter. A fuller treatment of the subject is promised; at present the author is of opinion that the sodium chloride, as a disinfectant, slightly active accentuates the bactericidal value of the mercuric oxycyanide by promoting the absorption of the latter substance by the protoplasm. C. S.

Biochemical Reactions of Diphtheria-like Organisms. T. G. M. HINE (*J. Path. Bact.*, 1913, **18**, 75—80).—The chief point urged is that the diphtheria-like bacilli, *B. diphtheriae*, alone gives acid with dextrose and dextrin, and not with sucrose.

W. D. H

The Inhibition of the Cholera-Red Reaction by Certain Nitrite-destroying Organisms, and on the Mutual Inhibition of B. dysenteriæ (Flexner) and V. choleræ when Grown together. W. J. LOGIE (*J. Hygiene*, 1913, **13**, 162—167).—Certain nitrite-destroying organisms when grown along with *V. cholerae* prevent the appearance of the cholera-red reaction. This is not due to the non-formation of nitrite, but to its rapid destruction by the nitrite-destroying organisms. There are, on the other hand, certain nitrite-destroying organisms which fail to prevent the cholera-red reaction. In the case of *B. dysenteriae* the failure to prevent the cholera-red reaction is due to an inhibition of the growth of both organisms when grown together. W. D. H.

Spore-producing Bacillus lactis fermentens, a Ferment Producing Butylene Glycol from Lactose. RUOT (*Compt. rend.*, 1913, **157**, 297—299).—*Bacillus lactis fermentens* is a very mobile, anaerobic bacillus, which produces spores after three days on gelose at 30°, which resist a temperature of 90° for five minutes, and can be heated at 100° for half a minute without being killed. It ferments dextrose, sucrose, lactose, mannitol, and glycerol, the products from the sugars being carbon dioxide, hydrogen, alcohol, butylene $\beta\gamma$-glycol, acetylmethylcarbinol, and formic and acetic acids, no lactic or succinic acids being found. The fermentation of milk by this bacillus is very rapid, the products being as above. W. G.

Isolation of B. typhosus from Fæces by means of Brilliant-Green. C. H. BROWNING, W. GILMAN, and T. J. MACKIE (*J. Path. Bact.*, 1913, **18**, 146—148).—The method described is based on the observation that brilliant-green exerts a much more marked inhibitory effect on *B. coli* than on *B. typhosus*. W. D. H.

Bactericidal Action and Chemical Constitution with Special Reference to Basic Benzene Derivatives. C. H. BROWNING and W. GILMAN (*J. Path. Bact.*, 1913, **18**, 144—146).—*Staphylococcus aureus* and *B. anthracis* are more susceptible to basic benzene derivatives than are organisms of the *Coli* group. It is not possible to differentiate generally that gram-positive organisms are susceptible, and gram-negative organisms are not susceptible to crystal-violet. Salts of the heavy metals do not act less powerfully on the coli-typhoid group than on *S. aureus* and *B. anthracis*. Preliminary details are given of the effects of substituting radicles in benzene derivatives on their bactericidal power; and on the effect of serum on bactericidal action. W. D. H.

Influence of Ozone on Yeast and Bacteria. CARL A. NOWAK (*J. Ind. Eng. Chem.*, 1913, **5**, 668).—Results of experiments with bottom-fermentation yeast showed that ozonisation is not only of value in freeing the yeast from objectionable organisms which are susceptible to the action of ozone to a larger degree than the yeast itself, but also in eliminating the weakened cells and stimulating the fermentative power of the surviving ones. W. P. S.

Influence of Mineral Salts on Alcoholic Fermentation. Salts of Tin and Bismuth. MARIUS EMMANUEL POZZI-ESCOT (*Bull. Assoc. chim. Sucr. Dist.*, 1913, **31**, 49—53).—Stannous chloride even in small amounts retards fermentation. Yeast can be acclimatised so as to ferment well in presence of considerably more stannous chloride than will retard fermentation with ordinary yeast; the yeast, however, rapidly degenerates. Stannic chloride is much more toxic than stannous chloride.

With regard to bismuth, the basic nitrate, with which Gimel obtained favourable results, is quite insoluble when washed with hot water. N. H. J. M.

The Enrichment of the Invertase Content of Living Yeasts. JAKOB MEISENHEIMER, STEFAN GAMBARJAN, and L. SEMPER (*Biochem. Zeitsch.*, 1913, **54**, 122—154).—The effect of allowing various yeasts to remain in contact with various sugars on their content in invertase was investigated. It was found that the amount largely increased by this treatment. Large quantities of the organism were allowed to remain for one to two days in sucrose solutions, which were then cooled on ice, and poured off. A portion of the yeast was then removed, the juice expressed and treated with acetone. The invertase reaction constant of this preparation was then determined. The main portion of the yeast was again treated in a similar way, and the reaction constant of a portion also determined; the main bulk was again treated with sugar, and these processes repeated until the yeast was exhausted. During these successive treatments the invertase content increased, although the zymase content diminished. The relative influence of various sugars on the increase of invertase content was also investigated. In the majority of cases, the yeasts were allowed to grow in a Lindner solution, to which was added the various sugars. It was found that in most of the experiments invert sugar and lævulose caused a larger increase in the invertase than dextrose or sucrose. The lævulose was generally more effective than the invert sugar, and the sucrose slightly more effective than dextrose. The results may possibly be explained on the assumption that a lævulose-invertase combination is somewhat more stable than the combination of invertase with other sugars, and the ferment is thereby more efficiently guarded against change during the autolysis of the yeast. S. B. S.

The Dominance of Roquefort Mould in Cheese. CHARLES THOM and JAMES N. CURRIE (*J. Biol. Chem.*, 1913, **15**, 249—258).—The low percentage of oxygen in the open spaces within the cheese accounts for the dominant activity of *Penicillium roqueforte* in Roquefort and similar cheese. Gas analyses from cultures of various kinds of moulds are presented. W. D. H.

Phenomena of Imbibition in the Seeds of Avena sativa. F. PLATE (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 133—140).—From experiments with solutions of potassium, sodium, barium,

and calcium hydroxides, and of hydrochloric, nitric, sulphuric, and phosphoric acids, the author finds that both cation and anion have specific functions in regard to this phenomenon. The solutions accelerate germination, and considerable concentrations do not spoil germination, but even favour it. R. V. S.

Compounds Obtained from Plant Seeds by the Methods for Extracting Lecithin. IV. Peas, Larch, Rice. GEORG TRIER (*Zeitsch. physiol. Chem.*, 1913, **86**, 407—414).—Peas contain rather over 1% of lecithin. This yielded galactose on acid hydrolysis and colamine when hydrolysed with barium hydroxide.

The lecithin from larch seeds contained about 3·3% of phosphorus, 0·75% of nitrogen, and 4% of galactose.

Rice which had not been deprived of the husk yielded a lecithin compound having the properties of a cerebroside. E. F. A.

Distribution of Carboxylase in Plants. W. ZALESKI (*Ber. deut. bot. Ges.*, 1913, **31**, 349—353).—Carboxylase was found in various seeds, such as peas, lupines, *Vicia Faba*, wheat, and maize, in etiolated seedlings, and in moulds.

Although anærobic, carboxylase is active in presence of oxygen; and some of these substances decompose pyruvic acid equally well in air and in hydrogen. Some, however, such as ripening pea seeds, fail to decompose pyruvic acid in presence of air, whilst they are very active in a vacuum. The stem points of *Vicia Faba* decompose pyruvic acid in presence of air if previously extracted with methyl alcohol. N. H. J. M.

Chemical Composition of Cooked Vegetable Foods. KATHARINE I. WILLIAMS (*J. Ind. Eng. Chem.*, 1913, **5**, 653—656).—Analyses of cooked vegetables, cereals, and leguminous seeds, etc., are recorded (compare P., 1903, **19**, 26). W. P. S.

Chlorophyll Assimilation. K. VON KŐRÖSY (*Zeitsch. physiol. Chem.*, 1913, **86**, 368—383).—In acacia leaves immersed in nutritive fluids the assimilation of starch and sugar was about 10%, but the fat in the leaves was not increased. W. D. H.

Composition of the Fruit and Seeds of Adansonia digitata. RUSSELL GEORGE PELLY (*J. Soc. Chem. Ind.*, 1913, **32**, 778—779). —The seeds of the baobab tree (*Adansonia digitata*) consist of a very tough husk enclosing a soft, oily kernel, devoid of starch. Analysis gave, in percentages: moisture, 12·1; ash, 3·5; oil, 11·6; protein (total nitrogen multiplied by 6·25), 11·2; fibre, 22·5; carbohydrates (by difference), 39·1. The ash of the kernels contained: potash, 31·0; soda, 7·2; and phosphoric acid, 34·2%. The oil as extracted by light petroleum had D_{15}^{15} 0·915, saponification value, 190·5—191·7, and iodine value (Hübl, seventeen hours), 76·7—77·8. The seeds are free from alkaloids and cyanogenetic glucosides.

The fruit pulp gave: moisture, 15—16%; ash, 4·76—6·10%;

matter soluble in alcohol, 16·7—18·7%. The ash consisted largely of alkali carbonates, and contained: silica, 4·74; lime, 8·88; potash, 48·90; soda, 4·20; and phosphoric acid, 1·08%. The pulp consisted largely of pectous matter. The free acid extracted by 95% alcohol was found to be citric acid; no indications of tartaric acid were obtained, but small amounts of malic acid may be present. The pulp also contains an acid or acids of the pectic type, possibly present as acid potassium salts and insoluble in alcohol. T. S. P.

Application of the Biochemical Method to the Detection of Sucrose and Glucosides in Certain Ericaceæ. ÉMILE BOURQUELOT and (Mlle.) A. FICHTENHOLZ (*J. Pharm. Chim.*, 1913, [vii], **8**, 158—164).—The presence of sucrose, of a β-glucoside which is hydrolysed by emulsin, and of invertase and emulsin is demonstrated in *Arbutus unedo*, *Arbutus Menziezii*, *Azalea mollis*, *Calluna vulgaris*, *Kalmia latifolia*, and *Vacinium myrtillus*. E. F. A.

Plant Chemistry. P. Q. KEEGAN (*Chem. News*, 1913, **108**, 61—62. Compare A., 1912, ii, 1085).—A brief résumé and discussion of our present knowledge of the occurrence and composition of the bitter principles, fat-oils, and oxydases in plants, special reference being made to analyses of the bearberry (*Arbutus uva-ursi*). W. G.

The Nature of the Sugar Found in the Tuber of Arrowhead. K. MITAKE (*J. Biol. Chem.*, 1913, **15**, 221—229).—Dextrose, lævulose, and sucrose were found; galactose and raffinose are doubtful; maltose, pentose, and mannose are absent. W. D. H.

Capoc Seeds and Capoc Oil. HERMANN MATTHES and HEINRICH HOLTZ (*Arch. Pharm.*, 1913, **251**, 376—396).—Capoc seeds, obtained from *Eriodendron anfractuosum* and other trees and plants allied to the *gossypium*, contain 7·5% of water, 25·6% of fatty oil, and 5·6% of ash; the last consists essentially of potassium phosphate, and contains also considerable quantities of calcium, magnesium, and sulphuric acid. Capoc oil, which is expressed from the seeds, is a pale yellow, viscous liquid, having a faint, pleasant odour and taste; after long keeping it deposits solid constituents. It resembles cotton-seed oil, with which it is often adulterated. The oil has D^{15} 0·9218, n^{40} 1·4630, and is optically inactive. It has iodine number 88·7 (93·3) [the numbers in brackets are the values given by a capoc oil extracted from the seeds by petroleum], acid number 21·6 (3·4—4·6), saponification number 192·3 (196·3), Reichert-Meissl value 0·8, and Polenske value 0·14—0·34. The m. p. of the fatty acids (Hehner's method) is 34—35° and the solidifying point 28—30°, the values of the m. p. and of the solidifying point being 36° and 31—32° respectively after the acids have been freed from phytosterol. The very high m. p. of the fatty acids serves to identify capoc oil in the presence of other oils, as also do Halphen's reaction Milliau's modification of Becchi's reaction, and the nitric

acid test. The behaviour of the oil with Welman's, Serger's, and Kreis's reagents, and in the elaidic acid test is also described. Capoc oil is a drying oil, but does not become hard even after four months' exposure.

Capoc oil consists essentially of the triglycerides of palmitic, oleic, and linolic acids. The fatty acids are 26—28% palmitic acid and 72—74% liquid acids (40% linolic acid and 60% oleic acid); volatile acids are present only in small quantity. The oil contains 1·04% of unsaponifiable matter.

The crude phytosterol obtained from the oil contains 74% of reddish-brown, slightly dextrorotatory liquid constituents (iodine number 74·7), and 26% of a solid *phytosterol*, m. p. 136°, $[\alpha]_D$ $-29·97°$ in alcohol and ether (*acetate*, m. p. 126°, needles).
C. S.

Presence of Quinine in the Seed of Cinchona Ledgeriana (Moens). P. VAN LEERSUM (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 153—155).—In order to investigate the formation of quinine in *Cinchona* the author has examined the seeds of *C. Ledgeriana*. The finely powdered seed was first extracted with light petroleum, which removed a pale green oil, D^{18} 0·930, $[\alpha]_D^{20}$ $-26°$, which formed 18·6% of the material, and then digested with lime and sodium hydroxide and extracted with benzene. The total alkaloid so obtained (about 0·38% of the dry seed) was purified, and finally concentrated as the hydrochloride on a microscope slide, when quinine was detected by the herapathite reaction (compare A., 1905, ii, 620).
J. C. W.

The Availability of Glucosamine Hydrochloride as a Source of Nitrogen for the Nutrition of Maize (Zea Mays) and Beans (Phaseolus multiflorus). MARSTON LOVELL HAMLIN (*J. Amer. Chem. Soc.*, 1913, **35**, 1046—1049).—When, for the purpose of comparison, the above-named plants were grown in an ordinary culture solution, in a nitrogen-free solution and in a solution containing glucosamine hydrochloride as the sole source of nitrogen, it was invariably found that the glucosamine had a deleterious effect, and caused withering.

It is evident, therefore, that under the conditions of the experiment, glucosamine cannot be utilised as a source of nitrogen for nutrition.
D. F. T.

A New Species of Prostanthera and its Essential Oil. R. T. BAKER and HENRY G. SMITH (*J. Roy. Soc., New South Wales*, 1913, **46**, 103—110).—The stalks and leaves of the new shrub, for which the name *Prostanthera cineolifera* is proposed, yield 0·71% of a yellow oil, which rapidly darkens on exposure to light. The crude oil has D^{15} 0·9204, n^{22} 1·4711, and is soluble in 1·7 volumes of 70% alcohol. After removal of phenols and aldehydes, the cleared oil has D^{15} 0·9199; n^{22} 1·4706, α_D $+4·1°$. Saponification number of ester + free acid = 9·9 by boiling and 8·5 by cold saponification with two hours' contact; saponification number after acetylation 34·2 by

boiling, 18·3 by cold saponification. It is probable that the principal ester in the oil of this plant is geranyl acetate, constituting 2·9% of the crude oil. The isolation of geraniol was not, however, practicable owing to the small quantity of oil obtainable. The phenols present constitute 0·65% of the oil, and are composed of carvacrol and thymol. Cuminaldehyde is present to the extent of 0·142%.

The main constituents of the oil are cineole (61 per cent.) and cymene. A small quantity of a dextrorotatory terpene, probably pinene, is also present, whilst, by the action of alcoholic potassium hydroxide on the portion of the oil boiling above 224°, a substance is obtained which is possibly a sesquiterpene, but the amount of which is insufficient for identification. H. W.

Condition of Soil Phosphoric Acid Insoluble in Hydrochloric Acid. William H. Fry (*J. Ind. Eng. Chem.*, 1913, **5**, 664—665).—Whilst it is probable that soils may contain small quantities of phosphoric acid compounds which are not soluble in hydrochloric acid, mineralogical analyses have shown that a very large number of soils contain apatite (a soluble phosphate) enclosed in quartz grains. The quartz acts as a protective coating, and the phosphate is apparently insoluble in hydrochloric acid. W. P. S.

Organic Soil Constituents in their Relation to Soil Fertility. Oswald Schreiner (*Eighth Inter. Cong. App. Chem.*, 1912, **15**, 231—245).—In water-culture experiments with wheat, it was shown that creatinine, creatine, hypoxanthine, arginine, histidine, and nucleic acid are all assimilated, both when supplied as the only source of nitrogen and in presence of nitrate. When nitrates are present in addition to the organic compounds, there is a decrease in the amount of nitrate assimilated as compared with the amount when nitrate alone is supplied. The lowest decrease in nitrate absorbed was 17% with creatine, and the highest, 45%, with hypoxanthine. Further experiments on the effect of histidine, creatinine, and asparagine, used singly and together, showed increased growth with the single substances, in the order as given; and a further increase when all were present simultaneously, although the amount of nitrogen supplied was the same. N. H. J. M.

Organic Phosphorus in the Soil. John Stewart (*Eighth Inter. Cong. App. Chem.*, 1912, **15**, 273—300).—The Grandeau method for estimating organic phosphorus in soils gives somewhat low results, since some of the phosphorus dissolves in the acid, and some remains undissolved after treatment with alkali. The method is, however, one of the best hitherto proposed.

The iron and aluminium of humus are organically combined, except the small amount in colloidal form.

The decaying organic matter of soils interacts with the phosphates present with production of various organic compounds containing phosphoric acid and the different bases. Acid and basic mineral phosphates are probably found as intermediate products.

Barium chloride, magnesia mixture (both in alkaline solutions), phenylhydrazine in faintly acid solution, and ammonium hydroxide in presence of sufficient iron or aluminium, reprecipitate inorganic phosphorus quantitatively in presence of organic matter, in some cases at least. No precipitate is formed in absence of organic matter. N. H. J. M.

Biochemical Factors in Soils. MICHAEL X. SULLIVAN (*Eighth Inter. Cong. Appl. Chem.*, 1912, **15**, 305—312).—The oxidising power of soils, as indicated by aloin, is greater in productive than in less productive soils, and in surface soils as compared with subsoils. The catalytic power of soils shows similar differences.

It is evident from the presence of such compounds as histidine, arginine, and cytosine, that soils contain enzymes, either intra- or extra-cellular No soil extract has hitherto been found to contain diastatic, inverting, lipolytic, proteolytic, oxidising, or catalysing enzymes; and it has been found that when diastase is added to soil it is either fixed or destroyed in a few days.

The oxidising and catalysing powers of soils are probably due to the inorganic and organic substances rather than to enzymes. Both properties are retained for years by air-dried soils. Many substances present in soils result from the metabolism of micro-organisms. In mould cultures, fatty acids, especially oleic and palmitic acids, purine bases, such as guanine, adenine, and hypoxanthine, histidine, and probably thymine, are present.

N. H. J. M.

Increasing the Manurial Action of Cyanamide under the Influence of Ferric Oxide. ALBERT STUTZER (*Eighth Inter. Cong. App. Chem.*, 1912, **15**, 301—304).—The results of pot experiments with oats grown in sandy loam showed that the manurial value of cyanamide is increased by addition of molasses, owing to the increased production of carbon dioxide in the soil.

In further experiments, it was found that addition of ferric oxide, in the form of bog ore, greatly increased the yield of oats. It was found that ferric oxide accelerates the production of carbamide from cyanamide, and there may be a stimulating action in addition.

As a rule, 50 kilos. of bog ore per hectare will suffice.

N. H. J. M.

Boron as Catalytic Manure. HENRI AGULHON (*Eighth Inter. Cong. App. Chem.*, 1912, **15**, 9).—In pot experiments with peas, haricots, beet, and radish, the yields were increased by boric acid up to 34%. In field experiments with oats, the yield was increased by 54% when 1·5 kilo. of boric acid per hectare was applied. Applications of 20—50 kilos. were found to be too much for wheat, oats, maize, lucerne, peas, colza, and lupines; the yields, weighed fresh, were frequently increased without any gain in dry matter.

N. H. J. M.

Organic Chemistry.

Preparation of Hydrocarbons with Two Conjugated Double Linkings. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 261642).—When $\alpha\gamma$-glycols of the general formula

$$RRC(OH)\cdot CHR\cdot CR(OH)\cdot CHRR$$

(where R is an alkyl group or hydrogen) are heated with agents that withdraw water, they furnish compounds of the general formula

$$RRC:CR\cdot CR:CRR.$$

Butane-$\alpha\gamma$-diol when heated with 30% sulphuric acid at 170—180° yields a 10% yield of erythrene; with phosphoric acid at 300° the yield is 60%, and with magnesium sulphate at 300—400° about 50%, whilst β-methylbutane-$\beta\delta$-diol with potassium hydrogen sulphate at 160—170° gives rise to a 20% yield of isoprene.

$\alpha\alpha$-Dimethylerythrene, b. p. 74°, is obtained in 40% yield from β-methylpentane-$\beta\delta$-diol at 160° with aluminium chloride.

F. M. G. M.

Di*iso*butenyl from Tribromo*iso*butane. VL. KRESTINSKI and K. KRIVOROTKO (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 946—949).—The action of magnesium on $\alpha\beta\gamma$-tribromo*iso*butane, $CH_2Br\cdot CMeBr\cdot CH_2Br$ (compare Pogorshelski, A., 1905, i, 315), in presence of ether and treatment of the product obtained with water, yields, as principal product, $\beta\epsilon$-dimethyl-$\Delta^{\alpha\epsilon}$-hexadiene, $CH_2:CMe\cdot CH_2\cdot CH_2\cdot CMe:CH_2$, D^{20} 0·7512, n_D^{20} 1·4309 (compare Pogorshelski, A., 1899, i, 785). Treatment of the latter with hydrogen bromide yields the $\beta\epsilon$-dibromo-$\beta\epsilon$-dimethylhexane, $CMe_2Br\cdot CH_2\cdot CH_2\cdot CMe_2Br$, m. p. 68°. T. H. P.

Preparation of Halogen Derivatives of the Paraffin Series. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 261677, 263716).—A satisfactory yield of chlorinated or brominated hydrocarbons is obtained by mixing the parent hydrocarbons in a gaseous condition with the vapour of the required halogen. Mixtures of chloro- and dichloro-, and of bromo- and dibromo-hexane were thus obtained; chloro*iso*pentane furnished $\alpha\beta$-dichloro-β-methylbutane, whilst chloropentane gave rise to a *dichloropentane*, b. p. 130—150°. In the second patent it is shown that the halogenation can be effected by means of the silent electric discharge; thus *n*-pentane furnishes a mixture of α- and γ-chloropentane. F. M. G. M.

Addition of Bromine to Chlorinated Olefines. WALTHER HERZ and W. RATHMANN (*Ber.*, 1913, **46**, 2588—2590. Compare this vol., ii, 26, 765).—The reactions between bromine and di-, tri-, and tetrachloroethylene have been studied. Known quantities of the two substances, with or without diluents, were sealed up in test-tubes of dark brown glass, and kept at 25° for different intervals, when the tubes were broken under potassium iodide and the unabsorbed bromine

titrated. By employing a large excess of hydrocarbon the reaction could be expressed in the form, $1/t \log a/(a-x)$, where a is the initial concentration of bromine and x the amount absorbed after the time t.

cis-Dichloroethylene was found to absorb bromine nearly twice as fast as the *trans*-modification. No constant values could be obtained in the case of trichloroethylene, but *aaβ-trichloro-aβ-dibromoethane* was isolated as a pale yellow, pungent smelling liquid, b. p. 126°/85 mm. The influence of diluents was studied in the case of tetrachloroethylene.

J. C. W.

The Action of Sodium Ethoxide on Tetranitromethane. A Caution. ALEXANDER K. MACBETH (*Ber.*, 1913, **46**, 2537—2538; *Chem. World*, 1913, 2, 328).—The addition of sodium ethoxide to tetranitromethane may give rise to serious explosions.

In an experiment in which 30 grams of tetranitromethane were being treated with an alcoholic solution of solium ethoxide, the formation and separation of the sodium derivative of trinitromethane appeared to be proceeding in a normal manner when a violent explosion occurred doing serious damage to the experimenter and to the laboratory.

D. F. T.

Mechanism of the Reactions between Alcohols and Mineral Acids. Oxonium Compounds of Hydrogen Haloids. ALEXEI E. FAVORSKI (*J. pr. Chem.*, 1913, [ii] **88**, 480—495. Compare McIntosh, T., 1904, **85**, 919; 1905, **87**, 784; A., 1905, i, 254, 677; 1906, i, 481, and Mokievski, A., 1899, i, 729).—Di*iso*propylcarbinol, ethyl*tert.*-butylcarbinol, and *iso*propyl*tert.*-butylcarbinol (this vol., i, 12) readily form with hydrogen haloids, crystalline oxonium salts of the following types:

$$\text{(I.)}\ {}^{R}_{H}\!\!>\!O\!<\!{}^{H}_{X} \qquad \text{(II.)}\ {}^{R}_{H}\!\!>\!O\overset{H\quad H}{\diagup\!\!\!-\!\!\!-\!\!\!-\!\!\!\diagdown}O\!<\!{}^{R}_{X}$$

The compounds of the second type are the more stable, and are obtained by the action of the hydrogen haloid on the alcohols at 0° or the ordinary temperature; at lower temperatures compounds of the first type are produced. The oxonium compounds derived from glycols (Mokievski, *loc. cit.*) and diethylene ether are formulated as follows:

$$\begin{array}{l} CH_2\cdot O\!<\!{}^{H}_{H} \\ \vert \qquad \vert \\ CH_2\cdot O\!<\!{}^{H}_{X} \end{array} \quad \text{and} \quad \begin{array}{l} CH_2\cdot OH\cdot CH_2 \\ \vert \qquad \vert \qquad \vert \\ CH_2\cdot OX\cdot CH_2 \end{array}.$$

The author considers that the intermediate formation of oxonium compounds of this kind must be taken into account in explaining the mechanism of all reactions in which alcohol and mineral acids simultaneously take part, and illustrates his views by reference to the formation of ethers and hydrocarbons by the action of acids on alcohols, and the transformation of glycols into ketones and aldehydes under the influence of acids.

[With ANNA I. UMNOVA.]—The *compounds* of di*iso*propylcarbinol with hydrogen iodide and hydrogen bromide, $2C_7H_{15}\cdot OH,HX$,

separate in colourless crystals, m. p. 77—78° and 68—69° respectively, by passing the hydrogen haloids into the carbinol at the ordinary temperature; the corresponding *hydrochloride* is very hydroscopic.

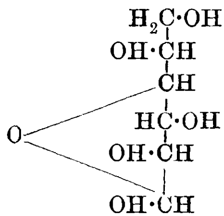
[With P. Aschmarin.]—The following *compounds* of ethyl *tert.*-butylcarbinol are described: $2C_7H_{15}·OH,HI$, m. p. 74—76°; $2C_7H_{15}·OH,HBr$, m. p. 52—54°; $C_7H_{15}·OH,HBr$, m. p. 13—17°; $C_7H_{15}·OH,HCl$, m. p. 23—25°; $2C_7H_{15}·OH,HCl$.

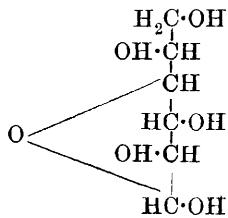
[With Ernst Fritzmann.]—The compounds of *iso*propyl*tert.*-butylcarbinol with hydrogen iodide, $2C_8H_{17}·OH,HI$, and hydrogen bromide, $2C_8H_{17}OH,HBr$, have m. p. 78—80° and 77—78° respectively.

F. B.

The Spacial Arrangement of the Hydroxyl Groups of Polyhydroxy-compounds. The Configuration of the Saturated Glycols and of α- and β-Dextrose. Jacob Böeseken (*Ber.*, 1913, **46**, 2612—2627).—The influence of hydroxy-compounds on the conductivity of boric acid solutions is set forth in a series of experiments, most of which have already been described (this vol., ii, 147; i, 742). The main conclusion arrived at by the author, that exaltation of the conductivity is caused by those compounds in which two hydroxyl groups attached to neighbouring carbon atoms are also in the same plane, thus permitting the formation of ring combinations with the boric acid, is further exemplified and extended to the determination of the configuration of saturated glycols and of α- and β-dextrose. Saturated glycols have no positive influence, and therefore the hydroxyl groups are arranged on opposite sides of the neighbouring carbon atoms. Alcohols with more than two hydroxyl groups are likely to have some pair or other in the favourable position, and glycerol, erythritol, β-nitro-αγδ-trihydroxy*iso*butane, pentaerythritol, mannitol, dulcitol, and sorbitol have positive influences in increasing degrees.

α- and β-Methylglucosides, sucrose, and raffinose have no pair of hydroxyl groups in the favourable position, and have only a minimal, negative influence on boric acid. α-Dextrose has a greater influence than β-dextrose, and the sugars are therefore represented by the formulæ I. and II. respectively, α-dextrose possessing one pair of neighbouring hydroxyl groups on the same side of the plane of the ring.

(I.) 

(II.) 

The gradual fall in the conductivity of α-dextrose–boric acid and the rise in conductivity of β-dextrose–boric acid coincide with the mutarotation, and the constants for the mutarotation and the alteration in

conductivity are equal. If the mutarotation were accompanied by the opening of the ring, a chain of five labile hydroxyl groups would be formed, and the conductivity of the boric acid solution would be increased. The fact that this does not happen supports E. F. Armstrong's view that mutarotation takes place without disturbing the γ-oxide ring (T., 1903, **83**, 1305). J. C. W.

Conversion of Cellulose into Dextrose. HERMANN OST (*Ber.*, 1913, **46**, 2995—2998).—In reply to the interpretation placed by Willstätter and Zechmeister (this vol., i, 955) on the optical activity of the dextrose obtained by Ost and Wilkening (A., 1910, i, 364) from the hydrolysis of starch by sulphuric acid, the author maintains that the other experiments of the latter investigators supply final evidence that the yield of dextrose was in reality over 90% of the starch used, and attributes the low optical activity to the well known considerable effect of the presence of traces of impurity. D. F. T.

Electrical Conductivity of Some Platinum Compounds of Organic Disulphides. LEO A. TSCHUGAEV and A. KOBLJANSKI (*Zeitsch. anorg. Chem.*, 1913, **83**, 8—26).—In order to avoid the complications introduced by water, the author has examined the conductivity of a large number of complex compounds in methyl alcohol. It is found that compounds of the type $[PtS''Cl_2]$, where S″ is a dithioether, are non-conducting, but that further addition of disulphide causes a rapid increase of conductivity. An equilibrium occurs: $[PtS''Cl_2] + S'' \rightleftharpoons [Pt2S'']Cl_2$, the latter compound then becoming ionised.

The compounds of ethylene-dithioglycol ethers have been compared with those from propylene-dithioglycol ethers. The platinum chloride compound of the *diethyl ether*, $[PtCl_2,C_3H_6(SEt)_2]$, crystallises in needles, m. p. 135°, and the *di-n-propyl ether* compound has m. p. 133°. It has not been found possible to prepare sufficiently pure compounds from αα- and αε-dithioglycol ethers, but the conductivity of mixed solutions of these sulphides with stable αβ-compounds has been determined. The αα-dithio-ethers have the least tendency to form complexes.

The conclusions are in accordance with Werner's co-ordination theory. C. H. D.

Compounds of Platinous Nitrite with Organic Dithio-ethers. LEO A. TSCHUGAEV and WITALIUS G. CHLOPIN (*Zeitsch. anorg. Chem.*, 1913, **82**, 401—419. Compare A., 1910, i, 354; 1912, i, 70).—Like the halogen compounds, platinous nitrite readily forms isomeric compounds with dithio-ethers. The bimolecular compound is the first product, and is more stable than in the case of the halogen compounds, so that the conversion into the unimolecular form takes place much less readily. The latter modifications are most readily obtained from the chlorides and soluble nitrites.

Diethyl ethylene dithioether and platinous nitrite form a *compound*, $[Pt2C_2H_4(SEt)_2]Pt(NO_2)_4$, m. p. 170—170·5°. It reacts with Reiset's chloride to form the yellow compound $[Pt4NH_3]Pt(NO_2)_4$. The former

compound is also obtained from the bimolecular chloride and sodium nitrite. The unimolecular *compound*, $C_2H_4(SEt)_2,Pt(NO_2)_2$, has m. p. 161—161·5°, and does not react with Reiset's chloride. Excess of the ether, together with potassium platinonitrite, convert it into the bimolecular modification.

Dimethyl ethylene dithioether and platinous nitrite yield the bimolecular *compound*, $[Pt2C_2H_4(SMe)_2]Pt(NO_2)_4$, m. p. 214·5—215°, which is slowly converted, even in the cold, into the unimolecular compound, m. p. 210·5—211°, by an excess of the ether.

The dipropyl dithioether also yields two *compounds*, m. p. 184·5—185° and 179—179·5° respectively, and the *compounds* from the di-*n*-butyl dithioether have m. p. 181—181·5° and 172—172·5° respectively.

Diethyl propylene dithioether yields a *compound* with m.p. 229—229·5°, the constitution of which is uncertain.

Diethyl β-hydroxypropylene $\alpha\gamma$-dithioether yields a sparingly soluble *compound*, m. p. 182—182·5° (decomp.), and probably bimolecular.

Dimethyl sulphide yields only a unimolecular compound with platinous nitrite, all attempts to prepare a bimolecular modification having failed. C. H. D.

Complex Compounds of Organic Sulphides with Quadrivalent Platinum. LEO A. TSCHUGAEV and J. BENEVOLENSKI (*Zeitsch. anorg. Chem.*, 1913, **82**, 420—425).—Isomerism has not hitherto been observed in compounds of quadrivalent platinum with organic sulphides. It is now found that compounds with two complex ions are obtained from hydrogen platinichloride and sulphides, but that their composition does not correspond with the expected formulæ

Methyl sulphide and platinic chloride yield a precipitate with the empirical composition $Pt,2Me_2SCl_3$, which at 110—115° suddenly changes from red to yellow, yielding a mixture of two substances, which may be separated by means of chloroform. The less soluble compound, $PtCl_4,2Me_2S$, darkens from 150°, whilst the other,

$$PtCl_2,2Me_2S,$$

has m. p. 157°. The original compound is thus $[Pt,4Me_2S]PtCl_6$. A similar compound is obtained from diethyl ethylene dithioether.

C. H. D.

Formic Acid as a Solvent. OSSIAN ASCHAN (*Chem. Zeit.*, 1913, **37**, 1117—1118).—The solubilities of a number of inorganic salts and organic compounds in 95% formic acid are given. A wide range of metallic salts is found to dissolve in this acid, but not so freely as in water. Easily reduced salts are liable to decomposition, but, whereas iodine is liberated from sodium iodide in the cold, potassium iodide is stable. The acid decomposes pinene nitrosochloride and the salts of weak organic acids, and esterifies certain alcohols, such as borneol. With these exceptions, it is a useful solvent for many organic compounds, including in addition to bromo-carboxylic acids, for which it has already received frequent application, polycyclic hydrocarbons, terephthalic acid, uric acid, indigotin, and alizarin.

The acid is easily volatilised on the water-bath, and deposits large

crystals of many substances, as, for example, suberic acid, citric acid, α-bromocamphor, α-nitronaphthalene, and *m*-dinitrobenzene. It is now cheaper than glacial acetic acid, and usually exhibits a greater difference of solvent power between the hot and cold liquid, and, in spite of its blistering effect, it is deserving of more extensive application. J. C. W.

Displacement of Acetic Acid from Solutions of its Salts by Carbon Dioxide Under High Pressure. VLADIMIR N. IPATIEV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 992—994. Compare Ipatiev and Verchovski, A., 1909, ii, 564; 1911, ii, 716).—The author has investigated the action of carbon dioxide under a pressure of 50 atmospheres on aqueous solutions of various acetates, both at the ordinary temperature and at 90°. With 12% calcium acetate solution, crystalline calcium carbonate was precipitated in some cases, but not in others; in one instance, 1 gram of the carbonate was obtained from 50 c.c. of the acetate solution after seven days at 90°. In a similar manner barium acetate yields the carbonate, and copper acetate the basic carbonate, $CuCO_3,Cu(OH)_2,H_2O$, but no precipitate was obtained from nickel acetate, even after several months. T. H. P.

The Action of Acetic Anhydride on Ferric and Chromic Nitrates. RUDOLF F. WEINLAND and HANS REIHLEN (*Zeitsch. anorg. Chem.*, 1913, **82**, 426—430).—The compounds described by Späth (A., 1912, i, 408) as normal ferric and chromic acetates are really acetates of the triferri-(chromi)hexa-acetato-base, and the method of preparation has no advantage over those usually adopted. Both compounds yield the characteristic platinichlorides. C. H. D.

Production of Hydrocarbons from a Solution of Sodium Stearate by Electrolysis. H. T. F. RHODES (*Chem. News*, 1913, **108**, 201).—The production of hydrocarbons by the electrolysis of aqueous solutions of the salts of aliphatic acids increases in difficulty with increasing molecular weight of the acid, probably owing to the partial hydrolysis which occurs when the salts are dissolved in water. By employing a small current, however, the author has succeeded in electrolysing an aqueous solution of sodium stearate which had been acidified with acetic acid, and has obtained a hydrocarbon very similar in physical properties to paraffin wax. The substance could only be detected after the solutions had been preserved for some time, and could not be identified owing to the small yield. H. W.

Oxidising Action of Potassium Permanganate in an Alkaline Medium on Normal, Saturated Fatty Acids. EVGENJI S. PRSHEVALSKI (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 891—905; *J. pr. Chem.*, 1913, [ii], **88**, 495—501. Compare A., 1911, i, 947).—The action of faintly alkaline potassiumpermanganate solution on various acids of the aliphatic series has been investigated.

With 1% permanganate solution, *n*-heptoic acid gives (1) valeric, butyric, and propionic acids; (2) a ketonic acid, probably

$$CH_3\cdot[CH_2]_4\cdot CO\cdot CO_2H,$$

m. p. 51—52°; (3) a dibasic dihydroxy-acid, $C_5H_8(OH)_2(CO_2H)_2$, and (4) adipic, glutaric, succinic, and oxalic acids. Under similar conditions, *n*-hexoic acid yields glutaric acid, in addition to the acids already mentioned (*loc. cit.*). *n*-Valeric acid gives butyric, propionic, oxalic, and succinic acids. At either 37—38° or 100°, *n*-butyric acid yields oxalic and propionic acids, whilst if 5% permanganate is used, β-hydroxybutyric and *iso*malic acids are also formed. Propionic acid gives carbon dioxide and oxalic acid, and if the oxidation is carried out in a solution containing 5% of alkaline hydroxide, hydroxypropionic acid.

The results obtained show that the difficulty of oxidising normal fatty acids increases with the shortness of the carbon-atom chain (compare Margulies, A., 1894, i, 491), and that the products obtained vary with the conditions of oxidation. In every case oxidation takes place at two points of the carbon-atom chain: (1) at the carbon atom adjacent to the carboxyl group, the next lower fatty acid being formed, and (2) at the carbon atom next to the methyl group.

Since the dibasic acids obtained never contained the same numbers of carbon atoms as the original acids, but always one less, the methyl group must undergo oxidation to carboxyl and then to carbon dioxide.

That oxidation of two carbon atoms simultaneously in one molecule of an acid may take place is shown by the formation of a dihydroxy-dicarboxylic acid from *n*-heptoic acid. As intermediate products of these oxidations, hydroxy- and keto-acids are formed.

In view of the ready oxidisability of the methyl group, which is adjacent to a partly oxidised carbon atom, the possibility of the formation of acetic acid in these oxidations seems doubtful.

With *n*-butyric acid, oxidation is accompanied by isomerisation of the normal propyl group to the iso-group. T. H. P.

Lignoceric Acid. HANS MEYER, LEO BROD, and WALTHER SOYKA (*Monatsh.*, 1913, **34**, 1113—1142).—Lignoceric acid is shown to occur in the "solid paraffin" fraction of tar distilled from Bohemian lignite. With a view to ascertaining whether lignoceric acid, $C_{24}H_{48}O_2$, has the normal structure it has been degraded to $C_{22}H_{44}O_2$ (A., 1904, i, 548; 1905, i, 405, 736), and attempts have also been made to synthesise it from normal behenic acid, $C_{22}H_{44}O_2$. The degradation product is not identical with behenic acid, and the synthetic product is not lignoceric acid, so that the latter cannot be the normal 24 carbon saturated fatty acid.

Lignoceric acid, $C_{24}H_{48}O_2$, m. p. 80—80·5°, prepared from groundnut oil, on treatment with bromine in presence of amorphous phosphorus yields *α-bromolignoceric acid*, m. p. 68·5°, which crystallises in colourless rhombohedra and on treatment with sodium ethoxide in dry alcohol furnishes with some difficulty *α-ethoxylignoceric acid*, m. p. 61—62°, crystallising in slender, colourless needles. *Methyl α-bromolignocerate*, m. p. 46—47°, forms small, colourless crystals. The bromo-acid when boiled with potassium iodide in alcohol yields *α-iodolignoceric acid*, m. p. 74°, which forms small, colourless prisms from a mixture of light petroleum and acetic acid, and when treated with potassium

hydroxide furnishes a mixture of *a-hydroxylignoceric acid* (m. p. 92°, small crystals) with the *unsaturated acid*, $C_{24}H_{46}O_2$, m. p. 59°, which forms a crystalline mass. The latter acid on oxidation with permanganate yields oxalic acid and *isobehenic acid*, $C_{22}H_{44}O_2$, m. p. 75°. The latter crystallises in glancing pearly leaflets, and furnishes a *methyl* ester, m. p. 54°, as colourless leaflets, and a crystalline *lithium* salt, m. p. 210° (decomp.). Melting-point curves for mixtures (1) of behenic and *iso*behenic acids, and (2) of the methyl esters of the two acids are given.

Behenic acid, m. p. 82—84°, was prepared by the catalytic reduction of erucic acid, and converted successively into the chloride (leaflets, m. p. 73—75°); methyl ester, m. p. 55°; amide, m. p. 111°, and the latter reduced to docosyl alcohol by means of sodium in amyl alcohol and this was converted into docosyl iodide, m. p. 46°. The latter was condensed with ethyl malonate to *docosylmalonic acid*, and this heated until carbon dioxide was no longer evolved when it yielded a *tetracosanic acid*, $C_{24}H_{48}O_2$, m. p. 85·5—86°, crystallising in pearly leaflets, and furnishing a *methyl* ester (m. p. 59·5—60°, glancing scales), a crystalline *lithium* salt, and an *a-bromo*-derivative, m. p. 73·5°, the *methyl* ester of which has m. p. 57°, and crystallises in glancing leaflets. Melting-point curves and tables for mixtures (1) of synthetic tetracosanic acid and lignoceric acid, and (2) of the methyl esters of these two acids are given.

In the synthesis of the tetracosanic acid the principal product is a *ketone*, $C_{47}H_{94}O$, which was not further characterised.

The synthetic method described was also used in preparing arachidic acid, m. p. 77°, from octadecyl iodide (compare Baczewski, A., 1897, i, 11). Melting-point curves for mixtures of lignoceric acid with (*a*) arachidic acid, (*b*) stearic acid, and (*c*) palmitic acid are given.

T. A. H.

Montanic Acid. HANS MEYER and LEO BROD (*Monatsh.*, 1913, **34**, 1143—1157. Compare Easterfield and Taylor, T., 1911, **99**, 2302).—Montanic acid has been exhaustively examined and purified by methods described in detail in the original, and shown to have the formula, $C_{28}H_{56}O_2$, first suggested by Ryan and Dillon (A., 1909, i, 629). A number of its derivatives are described.

Montanic acid melts at 85° and crystallises from acetic acid in small, pearly leaflets. The *chloride*, m. p. 67·5—68·5°, forms masses of leafy crystals and is readily soluble in benzene or petroleum. The *amide*, m. p. 112°, separates from alcohol as a crystalline powder. *a-Bromomontanic acid*, m. p. 77°, forms colourless scales from a mixture of acetic acid and light petroleum; with sodium ethoxide in alcohol, it yields *a-ethoxymontanic acid*, m. p. 71—72°, crystallising from acetic acid in colourless scales, and with ethyl alcohol in presence of mineral acids, *ethyl bromomontanate*, m. p. 62—63°, which forms colourless leaflets from alcohol. Attempts to eliminate hydrogen bromide and form the corresponding unsaturated acid were successful. T. A. H.

Ground-nut (Earth-nut) Oil. HANS MEYER and ROBERT BEER (*Monatsh*, 1913, **34**, 1195—1208).—The numerous researches already

conducted on the composition of ground-nut oil render it probable that it contains glycerides of arachidic, lignoceric, oleic and linoleic acids, and leave doubtful the presence of glycerides of palmitic, stearic, and hypogaeic acids. The authors confirm the occurrence in the oil of glycerides of the four first-named acids and also of palmitic acid, but they were unable to find any evidence of stearic or hypogaeic acid in the fatty acids prepared from the oil (compare Franz, *Diss.*, München, 1910). The supposed stearic acid obtained by Hehner and Mitchell's method (A., 1897, ii, 289) lowers the melting point of stearic acid and in reality consists of a mixture of arachidic and lignoceric acids. No trace of dihydroxypalmitic acid could be found in the oxidation products from the unsaturated fatty acids of ground-nut oil so that hypogaeic acid cannot be a constituent of these acids. Tables and curves of the melting points of mixtures of arachidic acid with (*a*) stearic acid and (*b*) palmitic acid are given in the original.

T. A. H.

Candelilla Wax. HANS MEYER and WALTHER SOYKA (*Monatsh.*, 1913, **34**, 1159—1172. Compare Olsson-Seffer, *Bull. Imp. Inst.*, 1909, **7**, 411; Hare and Bjerregard, *J. Ind. Eng. Chem.*, 1910, **2**, 203; Doiler, *ibid.*, p. 454; Sanders, P., 1911, **27**, 250, and *Anal. Inst. Nac. Med. Mex.*, 1905, **7**, 498, and Niederstadt, *Chem. Zeit*, 1911, **35**, 1190).—Candelilla wax on extraction with hot alcohol yields 18 to 20% of soluble soft resin, which gives the Liebermann-Storch reaction. The portion of the resin-free wax soluble in hot alcohol, but insoluble in the cold, consists principally of dotriacontane, not hentriacontane as Sanders (*loc. cit.*) supposed, which was isolated by extraction with ether and amounted to 74 to 76% of the crude wax. The remaining constituent not removed by ether is a lactone, $C_{30}H_{58}O_3$, m. p. 88°, which forms a colourless, crystalline mass, is neutral in reaction, but yields a *potassium* salt when boiled with potassium hydroxide in alcohol, and is partly esterified when treated with methyl alcohol and sulphuric acid. This substance appears to be that which Sanders mistook for myricyl alcohol (*loc. cit.*), and which Fraps and Ruther (*J. Ind. Eng. Chem.*, 1910, **2**, 454) described as a hydrocarbon. It is perhaps identical with Darmstädter and Lifschütz's lanoceric acid lactone (A., 1896, i, 522).

The authors doubt whether the hydrocarbon frequently found in plants and described as hentriacontane really consists of the latter.

T. A. H.

Water of Crystallisation of the Calcium Salt of Lauronolic Acid. CHARLES E. BURKE (*J. Amer. Chem. Soc.*, 1913, **35**, 1647—1648).—Although the rapid evaporation of a solution of calcium lauronolate on a water-bath gives surface crystals containing approximately $3H_2O$ (Noyes and Burke, A., 1912, i, 159), yet under the conditions of Bredt's method with slower evaporation (A., 1911, i, 417) the crystals, which separate in this case under the liquid, contain exactly $2H_2O$, as stated by Bredt. D. F. T.

Preparation of Di-iodotariric Acid. F. HOFFMANN-LA ROCHE & Co. (D.R.-P. 261211. Compare A., 1892, 470).—*Di-iodo-*

tariric acid, colourless needles, m. p. 48·5°, containing 47·5% of iodine and of therapeutic value, is obtained when a boiling aqueous solution of tariric acid containing sodium hydroxide is slowly treated with 9 parts of a mixture of iodine (100 parts), potassium iodide (160 parts), and water (740 parts); the product is separated by the addition of dilute sulphuric acid. F. M. G. M.

The Ability of Alcoholic Hydroxyl Groups to Form Complexes. II. GENNARO CALCAGNI (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 157—162. Compare A., 1910, i, 811; Weinland and Herz, A., 1912, i, 854).—The *basic glycollate* of a *hexaglycollatotriferri*-base, $[Fe_3(OH)_2(CO_2{\cdot}CH_2{\cdot}OH)_6]{\cdot}CO_2{\cdot}CH_2{\cdot}OH(FeOH)_3$, prepared by fractional precipitation of an alcoholic solution with ether, is an orange-yellow, amorphous substance which is hygroscopic and readily hydrolyses. The *basic nitrate*, $[Fe_3(OH)_2(CO_2{\cdot}CH_2{\cdot}OH)_6]NO_3{\cdot}Fe(OH)_3$, is similar in properties. The *basic lactate* of a *hexalactatotriferri*-base,

$$[Fe_3(OH)_2(CO_2{\cdot}CHMe{\cdot}OH)_6]CO_2{\cdot}CHMe{\cdot}OH{\cdot}Fe(OH)_3,4H_2O,$$

is an orange-yellow, hygroscopic substance which is readily hydrolysed.

When solutions of chrome alum and sodium benzoate are mixed, *chromous benzoate*, $Cr(CO_2Ph)_2,H_2O$, is precipitated. *Ferrous salicylate*, $Fe(CO_2{\cdot}C_6H_4{\cdot}OH)_2$, is a reddish-violet, amorphous substance. *Chromous salicylate* was also prepared. R. V. S.

Complex Oxalic Derivatives of Iridium. ALEXIS DUFFOUR (*Ann. Chim. Phys.*, 1913, [viii], **30**, 169—240).—A detailed, connected account of work already published (Abstr., 1909, i, 762—763; 1910, i, 541; 1911, i, 519; 1912, ii, 849). Apart from slight modifications of some of the views expressed already, the following new results are now recorded. *Thallous iridotetrachloro-oxalate*, $Tl_2IrCl_4C_2O_4$, forms maroon-coloured, microscopic, hexagonal lamellæ, which are pleochroic and faintly birefringent. *Argentous iridotetrachloro-oxalate* resembles the thallous salt, but only assumes a crystalline texture after prolonged contact with water. T. A. H.

Electrolytic Reduction of Aldehydes. WILHELM SCHEPSS (*Ber.*, 1913, **46**, 2564—2574).—An extension of the earlier investigation (Tafel and Schepss, A., 1911, i, 784) in which it was demonstrated that by electrolytic reduction the aldehyde group in anisaldehyde can be directly converted into the methyl group. The reduction of the aldehydes was effected in a mixture of alcohol and sulphuric acid.

Propaldehyde undergoes reduction to propane less readily than does acetone, and it was found that cathodes of lead or cadmium are much more effective than a mercury cathode. No formation of any organic lead or mercury compounds analogous to those observed in the reduction of acetone could be detected.

Reduction of heptaldehyde yielded *n*-heptane, and again the action proceeds less easily than with methyl *iso*amyl ketone (Tafel, A., 1909, i, 766). Benzaldehyde (compare Kauffmann, A., 1899, i, 152; Law, T., 1907, **91**, 755) at a cadmium cathode gave as hydrocarbon product a small quantity of toluene; no benzene could be detected (compare

Law, *loc. cit.*). *p*-Hydroxybenzaldehyde could be reduced to *p*-cresol; salicylaldehyde and *m*-hydroxybenzaldehyde appeared to undergo reduction only as far as the corresponding alcohols, and in attempts to reduce the former more energetically much resinification occurred.

Protocatechualdehyde gave 3:4-dihydroxytoluene, whilst vanillin gave the corresponding ether, 4-hydroxy-3-methoxytoluene. The experiments in the latter case were conducted with cadmium electrodes and the result is somewhat at variance with that of Law (*loc. cit.*). Piperonal underwent reduction to hydropiperoin and *methylenedioxytoluene*, an aromatic oil, b. p. 81—83°/11 mm., 197—198° (corr.)/741·5 mm., D_{16}^{16} 1·1353, n_D^{16} 1·53165.

When reduced in solution in the usual mixture of alcohol and sulphuric acid, *p*-dimethylaminobenzaldehyde was converted into the corresponding alcohol, which immediately condensed with the alcohol of the solvent; the product was therefore p-*dimethylaminobenzyl ethyl ether*, $NMe_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}OEt$, a liquid of characteristic amine odour, b. p. 269—271°/747 mm.; *methiodide*, m. p. 141·5—143°. Reduction of the aldehyde in alcohol-free diluted sulphuric acid gave as chief product *p*-dimethylaminobenzyl alcohol, as a viscous oil, b. p. 175—178°/28 mm. (compare Rousset, A., 1895, i, 176).

In the above examples it was generally found that the process of reduction became more speedy and complete with increased temperature and current density. The extent to which reduction was effected varied considerably, however, in different cases.

A repetition of the reduction of citral (Law, T., 1912, **101**, 1025, 1544) at a lead cathode certainly yielded a red product at the cathode, but it was of a resinous nature and not an organic lead compound. D. F. T.

Formation of Methylglyoxal. CARL NEUBERG and W. OERTEL (*Biochem. Zeitsch.*, 1913, **55**, 495—503).—The importance of methylglyoxal as an intermediary product of sugar degradation has been often discussed, and the substance has been obtained directly from dextrose by various methods (distillation in presence of weak alkalis, zinc carbonate, etc.). It is now shown that it can be obtained from sugars in larger quantities if solutions of these substances are heated with sodium carbonate or disodium hydrogen phosphate in the presence of phenylhydrazine. Particularly good yields were obtained in this way from lævulose, and moderate yields from dextrose. Mannose also yielded a small quantity. The methylglyoxal was in each case identified in the form of an osazone. S. B. S.

Plant Colloids. III. Processes of Solution and Removal of the Ash of Starch. MAXIMILIAN SAMEC and F. VON HOEFFT (*Koll. Chem. Beihefte*, 1913, **5**, 141—210. Compare A., 1912, ii, 144).—The influence of the removal of the ash from starch on the physicochemical properties of starch solutions has been studied, and the properties of solutions of such starch are compared with those of ordinary starch solutions prepared under identical conditions. It is shown that the three processes, removal of the ash, solution and ageing

occasion the same changes in the properties of starch solutions, namely, decrease of the viscosity, and decrease of the influence of acids and bases on the viscosity. These changes take place more rapidly the higher the temperature. At constant temperature in solutions of different concentrations the viscosity decreases in the same proportion in the same time. Simultaneously with the decrease of viscosity an increase in the electrical conductivity is brought about, and the electric transport and amount precipitated by alcohol decrease. The osmotic pressure is slightly decreased, whilst the optical rotation slightly increases and the quantity of titratable acid increases. Starch granules give practically no free electrolyte to water at ordinary temperatures, but at the swelling temperature this occurs fairly rapidly, and at the same time the power of the granules for taking up water increases in a series of sudden steps. The observations lead to the assumption that the ash of starch is present as an amylphosphoric acid, and this assumption brings observations of other observers into agreement. J. F. S.

Chemistry of Starch. Schardinger's Crystalline Dextrins. II. HANS PRINGSHEIM and FRANZ EISSLER (*Ber.*, 1913, **46**, 2959—2974. Compare A., 1912, i, 832).—Further observations on dextrin-β (hexa-amylose), dextrin-α (tetra-amylose), and their scission products are recorded and the properties of the crystalline "slime" prepared by Schardinger are described. Provisional formulæ for diamylose and *iso*-diamylose are advanced and discussed.

Schardinger's "slime" $[(C_6H_{10}O_5)_2]_x,C_2H_5\cdot OH$, was prepared by dissolving crude dextrin (precipitated by means of chloroform from the liquid produced by the action of *Bacillus macerans* on starch paste) in hot water, heating to remove chloroform and then diluting with water, when the slime was precipitated. It was isolated by means of a centrifuge, and crystallised from water containing 1·5% alcohol, when it formed hexagonal tablets. It has $[\alpha]_D^{20}$ +139·2°. On acetylation in presence of zinc chloride, it yields the hexa-acetate of diamylose (*loc. cit.*) and by the Baumann-Schotten method yields the *dibenzoate* of *diamylose*, m. p. 200° (approx.), an amorphous substance also obtained when tetra-amylose is benzoylated by this process, an observation which indicates that the slime belongs to the α-group of dextrins. Triamylose, the scission product of dextrin-β, yields a *tribenzoate*, m. p. 190°, which is also amorphous.

These amyloses (dextrins) all yield additive products with iodine when their aqueous solutions are treated with iodine in potassium iodide. The iodine additive products of the α-group form green-tinted needles, become blue when moistened with water, but form dark red solutions when much water is added; those of the β-group form dark reddish-brown prisms and give dark red solutions with water. *Tetra-amylose iodide*, $(C_6H_{10}O_5)_4,1\frac{1}{2}I$, and *hexa-amylose di-iodide*, $(C_6H_{10}O_5)_6.2I$, belonging respectively to these groups, have been prepared; the slime gives an iodide of the α-type.

When tetra-amylose is dissolved in glycerol by heating, and the liquid is heated at 200° during thirty minutes, a small part of the dextrin is converted into the slime and a little into iso*diamylose*, a new

amorphous amylose of the β-type. The latter is also obtained in the form of its amorphous *hexa-acetate* when tetra-amylose is acetylated with acetic anhydride in presence of sulphuric acid. Similarly, hexa-amylose when heated in water for a long time yields a small amount of the slime, and when acetylated in presence of sulphuric acid yields iso*triamylose-nonoacetate*, from which on hydrolysis iso*triamylose* is obtained; both these products are also amorphous. These new amyloses are hygroscopic, dextrorotatory, decompose without melting when heated, and reduce Fehling's solution. Some preliminary observations on the acetylation of "soluble" starch are also recorded.

Starch was separated by Gatin-Grużewska's method (A., 1911, i, 357) into amylopectin and Maquenne's amylose. These two products on treatment with *Bacillus macerans* fermented less easily than starch, but yielded the same products, viz., tetra-amylose, hexa-amylose, and the slime.

Takadiastase and *Penicillium africanum* hydrolyse hexa-, tetra-, tri-, and di-amyloses, whilst emulsin decomposes *iso*tri- and *iso*di-amyloses, but has no action on the other four. Yeast and diastase do not act on any of the six dextrins. T. A. H.

Hexabromoplatinates [Platinibromides]. ALEXANDER GUTBIER and A. RAUSCH (*J. pr. Chem.*, 1913, [ii], 88, 409—424. Compare A., 1910, i, 12; 1911, i, 32).—On account of their sparing solubility and superior powers of crystallisation, the platinibromides may be employed with advantage for the characterisation of amines in place of the platinichlorides.

A solution of hydrogen platinibromide, suitable for this purpose, is readily obtained by dissolving platinic chloride in 20—30 times its weight of hydrobromic acid (D 1·49), and evaporating its solution to half its bulk.

The platinibromides have no definite m. p., but become dark and sinter before liquefaction takes place.

The compounds described below form light red to dark red crystals having a magnificent lustre:

Tetramethylammonium platinibromide, $(NMe_4)_2PtBr_6$, lustrous, red crystals of octahedral habit. *Tetraethylammonium platinibromide*, felted crystals.

Tripropylammonium platinibromide, compact clusters of deep red, rhombic, double pyramids.

*Di*iso*butylammonium platinibromide*, elongated prisms. *Tri*iso*butylammonium platinibromide*, small, red crystals. iso*Amylammonium platinibromide*, bright red crystals. *Di*iso*amylammonium platinibromide*, tabular crystals. *Tri*iso*amylammonium platinibromide*, bright red prisms. *Allylammonium platinibromide*. *Guanidine platinibromide*, $C_2H_{12}N_6PtBr_6$, lustrous, red crystals of a complicated structure. *Triphenylguanidine platinibromide*,

$$2NPh:C(NHPh)_2,H_2PtBr_6,$$

slender, felted, orange-red needles.

Nitrosodimethylammonium platinibromide, $(NO\cdot NHMe_2)_2PtBr_6$, acicular, pleochroic prisms. *Nitrosodiethylammonium platinibromide*, dark red, fibrous crystals. *Nitrosodipropylammonium platinibromide*,

red prisms. *Nitrosodi*iso*butylammonium platinibromide*, dark red, felted crystals.

m-*Chlorophenylammonium platinibromide*, $(C_6H_4Cl\cdot NH_3)_2PtBr_6$, lustrous, red plates. p-*Chlorophenylammonium platinibromide*, bright red, elongated prisms. 2 : 4-*Dichlorophenylammonium platinibromide*, dark red platelets.

o-*Bromophenylammonium platinibromide*, prisms combined with pyramids. m-*Bromophenylammonium platinibromide*, small, dark red, felted crystals. p-*Bromophenylammonium platinibromide*, red, fibrous crystals.

m-*Nitrophenylammonium platinibromide*, prisms. p-*Nitrophenylammonium platinibromide*, elongated prisms. p-*Nitrosophenyldimethylammonium platinibromide*, $(NO\cdot C_6H_4\cdot NHMe_2)_2PtBr_6$, deep red, felted crystals.

o-*Tolyldimethylammonium platinibromide*, $(C_6H_4Me\cdot NHMe_2)_2PtBr_6$, lustrous, red plates.

p-*Tolyldimethylammonium platinibromide*, red plates. 2 : 4-*Tolylenediammonium platinibromide*, $C_7H_{12}N_2PtBr_6$, deep red prisms. 3 : 4-*Tolylenediammonium platinibromide*, vivid red prisms.

o-*Methoxyphenylammonium platinibromide*, vivid red, monoclinic prisms. p-*Methoxyphenylammonium platinibromide*, long, slender, lustrous, red prisms. o-*Ethoxyphenylammonium platinibromide*, stellar, feebly pleochroic discs, or long prisms. p-*Ethoxyphenylammonium platinibromide*, lustrous, red, fibrous crystals.

Tribenzylammonium platinibromide, dark red crystals. *Benzylmethylammonium platinibromide*, dark red prisms.

Benzylidenemethylammonium platinibromide,

$$(CHPh{:}NHMe)_2PtBr_6,$$

red, felted aggregates. *Benzylidene-ethylammonium platinibromide*, leaflets.

Phenylbenzylammonium platinibromide, dark red crystals. *Phenylbenzylmethylammonium platinibromide*, $(NHMePh\cdot C_7H_7)_2PtBr_6$, red, felted crystals. *Phenylbenzylideneammonium platinibromide*, elongated prisms. 2 : 4 : 5-*Trimethylphenylammonium platinibromide*, light red prisms.

3-*Methylpyridinium platinibromide*, dark red, regular crystals. *Dimethylpyridinium platinibromide*, dark red, felted crystals. *Trimethylpyridinium platinibromide*, clusters of deep red crystals. *Piperidinium platinibromide*, elongated prisms. iso*Quinolinium platinibromide*, lustrous, red, prismatic crystals. F. B.

Action of Ammonia on β-Aminocrotonates and β-Carbethoxyaminocrotonates. ERNST PHILIPPI (*Monatsh*, 1913, **34**, 1187—1193. Compare this vol., i, 598).—It is argued that the substance which Meister (A., 1888, 675) regarded as having the formula $OEt\cdot C(OH)(NH_2)\cdot CH{:}CMe\cdot NH\cdot CO\cdot NH_2$, may be equally well represented by the formula

$$CH_3\cdot CH(NH\cdot CO\cdot NH_2)\cdot CH(NH_2)\cdot CO_2Et$$

or $CH_3\cdot C(NH_2)(NH\cdot CO\cdot NH_2)\cdot CH_2\cdot CO_2Et$, so far as the reactions described by Meister are concerned. The author finds that the substance on treatment with hot alkali solution yields ethyl β-amino-

crotonate, and that the latter condenses with carbamide in dry alcohol to regenerate the parent substance, which must therefore be ethyl β-amino-β-carbamidobutyrate represented by the third formula given above.

It is remarkable that whilst the substance is formed by the action of alcoholic ammonia at 160—170° on ethyl β-aminocrotonate, it is not produced when liquefied ammonia is allowed to react with the ester in the cold even for several days. It is probable that in the former case part of the ester is decomposed with the formation of carbamide, which then condenses with the rest of the ester. T. A. H.

The Condensation of Carbamides with Esters. GEORG ROEDER (*Ber.*, 1913, **46**, 2560—2564).—In an attempt to prepare hydurilic acid from ethyl ethanetetracarboxylate and carbamide, Conrad (A., 1907, i, 985) obtained scarcely a trace of the desired substance, although the analogous reaction with guanidine in place of carbamide proved satisfactory. It is now shown that the reaction with carbamide follows a different course from that expected, giving rise to *ethanetetracarboxydi-imide*, which carbonises at 270°. The reaction was effected in warm alcoholic solution containing sodium ethoxide, and can be represented as: $CH(CO_2Et)_2{\cdot}CH(CO_2Et)_2 + 2CO(NH_2)_2 =$

$$NH{<}\begin{matrix}CO{\cdot}CH{\cdot}CO\\ \quad\;\,| \\ CO{\cdot}CH{\cdot}CO\end{matrix}{>}NH + 2NaOCN + 4EtOH.$$

With thiocarbamide, the ester behaves as ethyl dimalonate, and under similar conditions to the last gives rise to *dithiohydurilic acid*, according to the equation: $CH(CO_2Et)_2{\cdot}CH(CO_2Et)_2 + 2CS(NH_2)_2 =$ $CS{<}\begin{matrix}NH{\cdot}CO\\ NH{\cdot}CO\end{matrix}{>}CH{\cdot}CH{<}\begin{matrix}CO{\cdot}NH\\ CO{\cdot}NH\end{matrix}{>}CS + 4EtOH$; the product, which is unaltered at 250°, gives a yellow *pyridine* salt, and when suspended in water is coloured green by ferric chloride; it can be desulphurised to hydurilic acid by heating at 100° with concentrated sulphuric acid.

As might be expected from the above results, ethyl succinate condenses with carbamide under similar conditions to the above with formation of succinimide and sodium cyanate. It is suggested that in this and the analogous case above, the course of the reaction follows the stages: $CH_2(CO_2Et){\cdot}CH_2{\cdot}CO_2Et \longrightarrow \begin{matrix}CH_2{\cdot}CO\\ | \quad\;\; \\ CH_2{\cdot}CO\end{matrix}{>}N{\cdot}CO{\cdot}NH_2 \longrightarrow$ $\begin{matrix}CH_2{\cdot}CO\\ | \quad\;\; \\ CH_2{\cdot}CO\end{matrix}{>}NH + NH_2{\cdot}CO_2Et$; the last substance, the formation of which is attributed to the action of the alcohol on the primary condensation product, then decomposes under the influence of sodium ethoxide into alcohol and sodium cyanate.

When ethyl phthalate is subjected to this reaction, either with carbamide or thiocarbamide, the product is phthalimide. D. F. T.

Chloro-glyoxime, Oxime Derivatives of Oxalyl Chloride and Oxalyl Semichloride, and Cyanoformylchloride Oxime. JOSEF HOUBEN and H. KAUFFMANN (*Ber.*, 1913, **46**, 2821—2835).—By careful chlorination in cold hydrochloric acid solution, both chloro-

amphi- and chloro-*anti*-glyoxime are converted into the same dichloro-*anti*-glyoxime. The chloro-*anti*-glyoxime is the more readily chlorinated. It is established that fuming hydrogen chloride converts chloro-*amphi*-glyoxime into the *anti*-modification contrary to the statement of Hantzsch, (A., 1892, 693).

Dichloro*anti*glyoxime, OH·N:CCl·CCl:N·OH, has decomp. 221° when crystallised from water, or 212° when crystallised from toluene. It gives a reddish-brown coloration with ferric chloride.

Dichloroglyoxime diacetate, OAc·N:CCl·CCl:N·OAc, separates in well formed crystals, m. p. 162—163°. Dry ammonia gas converts it into dioximino-ethylenediamine, which differs from the known compound, firstly, in forming a *diacetyl* derivative, m. p. 206° when crystallised from water, or 212° when crystallised from chloroform, and secondly, in not yielding a dibenzoyl derivative. The difference is attributed to a changed configuration.

Thionyl chloride converts chloro*amphi*glyoxime into *chloro-oximino-acetonitrile*, OH·N:CCl·CN. This is purified by distillation and the crystals formed, which are extremely hygroscopic, filtered and dried in a current of air in a specially constructed apparatus. It has m. p. 55—56°; the vapour has a very irritant action. It crystallises in monoclinic prisms and plates giving no coloration with ferric chloride until it has been warmed with water for a few seconds. The substance is a mixture of the two forms: $\begin{matrix}\text{Cl·C·CN}\\ \text{HO·N}\end{matrix}$ and $\begin{matrix}\text{Cl·C·CN}\\ \text{N·OH}\end{matrix}$, in which one greatly preponderates. The form present in the smaller proportion is much more easily decomposed by water. Probably the conversion of one form into the other takes place during the distillation.

Solution of the nitrile in water yields very soon a voluminous, flocculent precipitate which does not contain halogen. Its investigation is not yet completed, but it is probably *dioximino-oxalonitrile* NC·C(N·OH)·C(N·OH)·CN. It explodes violently at 250—260°.

Whereas both chloro-*amphi*- and *anti*-glyoxime diacetate and chloro-*amphi*-glyoxime monoacetate distil unchanged in a vacuum, the *anti*-diacetate at the ordinary pressure is decomposed, losing acetic acid and forming *chloro-oximinoacetonitrile acetate*, CN·CCl:N·OAc, a clear liquid, b. p. 74—75°/13 mm.

Fuming hydrochloric acid converts it into *chloro-oximinoacetamide*, OH·N:CCl·CO·NH_2, which crystallises in well-formed, pointed needles, m. p. 162°, crystallised from water, or 166° crystallised from benzene (decomp.).

On acetylation, *acetoximinochloroacetamide*, OAc·N:CCl·CO·NH_2, m. p. 134°, is formed. This compound serves to distinguish the oximinoacetamide from the chloroglyoximes.

The *hydrochloride* of *chloro-oximinoacetiminomethyl ether*,

OH·N:CCl·CCl(NH_2)·OMe,

forms crystals, m. p. 161°. The analogous *ethyl* ether has m. p. 155—164° according to the rate of heating.

When hydrolysed in fuming hydrochloric acid, *chloro-oximinoacetic acid*, OH·N:CCl·CO_2H, is formed. This has m. p. 125° (decomp.)

The acid is also obtained from chloro-oximinoacetic ester as prepared by Jovitschitsch (A., 1906, i, 732).

It has a strong acid astringent and yet sweet taste. It gives a deep, dark red coloration with ferric chloride. E. F. A.

Crystals of Diamminedimethylglyoximinecobalt Chloride. D. N. ARTEMÉEV (*Zeitsch. Kryst. Min.*, 1913, **52**, 632; from *Ann. Inst. Mines, St. Petersburg*, 1910, **2**). **Crystals of Chloroammine-dimethylglyoximinecobalt.** D. N. ARTEMÉEV and D. TH. MURASCHEV (*ibid.*, 1913, **52**, 627—628; from *ibid.*, 1910, **2**, 272—274). **Crystals of Nitroaquodimethylglyoximinecobalt.** D. N. ARTEMÉEV and W. M. LOMBERG (*ibid.*, 1913, **52**, 632—633; from *ibid.*, 1910, **2**, 352—356).—Descriptions are given, in Fedorov's nomenclature, of the crystals of these compounds prepared by L. A. Tschugaev (A., 1906, i, 814). Their formulæ are respectively $Co(NH_3)_2D_2H_2Cl,5H_2O$, $CoNH_3ClD_2H_2$, and $CoNO_2D_2H_2,H_2O$, where $D = \begin{matrix} CH_3\cdot C\colon NO \\ | \\ CH_3\cdot C\colon NO \end{matrix}$. L. J. S.

Complex Compounds of Rhodium. LEO A. TSCHUGAEV and W. LEBEDINSKI (*Zeitsch. anorg. Chem.*, 1913, **83**, 1—7).—Rhodium forms complex compounds with α-dioximes, completely resembling those of tervalent cobalt (A., 1906, i, 814; 1907, i, 904). Two series of compounds are formed, one being salts of a mono-acid base, $[Rh,2NH_3,D_2H_2]X$, and the other salts of a monobasic complex acid, $[RhCl_2D_2H_2]H$ (D = dimethylglyoxime, X = halogen). The complex acid is remarkably stable.

Diamminedimethylglyoximinerhodium chloride,

$$[Rh,2NH_3,D_2H_2]Cl,5H_2O,$$

from dimethylglyoxime and chloropentamminerhodium chloride at 150°, crystallises from hot water. The *iodide* is anhydrous. The *nitrate* is precipitated in microscopic tablets; the *perchlorate, platinichloride*, and *platinibromide* are very insoluble.

Rhodidichlorodimethylglyoximinic acid, $[RhCl_2,D_2H_2]H$, from sodium rhodihexachloride and dimethylglyoxime, boiled with water, crystallises from water containing a little hydrochloric acid. The *ammonium* salt, with $1H_2O$, forms large, brownish-yellow crystals. The *guanidinium* salt is anhydrous and sparingly soluble. C. H. D.

Decomposition of Alkylidenehydrazines. NICOLAI M. KISHNER (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 973—986).—The action of magnesium methyl iodide on *cyclo*butanecarboxylamide yields acetyl*cyclo*butane, b. p. 137—139°/761 mm., and the latter, on decomposition of its hydrazone, gives *ethylcyclobutane*, $CH_2{<}{\begin{matrix}CH_2\\CH_2\end{matrix}}{>}CHEt$, b. p. 70°/754 mm., D_0^0 0·7461, D_0^{20} 0·7284, n_D^{15} 1·4032, n_D^{20} 1·4004, which is extremely stable towards permanganate, towards fuming hydrobromic acid in a sealed tube at 100°, and unlike derivatives of three-membered rings, towards concentrated sulphuric acid at the ordinary temperature. Reduction of ethyl*cyclo*butane by means of fuming hydriodic

acid in a sealed tube at 210° yields γ-methylpentane, but no *n*-hexane; as would be expected from the presence of a CH-group in the molecule, γ-methylpentane is readily attacked by fuming nitric acid.

1 : 1-Dimethyl*cyclo*pentane (compare A., 1908, i, 864) may be obtained by distilling 1 : 1-dimethyl-2-*cyclo*pentanonehydrazone (A., 1911, i, 42) with potassium hydroxide and platinised porous tile.

Allylacetonehydrazone [Δ^{α}-*hexylen-ε-onehydrazone*],

$$CH_2:CH\cdot CH_2\cdot CH_2\cdot CMe:N\cdot NH_2,$$

b. p. 187—188°/757 mm., $D_0^{17\cdot5}$ 0·8990, mixes with water in all proportions and, when distilled with potassium hydroxide and platinised porous tile, yields Δ^{α}-*hexene*, $CH_2:CH\cdot CH_2Pr$, b. p. 64°/756 mm., D_0^{20} 0·6734, n_D^{20} 1·3870.

Distillation of β-methyl-Δ^{β}-hepten-ζ-onehydrazone with potassium hydroxide and platinised porous tile yields *β-methyl-*Δ^{β}*-heptene*, $CMe_2:CH\cdot CH_2Pr$, b. p. 122·4°/756 mm., D_0^{20} 0·7254, n_D^{20} 1·4169, which gives β-methylheptane (compare Clarke, A., 1911, i, 345) on reduction by Sabatier and Senderens' method, and forms the *nitrosochloride*, $CMe_2Cl\cdot C(:NOH)\cdot CH_2Pr$, m. p. 48—51°, this exhibiting normal cryoscopic behaviour in benzene. By removal of hydrogen chloride from the nitrosochloride, conversion of the oxime thus obtained into the corresponding ketone, and distillation of the hydrazone of this ketone with potassium hydroxide and platinised porous tile, β-methyl-Δ^{β}-heptene is again obtained.

Distillation of pentan-α-ol-δ-onehydrazone gives *n*-amyl alcohol.

βζ-Dimethyl-Δ^{β}-octene, $CMe_2:CH\cdot CH_2\cdot CH_2\cdot CHMeEt$, obtained by distillation of the hydrazone of the keto-alcohol,

$$OH\cdot CMe_2\cdot CO\cdot CH_2\cdot CH_2\cdot CHMeEt$$

(A., 1911, i, 1027), with potassium hydroxide and platinised porous tile, seems to be identical with the hydrocarbon obtained from citronellaldehydehydrazone (A., 1911, i, 1027). T. H. P.

Complex Mercury Compounds from Ethylene and Carbon Monoxide. WALTER SCHOELLER, WALTER SCHRAUTH, and WALTER ESSERS (*Ber.*, 1913, **46**, 2864—2876).—Mercury acetate in methyl alcohol reacts with a molecule of ethylene to form *acetatomercuriethyl methyl ether*, $CH_3\cdot CO\cdot O\cdot Hg\cdot CH_2\cdot CH_2\cdot OMe$, crystallising in colourless, slender, pointed needles, m. p. 42°. The *bromide* of the ether forms bunches of needles, m. p. 58°; the *iodide* crystallises in stellate aggregates of needles or platelets.

In presence of ethyl alcohol reaction between the mercury salt and ethylene is slower, and *acetatomercuridiethyl ether*,

$$CH_3\cdot CO\cdot O\cdot Hg\cdot C_2H_4\cdot OEt,$$

is formed. This sinters at 33°, m. p. 36°. The *chloride* crystallises in colourless needles, m. p. 92°.

When carbon monoxide is substituted for ethylene, *methyl acetatomercuriformate*, $CH_3\cdot CO\cdot O\cdot Hg\cdot CO\cdot OMe$, is formed. It crystallises in stellate aggregates of needles, m. p. 110° (corr. decomp.). The *chloride* separates in long needles, m. p. 110° (corr. decomp.); the *bromide* is composed of colourless platelets, decomp. 127—128°, and the *iodide* is similar in appearance.

Treatment with hydrogen sulphide in methyl alcohol gives rise to

the formation of *methyl sulphidomercuriformate*, $S(Hg\cdot CO\cdot OMe)_2$, obtained as a colourless, cheese-like precipitate.

Mercury acetate ethyl formate crystallises in aggregates of needles which sinter at 65°, decomp. 125°. The *chloride* forms plates, m. p. 88° (corr. decomp.); the *bromide* and *iodide* are very similar. The *sulphide* was obtained as a yellowish-white precipitate. E. F. A.

Decomposition of Pyrazoline Bases. Conversion of Phorone into 1:1-Dimethyl-2-*iso*butenyl*cyclo*propane. NICOLAI M. KISHNER (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 957—972).—The similarity in structure between mesityl oxide and phorone suggests the possibity of transforming the latter ketone into a pyrazoline base and thence into a hydrocarbon containing a trimethylene ring (compare A., 1912, i, 245). This possibility has been realised by the author.

Phorone and hydrazine react according to the equation:

$$CMe_2{:}CH\cdot CO\cdot CH{\cdot}CMe_2 + N_2H_4 \longrightarrow CMe_2{:}CH\cdot C\begin{cases}CH_2\cdot CMe_2\\ N{-\!-}NH\end{cases}.$$

When distilled with potassium hydroxide in presence of platinised porous tile, this pyrazoline base decomposes in two ways, giving (1) 1:1-dimethyl-2-*iso*butenyl*cyclo*propane, or (2) the trimethylpyrazoline and acetone, $CMe\begin{cases}CH_2\cdot CMe_2\\ N{-\!-}NH\end{cases} + COMe_2$.

1:1-*Dimethyl*-2-iso*butenyl*cyclo*propane*, $CH_2\begin{cases}CMe_2\\ CH\cdot CH{:}CHMe_2\end{cases}$, is a liquid, b. p. 132°/758 mm., D_0^{20} 0·7677—0·7681, n_D 1·4414—1·4420. Although the chemical properties of this hydrocarbon are in complete accord with the structure given above, yet the magnitude of the molecular refraction is virtually identical with that calculated for a compound with two double linkings; this exaltation may depend on the relation of the trimethylene ring to the grouping $:CMe_2$, such relation possibly resembling that between two conjugated double linkings.

Oxidation of 1:1-dimethyl-2-*iso*butenyl*cyclo*propane by means of 1% potassium permanganate solution proceeds according to the scheme:

$$CH_2\begin{cases}CMe_2\\ CH\cdot CH{:}CMe_2\end{cases} \longrightarrow CH_2\begin{cases}CMe_2\\ CH\cdot CH(OH)\cdot CMe_2\cdot OH\end{cases} \longrightarrow$$
$$CH_2\begin{cases}CMe_2\\ CH\cdot CO\cdot CMe_2\cdot OH\end{cases} \longrightarrow CH_2\begin{cases}CMe_2\\ CH\cdot CO_2H\end{cases} + CH_3\cdot COMe;$$

the intermediate glycol was not isolated.

The *ketol*, $CH_2\begin{cases}CMe_2\\ CH\cdot CO\cdot CMe_2\cdot OH\end{cases}$, is a viscous liquid with an odour resembling terpineol, b. p. 200°/758 mm., $D_0^{16\cdot5}$ 0·9377, D_0^{20} 0·9347, $n_D^{16\cdot5}$ 1·4500, n_D^{20} 1·4490; it exhibits an optical exaltation of 1·43, although that due to the trimethylene ring is usually less than 1. Its *semicarbazone*, $C_9H_{16}O{:}N_2H\cdot CO\cdot NH_2$, m. p. 127°, and its *phenylurethane*, $C_9H_{15}O\cdot O\cdot CO\cdot NHPh$, crystallise in needles.

1:1-*Dimethyl*cyclo*propane-2-carboxylic acid*, $CH_2\begin{cases}CMe_2,\\ CH\cdot CO_2H,\end{cases}$ is an oily liquid, b. p. 198°/751 mm., D_0^{18} 0·8990, n_D 1·4385, optical exaltation 0·83; it is stable towards alkaline permanganate solution.

Reduction of 1 : 1-dimethyl-2-*iso*butenyl*cyclo*propane by the method of Sabatier and Senderens, either at 120—125° or at 170°, yields a mixture of (1) a *cyclo*propane derivative, probably 1 : 1-dimethyl-2-*iso*butyl*cyclo*propane, and (2) *ββε-trimethylhexane*,

$$CMe_3\cdot CH_2\cdot CH_2\cdot CHMe_2,$$

b. p. 124—125°/763 mm., D_0^{20} 0·7082—0·7086, n_D 1·3987—1·3998. Treatment of the 1 : 1-dimethyl-2-*iso*butyl*cyclo*propane with hydrogen bromide and subsequently with 2% potassium hydroxide solution yields *βγε-trimethylhexan-β-ol*, $OH\cdot CMe_2\cdot CHMe\cdot CH_2\cdot CHMe_2$, b. p. 171—172°/755 mm., D_0^{20} 0·8316, n_D 1·4313.

1 : 1-Dimethyl-2-*iso*butenyl*cyclo*propane combines rapidly with 1 mol. of hydrogen bromide, giving the *monobromo*-derivative,

$$CH_2<\begin{matrix}CMe_2\\ |\\ CH\cdot CH_2\cdot CMe_2Br\end{matrix} \text{ or } CH_2<\begin{matrix}CMe_2\\ |\\ CH\cdot CHBr\cdot CHMe_2\end{matrix},$$

b. p. 94—96°/31 mm., D_0^{20} 1·1046, whilst the prolonged action of hydrogen bromide yields *δζ-dibromo-βζ-dimethylheptane*,

$$CHMe_2\cdot CH_2\cdot CHBr\cdot CH_2\cdot CMe_2Br,$$

b. p. 134—136°/31 mm., D_0^{20} 1·3846. When distilled with aniline, both the mono- and dibromo-compounds yield *βζ-dimethyl-$\Delta^{\beta\delta}$-heptadiene*, $CMe_2:CH\cdot CH:CH\cdot CHMe_2$, which contains a small admixture of another hydrocarbon with different positions of the double linkings and has the following approximate physical constants: b. p. 139—141°/758 mm., D_0^{20} 0·7482—0·7510, n_D 1·4456—1·4470. Reduction of this hydrocarbon by Sabatier and Senderens' method at 170° results in the formation of *βζ*-dimethylheptane. T. H. P.

Decomposition of Pyrazoline Bases. Conversion of Cinnamaldehyde into Phenyl*cyclo*propane. NICOLAI M. KISHNER (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 949—957).—*Phenyl*cyclo*propane*, $CHPh<\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}$, prepared by distilling phenylpyrazoline (from cinnamaldehyde and hydrazine) in presence of potassium hydroxide and platinised porous tile, is a liquid, b. p. 173·6°/758 mm., D_0^{15} 0·9449, D_0^{20} 0·9401, n_D^{15} 1·5342. Under the influence of moderately dilute sulphuric acid, it is converted into the same dimeride, $C_{18}H_{20}$, of α-phenyl-Δ^{α}-propylene as is obtained by boiling the latter with sodium.

Phenyl*cyclo*propane combines slowly with hydrogen bromide, yielding *α-bromopropylbenzene*, $CHPhBr\cdot CH_2Me$, b. p. 129—130°, 43 mm., D_0^{16} 1·3124, n_D 1·5528. When boiled with aqueous potassium hydroxide, the latter gives (1) the hydrocarbon, $C_{18}H_{20}$, referred to above; (2) phenylethylcarbinol, and (3) allylbenzene, which is also obtained when α-bromopropylbenzene is distilled in presence of quinoline.

In acetic acid solution, the action of bromine on phenyl*cyclo*propane results mainly in the replacement of the nuclear hydrogen, combination of bromine with the trimethylene ring occurring to a very limited extent:

$$CHPh<\begin{matrix}CH_2\\ |\\ CH_2\end{matrix} + Br_2 \longrightarrow C_6H_4Br\cdot CH<\begin{matrix}CH_2\\ |\\ CH_2\end{matrix} + HBr \longrightarrow C_6H_4Br\cdot CHEtBr.$$

The last compound readily loses hydrogen bromide, giving the unsaturated bromo-derivative, $C_6H_4Br\cdot CH\colon CHMe$, which yields *p*-bromobenzoic acid on oxidation.

αγ-Dibromopropylbenzene, $CHPhBr\cdot CH_2\cdot CH_2Br$ (?), formed in small proportion in the action of bromine on *cyclo*propane in acetic acid solution, crystallises in prisms, m. p. 125°.

4-*Bromo*-1-*allylbenzene*, $C_6H_4Br\cdot CH\colon CHMe$, is a liquid, b. p. 240—241°/764 mm., 124°/20 mm., D_0^{18} 1·3147, n_D 1·5692 ; owing to the conjugated nature of the double linkings in the ring and the side-chain, it exhibits optical exaltation. On reduction by means of hydriodic acid in a sealed tube, it yields propylbenzene. T. H. P.

Decomposition of Pyrazoline Bases : Synthesis of 1-Methyl-2-*iso*propyl*cyclo*propane. NICOLAI M. KISHNER (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 987—992).—iso*Butylideneacetone* [*β-Methyl-Δγ-hexylene-ε-one*], $CHMe_2\cdot CH\colon CH\cdot COMe$, prepared by the condensation of *iso*butyraldehyde and acetone in presence of sodium hydroxide, is a liquid, b. p. 156°/757 mm., D_0^{18} 0·8484, $n_D^{18\cdot5}$ 1·4394 ; its *semicarbazone*, $C_7H_{12}N\cdot NH\cdot CO\cdot NH_2$, forms hexagonal plates, m. p. 162—163°.

3-*Methyl*-5-iso*propylpyrazoline*, $NH<\begin{array}{l}CHPr^{\beta}\cdot CH_2\\ N{=\!=\!=}CMe\end{array}$, prepared by the action of hydrazine hydrate on *iso*butylideneacetone, is a liquid, b. p. 188·5—189·5°/754 mm., D_0^{17} 0·9081, n_D 1·4640 ; it oxidises readily in the air, its hot vapours igniting. Its *thioureide*, $C_7H_{13}N_2\cdot CS\cdot NHPh$, crystallises in needles, m. p. 95—100°.

1-*Methyl*-2-iso*propyl*cyclo*propane*, $CH_2<\begin{array}{l}CHMe\\ CHPr^{\beta}\end{array}$, prepared by decomposition of the preceding compound in a sealed tube at 230°, is a liquid, b. p. 80—81°/748 mm., D_0^{20} 0·7102, n_D^{20} 1·3927, which is extremely stable towards potassium permanganate, combines slowly with bromine in acetic acid solution, and reacts vigorously with fuming nitric acid with formation of a heavy oil. Reduction of 1-methyl-2-*iso*propyl*cyclo*propane by Sabatier and Senderens' method takes place less readily than that of 1 : 1 : 2-trimethyl*cyclo*propane, but at 170° it seems to yield a mixture of *βδ*-dimethylpentane and *βγ*-dimethylpentane. With fuming hydrobromic acid it yields *γ-bromo-βδ-dimethylpentane*, b. p. 158—161°/763 mm., D_0^{20} 1·1585, n_D 1·4548, which gives *βδ*-dimethylpentane on reduction with hydriodic acid. T. H. P.

Catalytic Reactions at High Temperatures and Pressures. XXXII. VLADIMIR N. IPATIEV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 994—995. Compare this vol., i, 693, 694).—In presence of nickel oxide, indene unites with hydrogen at 250—260° and 110 atmospheres, yielding *octahydrindene*, $\begin{array}{l}CH_2\cdot CH_2\cdot CH\cdot CH_2\\ CH_2\cdot CH_2\cdot CH\cdot CH_2\end{array}>CH_2$, which is a liquid, b. p. 165—166°/767 mm., D^{20} 0·8334, n_D^{20} 1·46287 (compare Padoa and Fabris, A., 1908, i, 255). T. H. P.

Metaquinonoids. OTTO STARK, O. GARBEN, and L. KLEBAHN, (*Ber.*, 1913, **46**, 2542—2544. Compare this vol., i, 362, 849).—It is

found that the hydrocarbon, *m-xylylene*, described earlier decomposes at 303—305°, the lower figure given previously being due to insufficient drying.

The substance in the solid state is in a polymerised condition, but the chloroform solutions give ebullioscopic results agreeing with a depolymerised unimolecular product; the solution in chloroform is, however, much more sensitive than that in benzene. The benzene solutions of the substance obtained in the original preparation exhibit a decided fluorescence, and dye paper and linen, whilst the chloroform solutions of the previously separated substance do not possess these characteristics.

A preliminary examination of the absorption spectra of the two solutions indicated complete analogy with the behaviour of Thiele's tetraphenyl-*p*-xylylene; an absorption of blue and violet light which commenced in the green portion of the spectrum was observed both with the chloroform and the original benzene solutions. D. F. T.

Elimination of Halogen Acids by Phosphoric Oxide. I. HANS LECHER (*Ber.*, 1913, **46**, 2664—2668).—Recent publications by Leuchs and his co-workers (this vol., i, 855, 972), in which mention is made of the catalytic action of compounds of phosphorus on the elimination of hydrogen chloride from certain acid chlorides, have led the author to publish a preliminary account of the use of phosphoric oxide in this direction.

Benzoyl chloride does not react with an excess of naphthalene at 180—200°. If, however, a small quantity of phosphoric oxide is added, a vigorous evolution of hydrogen chloride occurs, at the conclusion of which a mixture of much *α*- and less phenyl *β*-naphthyl ketone can be isolated, the total amount being 90% of that theoretically possible. Phosphoric oxide has the advantage over aluminium chloride that only small quantities of it are necessary, larger amounts having an unfavourable influence on the course of the reaction. On the other hand, the requisite temperature is high, and, in those cases in which the b. p. of the mixture lies below this temperature, the operation must be performed in sealed tubes. In these circumstances, the liberated hydrogen chloride can only be removed periodically, and greatly diminishes the velocity of the reaction. Thus, only small yields of benzophenone could be obtained by this method from benzoyl chloride and benzene.

Boiling benzyl chloride rapidly and completely eliminates hydrogen chloride in the presence of phosphoric oxide, forming a mixture of hydrocarbons which has not yet been completely investigated. *ω*-Chlorotriphenylmethane is similarly decomposed at about 150° into 9-phenylfluorene and much triphenylmethane.

A series of experiments has been performed to determine the exact nature of the catalyst. Bailey and Fowler (T., 1888, **53**, 755) have shown that phosphoric oxide reacts with hydrogen chloride according to the equation: $P_4O_{10} + 3HCl = POCl_3 + 3HPO_3$, but the author finds that no appreciable action occurs within a reasonable time at temperatures up to 260°, and, hence, that phosphoryl chloride cannot

be the actual catalyst. Direct experiment with metaphosphoric acid has shown that this substance is also inactive.

Finally, the active catalyst can easily be recovered by the removal of organic matter by extraction with benzene. In this manner, a mixture of a phosphorus compound (which yields metaphosphoric acid with water) and small quantities of carbon is obtained, which can be employed in the same manner as fresh phosphorus pentoxide.

H. W.

Morphological Studies in the Benzene Series. IV. The Crystalline Form of Sulphonates in Relation to their Molecular Structure. ERNEST H. RODD (*Proc. Roy. Soc.*, 1913, *A*, **89**, 292—313. Compare T., 1910, **97**, 1578; A., 1912, i, 756).—A number of salts of *p*-dichlorobenzenesulphonic acid have been prepared, and their crystallographic constants have been compared. Lanthanum *p*-dichlorosulphonate, $La(C_6H_3Cl_2SO_3)_3,15H_2O$, is deposited from solution between 10° and 50°; it forms triclinic prisms, which rapidly effloresce [$a:b:c = 1\cdot6193:1:1\cdot6028$; $\alpha = 76°26'$; $\beta = 113°48'$; $\gamma = 68°6'$]. Neodymium *p*-dichlorobenzenesulphonate,

$$Nd(C_6H_3Cl_2SO_3)_3,12H_2O,$$

crystallises in short, thick, rose-coloured, monoclinic prisms between 15° and 50°, closely isomorphous with $Gd(C_6H_3Br_2SO_3)_3,12H_2O$ [$a:b:c = 0\cdot5872:1:0\cdot3810$; $\beta = 76°34'$]. Praseodymium *p*-dichlorobenzenesulphonate, $Pr(C_6H_3Cl_2SO_3)_3,12H_2O$, forms pale green, monoclinic prisms isomorphous with the corresponding neodymium salt [$a:b:c = 0\cdot5887:1:0\cdot3819$: $\beta = 76°26'$]. A salt of the composition $Pr(C_6H_3Cl_2SO_3)_3,15H_2O$, isomorphous with the corresponding lanthanum salt, is formed when a supersaturated solution is allowed to spontaneously crystallise at the ordinary temperature. A number of other sulphonates have also been prepared and measured. Gadolinium *p*-dibromobenzene sulphonate, $Gd(C_6H_3Br_2SO_3)_3,7H_2O$, monoclinic prisms [$a:b:c = 1\cdot2595:1:0\cdot6031$; $\beta = 89°16'$]. Didymium benzenesulphonate, $Di(C_6H_5\cdot SO_3)_3,9H_2O$, crystallises from a mixture of aqueous alcohol and ethyl acetate in thin, hexagonal-shaped plates belonging to the rhombic system [$a:b:c = 2\cdot0795:1:1\cdot9374$]. Potassium *p*-dichlorobenzenesulphonate, $C_6H_3Cl_2SO_3K$, crystallises anhydrous from aqueous solutions between 20° and 37° in thin, monoclinic prisms [$a:b:c = 1\cdot5054:1:0\cdot7636$; $\beta = 83°27\cdot5'$]. Sodium *p*-dichlorobenzenesulphonate, $C_6H_3Cl_2SO_3Na,H_2O$, crystallises in large, monoclinic tablets at 37° [$a:b:c = 3\cdot0529:1:1\cdot9583$; $\beta = 88°46'$]. Zinc *p*-dichlorobenzenesulphonate, $Zn(C_6H_3Cl_2SO_3)_2,8H_2O$, forms long, monoclinic prisms, which are always distorted [$a:b:c = 2\cdot9985:1:2\cdot4539$; $\beta = 79°20'$]. Magnesium *p*-dichlorobenzenesulphonate,

$$Mg(C_6H_3Cl_2SO_3)_2,8H_2O,$$

crystallises in stout, monoclinic, hemimorphic plates [$a:b:c = 2\cdot9970:1:2\cdot4450$; $\beta = 79°41\cdot5'$]. Ferric *p*-dibromobenzenesulphonate, $Fe(C_6H_3Br_2SO_3)_3,13H_2O$; basic ferric *p*-dibromobenzenesulphonate, $Fe(OH)(C_6H_3Br_2SO_3)_2,12H_2O$; chromium *p*-dibromobenzenesulphonate, $Cr(C_6H_3Br_2SO_3)_3,14H_2O$; aluminium *p*-dibromobenzenesulphonate,

$$Al(C_6H_3Br_2SO_3)_3,18H_2O;$$

scandium *p*-dibromobenzenesulphonate, $Sc(C_6H_3Br_2SO_3)_3,14H_2O$, and

cobaltous *p*-dibromobenzenesulphonate, $Co(C_6H_3Br_2SO_3)_2,9H_2O$, have been prepared and described without crystallographic details. It is shown that similar conclusions may be drawn with regard to the structure of *p*-dichlorosulphonic acid as were drawn in the case of *p*-dibromosulphonic acid in the previous paper (*loc. cit.*). The structure of the sulphonates of monad and dyad metals is discussed; it is argued that in the formation of the latter the molecules of benzene in contiguous rows become separated by the intervention of the sulphonic radicles which are united in pairs by the metallic atom. The structure of the salts containing monad metals appears in some cases to be pseudo-trigonal like that of the acid; in others to resemble that of the dyad metals. J. F. S.

p- and o-Toluenesulphinic Acids. ALFRED HEIDUSCHKA and HANS LANGKAMMERER (*J. pr. Chem.*, 1913, [ii], **88**, 425—442).—An extension of the work of E. von Meyer and others (A., 1901, i, 264; 1903, i, 808) on the formation of aminodiaryl sulphides by the interaction of aromatic sulphinic acids and amines.

The authors find that the sulphides are obtained in a purer condition and better yield by fusing the sulphinic acids with the hydrochlorides of the amines, instead of with the free bases.

When *p*-toluenesulphinic acid is fused at 215° with aniline hydrochloride and the product extracted with ether, p-*aminophenyl* p-*tolyl sulphide* p-*toluenesulphonate*, $C_{20}H_{21}O_3NS_2$, is obtained in white needles, m. p. 216°; extraction of the residue with hydrochloric acid yields the corresponding *hydrochloride.*

p-Aminophenyl *p*-tolyl sulphide condenses with 4-bromo-2-hydroxybenzaldehyde in boiling alcoholic solution to form p-4-*bromo*-2-*hydroxybenzylideneaminophenyl* p-*tolyl sulphide*,

$$C_6H_4Me\cdot S\cdot C_6H_4\cdot N:CH\cdot C_6H_3Br\cdot OH,$$

which crystallises in lustrous, brownish-yellow leaflets, m. p. 148°; the m-*xylylidene* derivative, $C_6H_4(CH:N\cdot C_6H_4\cdot S\cdot C_6H_4Me)_2$, from *m*-phthalaldehyde, has m. p. 163°.

The *benzylidene* derivative, $C_6H_4Me\cdot S\cdot C_6H_4\cdot N:CHPh$, is obtained in the form of its *hydrochloride* (yellow needles, m. p. 164°, which rapidly acquire a greenish colour) by condensing benzaldehyde with *p*-aminophenyl *p*-tolyl sulphide hydrochloride; the *hydrochlorides* of the *salicylidene* and *vanillylidene* derivatives have m. p. 175° and 195° respectively.

The aqueous extract of the product obtained by fusing *o*-anisidine hydrochloride with *p*-toluenesulphinic acid at 225° yields o-*anisidine* p-*toluenesulphonate*, $C_{14}H_{17}O_4NS$, which has m. p. 150°, and has also been prepared directly from its components in alcoholic solution; extraction of the product with hydrochloric acid yields 4-*amino*-3-*methoxyphenyl* p-*tolyl sulphide hydrochloride*,

$$C_6H_4Me\cdot S\cdot C_6H_3(OMe)\cdot NH_2,HCl.$$

This has m. p. 215°, and on treatment with aqueous ammonia yields the free *base*, which, however, could not be obtained in a pure condition. The free base combines with phenylcarbimide in ethereal solution to form the *carbamide*, m. p. 163°,

$$NHPh\cdot CO\cdot NH\cdot C_6H_3(OMe)\cdot S\cdot C_6H_4Me.$$

o-*Anisidine* p-*toluenesulphinate*, prepared from its components in alcoholic solution, has m. p. 112°. o-*Chloroaniline* p-*toluenesulphonate*, m. p. 198°, and o-*chloroaniline* p-*toluenesulphinate*, m. p. 130°, were prepared in a similar manner.

3-*Chloro*-4-*aminophenyl* p-*tolyl sulphide hydrochloride*,

$$C_6H_4Me\cdot S\cdot C_6H_3Cl\cdot NH_2,HCl,$$

obtained by fusing *p*-toluenesulphinic acid with *o*-chloroaniline hydrochloride, forms colourless crystals, m. p. 150°, and on treatment with aqueous ammonia yields the free *base*, which combines with phenylcarbimide in ethereal solution to form the *carbamide*,

$$NHPh\cdot CO\cdot NH\cdot C_6H_3Cl\cdot S\cdot C_6H_4Me,$$

crystallising in white needles, m. p. 190°; the corresponding *thiocarbamide* prepared in a similar manner has m. p. 147°.

p-*Aminophenyl* o-*tolyl sulphide*, $NH_2\cdot C_6H_4\cdot S\cdot C_6H_4Me$, obtained in the form of its o-*toluenesulphonate*, $C_{20}H_{21}O_3NS_2$, m. p. 190°, by fusing aniline hydrochloride with *o*-toluenesulphinic acid and extracting the product with water, separates from ether in flat, hexagonal, brown pyramids, m. p. 50°, forms a *hydrochloride*, crystallising in slender, white needles, m. p. 137°, and condenses with benzaldehyde in alcoholic solution, yielding the *benzylidene* derivative, which was isolated in the form of its *hydrochloride*, $C_6H_4Me\cdot S\cdot C_6H_4\cdot N:CHPh,HCl$, as a yellow powder, m. p. 195°. It combines with phenylcarbimide in ethereal solution yielding the *carbamide*, $NHPh\cdot CO\cdot NH\cdot C_6H_4\cdot S\cdot C_6H_4Me$, crystallising in white needles, m. p. 164°. F. B.

Electrochemical Reduction of Organic Halogen Compounds. II. KURT BRAND (*Ber.*, 1913, **46**, 2935—2942).—This and the succeeding paper give the results of attempts to reproduce by electrochemical methods the conversion of diaryltrichloroethanes into stilbene derivatives, first effected by chemical methods by Goldschmidt, and later by Elbs (Abstr., 1893, i, 271). The results show that the products obtained depend in part on the nature of the cathode used. The apparatus used is described. The cathode liquid, which was kept boiling, consisted of the substance under examination in alcohol and hydrochloric acid.

Lead cathode.—$\beta\beta\beta$-Trichloro-$\alpha\alpha$-diphenylethane yielded stilbene (4% of the theoretical) and dichlorodiphenylethane. $\beta\beta\beta$-Trichloro-$\alpha\alpha$-di-*p*-tolylethane gave 6% of the theoretical yield of *p*:*p*′-dimethylstilbene. $\beta\beta\beta$-Trichloro-$\alpha\alpha$-di-*p*-anisylethane gave about 10% of the calculated yield of *p*:*p*′-dimethoxystilbene, and a similar yield of *p*:*p*′-diethoxystilbene was obtained from $\beta\beta\beta$-trichloro-$\alpha\alpha$-di-*p*-phenetylethane. These alkylstilbenes were identified by means of their dibromides.

Copper cathode.—The four diaryltrichloroethanes mentioned in the preceding paragraph were also submitted to electrolytic reduction in presence of a copper cathode, and then yielded the corresponding diaryldichloroethanes, but the first-named product gave only a small yield. The last-named substance also yielded a minute amount of the corresponding diethoxystilbene. The diaryldichloroethanes were identified by conversion into the corresponding ethylenes, which give characteristic colours with sulphuric acid. T. A. H.

Electrochemical Reduction of Organic Halogen Compounds. III. KURT BRAND and M. MATSUI (*Ber.*, 1913, **46**, 2942—2951).—It has been shown previously (Brand, *Zeitsch. Elektrochem.*, 1910, **16**, 669) that the principal product of the electrolytic reduction of hot alcoholic solutions of $\beta\beta\beta$-trichloro-$\alpha\alpha$-diphenylethane in presence of a lead cathode is a hydrocarbon, $C_{28}H_{22}$, which may have the constitution $CHPh_2\cdot C⋮C\cdot CHPh_2$ or $CPh_2:C:CH\cdot CHPh_2$ (see also preceding abstract). It is now shown that the cathodic reduction of $\beta\beta\beta$-trichloro-$\alpha\alpha$-di-*p*-tolylethane and of di-$\beta\beta\beta$-trichloro-$\alpha\alpha$-di-*p*-anisyl-ethane under analogous conditions furnishes similar substances, some reactions of which are described. These reactions do not enable a final decision as to the constitution to be arrived at, but on the whole they tend to support formulæ of the kind represented by the second given above.

$\beta\beta\beta$-Trichloro-$\alpha\alpha$ di-*p*-tolylethane furnishes the *hydrocarbon*, $C_{32}H_{30}$, m. p. 123°, which crystallises from boiling alcohol in colourless, small needles, shows a faint blue fluorescence, and on oxidation in acetone solution with potassium permanganate yields di-*p*-tolylacetic acid and di-*p*-tolyl ketone; the same products are formed with calcium permanganate in presence of pyridine, and with chromic acid in acetic acid, but in different amounts. On reduction with excess of sodium in amyl alcohol, the hydrocarbon yields the corresponding *tetra*-p-*tolylbutane*, m. p. 126°, crystallising from alcohol in colourless needles showing a slight blue fluorescence. With insufficient sodium, a *substance*, m. p. 186°, crystallising in glancing leaflets, is formed in small quantity. With sodium in absolute alcohol, the same reduction takes place. On treatment with sodium ethoxide in alcohol, the hydrocarbon is converted into $\alpha\alpha\delta\delta$-*tetra*-p-*tolyl*-$\Delta^{\alpha\gamma}$-*butadiene*,

$$C(C_6H_4Me)_2:CH\cdot CH:C(C_6H_4Me)_2,$$

m. p. 255°, which crystallises from methyl ethyl ketone in heavy, green, fluorescent needles, is sparingly soluble in boiling alcohol, but readily so in chloroform or benzene, giving solutions which are green in colour and show absorption in the extreme violet end of the spectrum. The hydrocarbon, $C_{32}H_{30}$, reacts with mercuric acetate to form an orange-yellow *compound* of uncertain composition, which with hydrogen chloride or with zinc and acetic acid yields the tetratolylbutadiene described above.

Di-*p*-anisyltrichloroethane yields in addition to di-*p*-methoxystilbene (preceding abstract) the *phenol ether*, $C_{32}H_{30}O_4$, which, as indicated above, is probably $\alpha\alpha\delta\delta$-tetra-*p*-anisyl-$\Delta^{\alpha\beta}$-butadiene,

$$(C_6H_4\cdot OMe)_2C:C:CH\cdot CH(C_6H_4\cdot OMe)_2.$$

It melts at 111°, crystallises from boiling alcohol in colourless needles, and on oxidation with chromic acid gives di-*p*-anisyl ketone and a small amount of di-*p*-anisylacetic acid. On reduction with sodium in amyl alcohol, $\alpha\alpha\delta\delta$-*tetra*-p-*anisylbutane*, m. p. 116°, crystallising in colourless needles with a blue fluorescence, is formed, whilst with sodium ethoxide in alcohol, $\alpha\alpha\delta\delta$-*tetra*-p-*anisyl*-$\Delta^{\alpha\gamma}$-*butadiene*, m. p. 149°, which crystallises from methyl ethyl ketone in green, fluorescent needles, is produced. These two substances closely resemble their analogues described in the preceding paragraph.

T. A. H.

Dehydrobenzylidenebisfluorene. ROBERT STOLLÉ (*Ber.*, 1913, **46**, 2979).—In preparing benzoylfluorene by Werner's method (A., 1906, i, 436), but using potassium ethoxide instead of sodium, the author has obtained a small quantity of *dehydrobenzylidenebisfluorene*, $C_{32}H_{22}$, m. p. 350°, which crystallises from chloroform in small, orange needles, and on heating sublimes to form red crystals. It is hardly soluble in ether or alcohol, and sparingly soluble in hot benzene or acetic acid. The analogous ethylidene compound has been described by Pummerer and Dorfmüller (this vol., i, 963). T. A. H.

Studies in the Fluorene Series. FRITZ MAYER (*Ber.*, 1913, **46**, 2579—2587).—The author has attempted to synthesise fluoranthene by the ring condensation of 9-ethylfluorene, fluorene-9-acetic acid or fluorenepropionic acid, but without success. On heating distilled ethylfluorene with litharge and distilling the product, 9-ethylidenefluorene, $\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}\!\!>\!C{:}CHMe$ (Ullmann, A., 1906, i, 77), which formed a picrate, m. p. 156°, was obtained. When crude ethylfluorene was employed, however, and the product was not distilled, a 9-fluorene-ethyl alcohol, which also gave a picrate, m. p. 155—156°, was formed. It was not identical with Ullmann's carbinol (*ibid.*) and has therefore the constitution $\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}\!\!>\!CH\cdot CH(OH)Me$ or $\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}\!\!>\!CH\cdot CH_2\cdot CH_2\cdot OH$. In each case, very small quantities of high-melting, red hydrocarbons of the formula $C_{15}H_{10}$ were obtained. It was expected that one of them would be identical with the compound,

$$\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}\!\!>\!CH\cdot CH{:}C\!<\!\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4},$$

described by Wislicenus and Densch (A., 1902, i, 291), but the author could not prepare this substance by any means.

Twenty grams of crude 9-ethylfluorene, from the action of ethyl iodide on ethyl fluorene-9-oxalate (*loc. cit.*), were heated for fifteen minutes at 310—360° with 40 grams of litharge, when the product was extracted with boiling chloroform. The solvent deposited a red *hydrocarbon*, $C_{15}H_{10}$ or $C_{27}H_{18}$, m. p. over 360°, on cooling, and the dark brown *picrate* of a fluorene-ethyl alcohol, $C_{21}H_{17}O_8N_3$, m. p. 155—156°, was obtained from the mother liquor. The *picrate* of Ullmann's carbinol has the same m. p., but not so a mixture of the two.

Two parts of distilled 9-ethylfluorene, b. p. 306—310°, were heated with five parts of litharge for one hour, the product was extracted with hot chloroform, which deposited a red *hydrocarbon*, $(C_{15}H_{10})_x$, m. p. 300—310°, and the residue, after evaporating the solvent, was distilled. The fraction, b. p. 310—320°, contained ethylidenefluorene and formed a *picrate*, $C_{21}H_{15}O_7N_3$, m. p. 155—156°.

For the preparation of *fluorene-9-acetic acid*, $\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4}\!\!>\!CH\cdot CH_2\cdot CO_2H$, ethyl fluorene-9-oxalate was treated with sodium in alcohol and ethyl bromoacetate, and the product was hydrolysed by 20% aqueous sodium hydroxide. The acid has m. p. 129—130°, forms a *methyl* ester,

$C_{16}H_{14}O_2$, m. p. 60°, an *amide*, $C_{15}H_{13}ON$, slender needles, m. p. 189°, and yields 9-methylfluorene (*ibid.*) on distillation with soda-lime. *Fluorene-9-propionic acid*, $C_{16}H_{14}O_2$, was also prepared, using ethyl β-iodopropionate; it forms white needles, m. p. 144°. Neither the acids themselves nor their chlorides gave definite products on condensation. J. C. W.

Tri-β-naphthylmethane and Certain of its Derivatives. Alexei E. Tschitschibabin and S. I. Korjagin (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 766—781; *J. pr. Chem*, 1913, [ii], **88**, 505—578).—Tri-β-naphthylcarbinol (compare Schmidlin and Huber, A., 1910, i, 832) may be readily obtained by the interaction of di-β-naphthyl ketone and magnesium β-naphthyl bromide (see A., 1911, i, 969) in presence of ether.

The authors were unable to prepare 2-bromonaphthalene by Darzens and Berger's method (A., 1909, i, 297), but obtained it readily from β-naphthylamine by passing through the diazo-compound.

Di-β-naphthyl ketone (compare Grucarevic and Merz, A., 1873, 263, 264) was prepared by the dry distillation of calcium β naphthoate, by oxidising di-β-naphthylcarbinol by the action of β-naphthoyl chloride on naphthalene in presence of zinc and by the action of magnesium β-naphthyl bromide on β-naphthoyl chloride. The first method gives poor, and the last good yields.

Tri-β-naphthylcarbinol, $C_{31}H_{22}O$, forms snow-white crystals, m. p. 204°, and dissolves in concentrated sulphuric acid with an intense coloration, which is greenish in thin layers or low concentrations, and violet-red when more concentrated. These solutions show an absorption band gradually weakening from the violet to the blue, with a maximum intensity at about 490 $\mu\mu$, and also a faint band in the red, beginning at about 755 $\mu\mu$. Unlike the isomeric tri-α-naphthylcarbinol (A., 1911, i, 969), it shows no inclination to oxidise in the air. *Tri-β-naphthylchloromethane*, $C_{31}H_{21}Cl$, forms white crystals, m. p. 199—201° (decomp.), the fused mass solidifying later, and then showing m. p. 231—236°; with sulphuric acid it gives the same coloration as the carbinol.

Tri-β-naphthylmethane, $C_{31}H_{22}$, prepared by reducing the above carbinol or chloride by means of hydriodic and glacial acetic acids (A., 1911, i, 277), forms colourless, prismatic crystals, m. p. 178—179°, and exhibits the normal molecular weight in freezing benzene. When crystallised from benzene, it yields crystals containing varying proportions of benzene, possibly owing to the formation of a solid solution.

β-Naphthyldi-ββ-naphthafluorene, $C_{31}H_{20}$, obtained on reduction of the impure tri-β-naphthylchloromethane or by heating the latter above its melting point in an atmosphere of carbon dioxide, forms white, nodular crystals, which melt at 235—237° in a sealed capillary filled with carbon dioxide. Its solutions exhibit intense blue fluorescence and react with magnesium methyl iodide with evolution of methane.

The action of copper-bronze or of Gomberg and Cone's molecular silver (A., 1906, i, 822) on a solution of tri-β-naphthyl-

chloromethane yields a dark violet-red liquid from which dark violet crystals were separated. These have not been analysed, but from their colour and ready oxidisability in the air, and the molecular weights indicated by cryoscopic measurements in benzene and naphthalene, it seems probable that they consist principally of *tri-β-naphthylmethyl*, $C(C_{10}H_7)_3$, and to a small extent of hexa-β-naphthylethane. T. H. P.

Phenyldichloroamine [Di-ω-chloroaniline]. STEFAN GOLDSCHMIDT (*Ber.*, 1913, **46**, 2728—2736).—The existence of di-ω-chloroaniline and ω-chloroaniline as intermediate products in the action of hypochlorites on aniline has already been indicated by Raschig (*Zeitsch. angew. Chem.*, 1907, **20**, 2065; compare also Bamberger, A., 1894, i, 238).

The dichloro-compound has now been isolated by the author by the interaction of aniline and hypochlorous acid in ethereal solution at a low temperature. The ethereal solution of hypochlorous acid is obtained by extracting an aqueous solution of the acid, prepared according to Wohl's method (A., 1907, i, 194), with ether, and rapidly cooling to $-15°$. At the ordinary temperature the solution is unstable and rapidly decomposes, yielding acetaldehyde and hydrogen chloride.

When treated with slightly less than the calculated amount of aniline in ethereal solution at $-15°$ to $-20°$, a yellow solution is obtained, which on evaporation at $-40°$ yields *di-ω-chloroaniline*, $NPhCl_2$, as a viscid oil, having a colour similar to that of potassium dichromate. Although in the free condition, the dichloroamine is very unstable and decomposes explosively when removed from the freezing mixture; in ethereal solution it may be kept for several hours without undergoing appreciable change. It liberates iodine from potassium iodide, and on treatment with ethereal hydrogen chloride rapidly decomposes, with the formation of 2:4-dichloroaniline and 2:4:6-trichloroaniline.

When treated with sodium hydroxide, alcoholic ammonia, sodium thiosulphate, aniline or copper powder, it yields *p*-aminodiphenylamine hydrazobenzene and benzoquinonephenyldi-imine; it is probable that the free radicle NPh: is formed as an intermediate product in these decompositions.

Attempts to prepare ω-chloroaniline by the interaction of molecular quantities of aniline and hypochlorous acid in ethereal solution at a low temperature were unsuccessful.

ωω-2:4:6-*Pentachloroaniline*, prepared from 2:4:6-trichloroaniline and hypochlorous acid in a similar manner to that described above for the preparation of di-ω-chloroaniline, is much more stable than the latter compound, and forms a viscid oil having the colour of diphenylketen. It has a sweet, disagreeable odour resembling that of chlorine, and solidifies at $-80°$ to a glassy mass. When heated, it becomes dark in colour and decomposes explosively with the production of flame. It dissolves in strong sulphuric acid, yielding violet solutions, which become yellow and evolve chlorine, when warmed.

On the addition of potassium iodide in aqueous alcoholic solution to an ethereal solution of the dichloro-compound, iodine (2 atoms) is liberated and 2 : 4 : 6 : 2′ : 4′ : 6′-hexachloroazobenzene is formed; in the presence of hydrochloric acid, 2 : 4 : 6-trichloroaniline is produced, the amount of iodine liberated in this case being twice that given above.

A sketch of the apparatus employed in the preparation of the dichloroamines is given. F. B.

A New Group of Metallic Compounds of the Aromatic Thiocarbamide Series. RUDOLF KRULLA (*Ber.*, 1913, **46**, 2669—2672).—Aryl thiocarbamides are readily prepared by the action of aryl amines on carbon disulphide in the presence of a substance which absorbs the liberated hydrogen sulphide. For this purpose, the author recommends nitrobenzene, which reacts in accordance with the equation: $5NH_2Ph + 3CS_2 + Ph{\cdot}NO_2 = 3(PhNH)_2CS + 2H_2O + 3S$. He has also employed a number of metallic oxides and salts for this purpose, and thus obtained a new series of organometallic derivatives, of which the *tin* compounds have been most completely investigated.

When an alcoholic solution of aniline and carbon disulphide is treated with tin hydroxide, a yellow tin salt, $Sn(S{\cdot}CS{\cdot}NHPh)_2$, is immediately precipitated in a practically pure condition. Like the similar salts of other metals, it is almost insoluble in most solvents except acetone and a mixture of acetone and alcohol, and is readily decomposed when warmed, even in solution. Warm acids immediately convert it into diphenylthiocarbamide and the corresponding metallic salt, whilst prolonged contact with aniline causes a similar change. Lead hydroxide similarly yields a *lead* salt, fine needles, when added to a dilute alcoholic solution of aniline and carbon disulphide; in concentrated solution, however, a dark green coloration is observed, and hydrogen sulphide is evolved with perceptible heat evolution. This appears to be the only case in which hydrogen sulphide is given off.

The *bismuth* salt forms long needles, readily soluble in alcohol.

In the cases of arsenic and antimony, the organometallic derivatives could not be isolated, the thiocarbamide and the metallic sulphide being the products of the action. Copper behaved similarly to the alkali metals, forming xanthates.

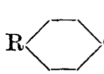
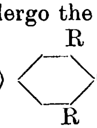
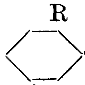
Homologues of aniline which do not contain too many acidic groups react analogously. In these cases it often occurs that lead oxide or hydroxide is active when tin is no longer useful. Organometallic derivatives have been obtained from *p*-toluidine, monomethylaniline, *p*-aminophenol, α- and β-naphthylamine. Diphenylamine did not react. H. W.

New Methods of Preparing Thiocarbanilides. HARRY S. FRY (*J. Amer. Chem. Soc.*, 1913, **35**, 1539—1546).—The method of preparing thiocarbanilides by the interaction of carbon disulphide and an aromatic amine frequently fails in its desired object, and the cause is attributed to the alcohol and potassium hydroxide which are generally introduced into the reaction mixture. By omitting the

alcohol and replacing the alkali by pyridine, the process is so improved that a better yield of a purer product is just as readily obtained. A specimen of di-*o*-chlorophenylthiocarbamide prepared in this manner had m. p. 130·5° (compare Grosch, A., 1899, i, 599).

By applying iodine together with pyridine, the former to remove the hydrogen sulphide from the primary reaction and the latter to combine with the hydriodic acid formed in the secondary reaction of the hydrogen sulphide, excellent yields of the various thiocarbanilide compounds can be obtained; the process in this respect is greatly superior to the previous one. The reaction may be summed up by the equation: $2NH_2R + CS_2 + I_2 + 2C_5H_5N = CS(NHR)_2 + 2C_5H_5N,HI + S$. An excess of carbon disulphide is applied (both in this and in the previous method), and during the action which occurs without warming, pyridine hydriodide separates. The reaction product is steam distilled, and the mixture of thiocarbanilide and sulphur obtained by filtration of the aqueous residue is then separated by extraction with alcohol.

In the preparation by the latter process with iodine it is important that only the theoretical proportions of aniline and iodine should be used. With excess of iodine, the reaction proceeds quantitatively to the formation of a thiocarbimide according to the equation: $NH_2R + CS_2 + I_2 + 2C_5H_5N = RNCS + 2C_5H_5N,HI + S$. Indeed, this reaction provides a convenient method for the estimation of aniline (dissolved in a mixture of carbon disulphide and pyridine) by direct titration with a solution of iodine in carbon disulphide. D. F. T.

Transformation of Phenyl Allyl Ethers into the Isomeric Allylphenols. LUDWIG CLAISEN and OTTO EISLEB (*Annalen*, 1913, **401**, 21—119).—It has been shown (A., 1912, i, 965) that the allyl ethers of several phenols change almost quantitatively by heating, sometimes even below the b. p., to the isomeric allylphenols. In order to test the generality of the change, a large number of aromatic allyl ethers have been examined; all without exception undergo the change. The ethers are of the types (i) $O\cdot C_3H_5$, (ii) $O\cdot C_3H_5$, and (iii) $O\cdot C_3H_5$. Those of type (i) change very easily to *o*-allylphenols, and those of type (ii) readily to *p*-allylphenols. Ethers of type (iii) yield *o*-allylphenols, so the allyl group preferentially enters the nucleus in the ortho-position to the hydroxyl group. The b. p.'s /0 mm. of the allylphenols and also the densities are generally higher than the corresponding constants of the isomeric allyl ethers; exceptions, however, are the allyl ethers of phenols containing a negative substituent in the ortho-position to the hydroxyl group, the b. p.'s of these being higher than the b. p.'s of the isomeric allylphenols.

With suitable ethers changes such as:

$$(o)OMe\cdot C_6H_4\cdot O\cdot C_3H_5 \longrightarrow OMe\cdot C_6H_3(C_3H_5)\cdot OH \longrightarrow OMe\cdot C_6H_3(C_3H_5)\cdot O\cdot C_3H_5 \longrightarrow OMe\cdot C_6H_2(C_3H_5)_2\cdot OH$$

proceed with good yields. Such changes occur particularly easily with allyl ethers of phenolaldehydes and phenolcarboxylic acids and their esters. However, when the aldehyde or carboxyl group occupies a position in the nucleus into which the allyl group desires to enter, it is eliminated as carbon monoxide or carbon dioxide respectively; for example, by alternate heating and allylation, esters of *o*-allyloxybenzoic acid are converted into 2-allyloxy-3 : 5-diallylbenzoates ; the latter then change to 2 : 4 : 6-triallylphenol by hydrolysis and heating.

In addition to the change to *o*-propenylphenols by heating with aqueous potassium hydroxide (*loc. cit.*), *o*-allylphenols are changed in another manner by heating with an acid catalyst, such as pyridine hydrochloride; this change, whereby dihydrocoumarones are produced, $OH\cdot C_6H_4\cdot CH_2\cdot CH:CH_2 \longrightarrow C_6H_4<\overset{CH_2}{\underset{O}{}}>CHMe$, will be described in a future communication.

The aromatic allyl ethers described below are prepared generally by boiling the phenol in acetone with allyl bromide and finely powdered potassium carbonate. For the preparation of the allyl bromide, Merling and Jacobi's hydrogen bromide method (A., 1894, i, 162) is recommended, the yield being 85%. An apparatus is figured and described by which 120—150 grams of hydrogen bromide per hour can be obtained quantitatively from its elements.

Although the change frequently occurs at lower temperatures, the optimum temperature, at which the change is complete usually in a few seconds or minutes, for the conversion of the aromatic allyl ether into the allylphenol is 230—250°. Difficultly volatile phenyl allyl ethers cannot have a b. p. under ordinary pressures, because they change to the allylphenol before the b. p. is reached.

p-*Chlorophenyl allyl ether*, $C_6H_4Cl\cdot OC_3H_5$, b. p. 106—107°/12 mm., D^{15} 1·131, a colourless liquid having an odour of aniseed, is converted by boiling for twenty to twenty-five minutes into 4-*chloro*-2-*allylphenol*, $OH\cdot C_6H_3Cl\cdot C_3H_5$, m. p. 48°, b. p. 256—260° or 124—125°/12 mm., D^{15} 1·171 (supercooled liquid), which develops an olive-green coloration with alcoholic ferric chloride and forms a p-*nitrobenzoate*, m. p. 82°. p-*Bromophenyl allyl ether*, b. p. 126°/14 mm., yields by boiling for a few minutes 4-*bromo*-2-*allylphenol*, m. p. 50°, b. p. 274—280° or 142—144°/14 mm. p-*Nitrophenyl allyl ether*, m. p. 18·5°, b. p. 160°/12 mm., faintly yellow prisms, yields about 40% of 4-*nitro*-2-*allylphenol* at 260°; the latter has m. p. 79°, b. p. 190°/11 mm., and crystallises in colourless leaflets. p-*Benzeneazophenyl allyl ether*,

$$C_6H_5\cdot N_2\cdot C_6H_4\cdot O\cdot C_3H_5,$$

m. p. 52°, yellowish-red needles and prisms, yields by heating in petroleum at 230° about 70% of o-*allylbenzeneazophenol*, m. p. 97—98°, yellow needles and prisms (*benzoate*, m. p. 92°, brownish-red crystals).

p-*Tolyl allyl ether*, b. p. 211—213° or 91°/12 mm., D^{15} 0·967, yields by boiling for one hour 3-*allyl*-p-*cresol*, b. p. 236—238° or 112°/12 mm., D^{15} 1·006 (p-*nitrobenzoate*, m. p. 69°). By heating with potassium hydroxide and water at 140—145°, 3-allyl-*p*-cresol is converted into 3-*propenyl*-p-*cresol*, b. p. 120—124°/11 mm., the *methyl ether* of which is oxidised to 4-methoxy*iso*phthalic acid by potassium permanganate. By allylation, 3-allyl-*p*-cresol yields 3-*allyl*-p-*tolyl allyl ether*, b. p.

123—127°/14 mm., from which is obtained by prolonged heating a very small quantity of a *substance*, b. p. 135—145°/14 mm., which is possibly *4-methyl-3 : 5-diallylphenol.*

Eugenyl allyl ether, b. p. 140°/9 mm., D^{15} 1·024, changes very easily at 230° to o-*allyleugenol*, b. p. 285—287° or 149°/10 mm., D^{15} 1·036, which develops a deep blue to deep green coloration with alcoholic ferric chloride and forms a p-*nitrobenzoate*, m. p. 136°.

The eugenol obtained previously (*loc. cit.*) by the transformation of guaiacyl allyl ether is now definitely proved to be *o*-eugenol (*o*-allylguaiacol), since it yields by treatment with aqueous potassium hydroxide at 170° a propenylguaiacol, m. p. 78°, which is identical with Pauly and Buttlar's *o*-*iso*eugenol, (A., 1911, i, 785). o-*Eugenyl allyl ether*, b. p. 128°/10 mm., D^{15} 1·016, changes at 200° to *o*-allyleugenol, identical with the substance obtained by the transformation of eugenyl allyl ether.

o-*Tolyl allyl ether*, b. p. 205—208° or 85°/12 mm., D^{15} 0·969, is changed by boiling to *2-methyl-3-allylphenol*, b. p. 231—233° or 106—107°/12 mm., D^{15} 1·007, which must contain the allyl group in the ortho-position to the hydroxyl group, since it is also obtained by heating 2-allyloxy-*m*-toluic acid (see below).

m-*Tolyl allyl ether*, b. p. 211—214° or 92—94°/12 mm., D^{15} 0·965, is changed by boiling to *3-methyl-2*(or 4)-*allylphenol*, b. p. 239—240° or 111—112°/11 mm., D^{15} 1·012; since the liquid has been separated into a liquid and a solid, m. p. 53°, possibly both allyl-*m*-cresols are present in it. By further allylation it yields *allyl*-m-*tolyl allyl ether*, which changes at 230° to *3-methyl-2 : 4-diallylphenol*, b. p. 272—274° or 140°/15 mm., to the extent of about 30%.

o-*Nitrophenyl allyl ether*, b. p. 155°/12 mm., is changed by heating at 180° for five hours to *6(?)-allyl*-o-*nitrophenol*, m. p. 9°, b. p. 130—135°/15 mm. (*barium* salt, golden-red leaflets).

a-Naphthyl allyl ether is an oil which cannot be distilled, even under diminished pressure, without partly changing to *2-allyl-a-naphthol*, b. p. 171°/12 mm. (p-*nitrobenzoate*, m. p. 99°). The allylnaphthol, which is obtained in 50—60% yield at 230°, condenses with benzenediazonium chloride to form *4-benzeneazo-2-allyl-a-naphthol*, m. p. 157—158°, red crystals with green reflex.

The behaviour of ethyl *o*-allyloxybenzoate has been recorded (*loc. cit.*). The position of the allyl group in the transformed product is proved by elimination of the carbethoxy group, whereby *o*-allylphenol is obtained. *Methyl* o-*allyloxybenzoate*, b. p. 143°/12 mm., D^{15} 1·118, changes by heating to *methyl 3-allylsalicylate*, b. p. 130°/10 mm., D^{15} 1·120°, with almost explosive violence; the latter gives a bluish-violet coloration with alcoholic ferric chloride, and yields *3-allylsalicylamide*, $C_3H_5{\cdot}C_6H_3(OH){\cdot}CO{\cdot}NH_2$, m. p. 99°, colourless plates, by prolonged keeping with concentrated methyl-alcoholic ammonia. By heating 2-allyloxybenzoic acid, the allyl does not displace the carboxyl group as in the cases recorded below, but enters position 3, as is proved by the conversion of the resulting 3-allylsalicylic acid into *o*-allylphenol at 300°. *o*-Allylphenol condenses with benzenediazonium chloride to form the benzeneazo-*o*-allylphenol mentioned above. *2-Methoxy-3-allylbenzoic acid*, m. p. 53°, is obtained by hydrolysing

the methyl ester, and *2-acetoxy-3-allylbenzoic acid*,

$$C_3H_5\cdot C_6H_3(OAc)\cdot CO_2H,$$

m. p. 96°, colourless needles, by boiling 3-allylsalicylic acid with acetic anhydride and potassium acetate.

Methyl 2-allyloxy-3-allylbenzoate, b. p. 152—162°/9 mm., obtained by heating methyl 3-allylsalicylate with allyl bromide and methyl alcoholic sodium methoxide, yields *2-allyloxy-3-allylbenzoic acid*, m. p. 57°, by hydrolysis. By heating at about 250—260°, the acid is converted into *3 : 5-diallylsalicylic acid*, m. p. 99°, and *2 : 6-diallylphenol*, b. p. 256—258°, whilst the methyl ester yields *methyl 3 : 5-diallylsalicylate*, b. p. 155—165°/9 mm., which develops a dark blue coloration with ferric chloride. *3 : 5-Diallylsalicylic acid*, m. p. 99°, colourless needles, gives an indigo blue colour with ferric chloride, and forms an *acetyl* derivative, m. p. 94°.

The allylation of methyl 3 : 5-diallylsalicylate yields *methyl 2-allyloxy-3 : 5-diallylbenzoate*, b. p. 180—182°/10 mm. This ester decomposes completely by heating under ordinary pressure, but the corresponding *acid*, m. p. 55°, is converted into *2 : 4 : 6-triallylphenol*, b. p. 293—295° or 152—153°/10 mm., D^{15} 0·978 (*phenylcarbamate*, m. p. 97°).

Methyl 2-allyloxy-3-methylbenzoate, b. p. 130—140°/10 mm., is converted by heating into *methyl 2-hydroxy-3-methyl-5-allylbenzoate*, b. p. 275—290°, whilst *2-allyloxy-3-methylbenzoic acid*, m. p. 59°, yields chiefly *2-methyl-3-allylphenol*, b. p. 231—233°, *2-hydroxy-3-methyl-5-allylbenzoic acid*, m. p. 127—129°, being obtained as a by-product.

Ethyl p-*allyloxybenzoate*, b. p. 156°/10 mm., is changed at 220—250° to *ethyl 4-hydroxy-3-allylbenzoate*, m. p. 78°, b. p. 185°/9 mm., the hydrolysis of which yields *4-hydroxy-3-allylbenzoic acid*, m. p. 128°.

4-Allyloxybenzoic acid, m. p. 162°, crystallises in colourless plates and leaflets. By heating with concentrated aqueous potassium hydroxide at 180°, 4-hydroxy-3-allylbenzoic acid is converted into *4-hydroxy-3-propenylbenzoic acid*, m. p. 169°.

Ethyl 4-allyloxy-3-allylbenzoate, b. p. 176°/9 mm., obtained by the allylation of ethyl 4-hydroxy-3-allylbenzoate (corresponding acid, $C_{13}H_{14}O_3$, m. p. 140°), is easily converted into *ethyl 4-hydroxy-3 : 5-diallylbenzoate*, m. p. 94°, b. p. 184—194°/9 mm., at 220—230°. *4-Hydroxy-3 : 5-diallylbenzoic acid* has m. p. 108°. By allylation its ester is converted into *ethyl 4-allyloxy-3 : 5-diallylbenzoate*, b. p. 190°/10 mm., which decomposes when heated under ordinary pressure; the *acid*, $C_{16}H_{18}O_3$, m. p. 97°, however, is converted into 2 : 4 : 6-triallylphenol quantitatively at 300°.

2-Allyloxybenzaldehyde, b. p. 130°/10 mm., D^{15} 1·094, obtained almost quantitatively by boiling salicylaldehyde with allyl bromide and potassium carbonate in absolute alcohol, changes at 220—230° to *3-allylsalicylaldehyde*, b. p. 245·5—246° or 111°/11 mm., D^{15} 1·098, which develops a bluish-violet coloration with alcoholic ferric chloride, forms a *copper* salt, $Cu(C_{10}H_9O_2)_2$, m. p. 181°, olive-brown needles, and *ferric* salt, $Fe(C_{10}H_9O_2)_3$, m. p. 110—111°, black crystals, condenses with benzenediazonium chloride in alkaline solution to form *benzene-azo-3-allylsalicylaldehyde*, $C_6H_5N_2\cdot C_6H_2(OH)(C_3H_5)\cdot CHO$, m. p. 71°, yellow needles or prisms, and forms an *aldoxime*,

$$C_3H_5\cdot C_6H_3(OH)\cdot CH{:}NOH,$$

m. p. 79°. The oxime is converted by acetyl chloride into the *acetyl*

derivative, $C_3H_5\cdot C_6H_3(OH)\cdot CH\colon NOAc$, m. p. 58° (from which the *nitrile* is obtained by heating), and the *hydrochloride*,

$$C_3H_5\cdot C_6H_3(OH)\cdot CH\colon NOH,HCl.$$

By methylation by the potassium carbonate method, 3-allylsalicylaldehyde is converted into *2-methoxy-3-allylbenzaldehyde*, b. p. 128°/9 mm., which is oxidised to 2-methoxy-3-allylbenzoic acid by alkaline hydrogen peroxide. The formation of this acid is the proof that the allyl group is in position 3 in the allylsalicylaldehyde obtained by the transformation of 2-allyloxybenzaldehyde.

2-Allyloxy-3-allylbenzaldehyde, b. p. 145—147°/11 mm., obtained by the allylation of 3-allylsalicylaldehyde, is converted at 200° into a 2 : 6-diallylphenol (75%) and *3 : 5-diallylsalicylaldehyde*, b. p. 138—143°/10 mm. (*semicarbazone*, m. p. 154—156°). 2 : 6-Diallylphenol condenses with benzenediazonium chloride to form *4-benzeneazo-2 : 6-diallylphenol*, m. p. 37°, reddish-yellow prisms.

2-Allyloxybenzyl alcohol, $C_3H_5O\cdot C_6H_4\cdot CH_2\cdot OH$, b. p. 133—150°/9 mm., obtained by the allylation of saligenin, yields formaldehyde and resinous products by heating.

4-Allyloxybenzaldehyde, b. p. 142°/10 mm., changes violently at 260—270°, and yields about 66% of *4-hydroxy-3-allylbenzaldehyde*, m. p. 66°, b. p. 179°/9 mm. By allylation, the latter yields *4-allyloxy-3-allylbenzaldehyde*, b. p. 164°/10 mm., which changes at 250° to *4-hydroxy-3 : 5-diallylbenzaldehyde*, m. p. 67·5°, b. p. 185—190°/10 mm., to the extent of about 66%. This in its turn, by allylation, yields *4-allyloxy-3 : 5-diallylbenzaldehyde*, which even by distillation under low pressures loses carbon monoxide and is converted into 2 : 4 : 6-triallylphenol.

The behaviour of *2-allyloxy-3-methoxybenzaldehyde* (o-*vanillin allyl ether*), b. p. 156—160°/12 mm., obtained by the allylation of *o*-vanillin, is particularly interesting. By heating at 170—240°, it yields mainly *o*-eugenol, carbon monoxide being eliminated; in addition, however, *2-hydroxy-3-methoxy-5-allylbenzaldehyde* (*5-allyl-*o*-vanillin*), m. p. 48—49°, pale yellow crystals, and *4-hydroxy-3-methoxy-5-allylbenzaldehyde* (*5-allylvanillin*), m. p. 86°, b. p. 173°/9 mm., are formed. 5-Allyl-*o*-vanillin is almost odourless, develops a dark blue coloration with alcoholic ferric chloride, dissolves in 10% aqueous sodium carbonate, forms a *semicarbazone*, m. p. 195°, and in alcohol reacts with concentrated aqueous ammonia to form an *imino*-derivative,

$$C_3H_5\cdot C_6H_2(OMe)(OH)\cdot CH\colon NH,$$

m. p. 114°, yellow needles. By allylation, it is converted into *3-methoxy-2-allyloxy-5-allylbenzaldehyde*, which changes at 170—285° into *o*-allyleugenol.

3-Methoxy-4-allyloxybenzaldehyde (p-*vanillin allyl ether*) changes very vigorously at ordinary pressure, and appreciably even at low pressures, to 5-allylvanillin; at 210—220°, the yield is 80%. *3-Methoxy-4-allyloxy-5-allylbenzaldehyde*, obtained by its further allylation, changes to *o*-allyleugenol by distillation, the amount of carbon monoxide evolved corresponding with an 82% yield. C. S.

Preparation of the Thymyl Ester of *iso*Valeryloxyacetic Acid. J. D. Riedel (D.R.-P. 260471. Compare this vol., i, 63).—*Thymyl chloroacetate*, a yellow oil, b. p. 262°, with a faint odour of thymol, is prepared by the condensation of thymol and chloroacetyl

chloride; when treated with sodium *iso*valerate it furnishes *thymyl isovaleryloxyacetate*, $C_6H_3MePr^\beta \cdot O \cdot CO \cdot CH_2 \cdot O \cdot CO \cdot CH_2 \cdot CHMe_2$, a yellow liquid, b. p. 207—209°/19 mm., D 1·037, and of therapeutic value.

F. M. G. M.

Action of Bromine and of Chlorine on Phenols. Substitution Products, ψ-Bromides, and ψ-Chlorides. XXVI. Action of Bromine on Di-*o*-cresoldimethylmethane [6 : 6′-Dihydroxy-ββ-di-*m*-tolylpropane]. THEODOR ZINCKE, J. KEMPF, and W. UNVERZAGT (*Annalen*, 1913, **400**, 27—47).—*m*- and *p*-Cresols condense with acetone in the presence of hydrogen chloride to form indifferent substances, $C_{20}H_{24}O_2$, which are probably ethers (Zincke and Gaebel, A., 1912, i, 442). *o*-Cresol (7 parts), acetone (1 part), and 0·7 part of hydrochloric acid, D 1·19, react at the ordinary temperature to form 6 : 6′-dihydroxy-ββ-di-*m*-tolylpropane,

$$CMe_2(C_6H_3Me \cdot OH)_2,$$

m. p. 136°, colourless needles, which is quite analogous to *pp*-dihydroxy-ββ-diphenylpropane (Zincke and Grüters, A., 1906, i, 172; Zincke, *ibid.*, i, 737) in its behaviour. It forms a *diacetyl* derivative, $C_{21}H_{24}O_4$, m. p. 88—89°, and reacts with bromine in cold glacial acetic acid to form 5 : 5′-*dibromo*-6 : 6′-*dihydroxy-ββ-di*-m-*tolylpropane*,

$$CMe_2(C_6H_2MeBr \cdot OH)_2,$$

m. p 119—120°, colourless plates or double pyramids (*diacetyl* derivative, m. p. 145°). When treated in the cold with an excess of bromine without a solvent, dihydroxy-ββ-di-*m*-tolylpropane or the preceding dibromo-derivative yields 3 : 4 : 5-tribromo-*o*-cresol, tetrabromo-*o*-cresol (in one experiment a *substance*, $C_{10}H_9Br_5$, m. p. 250—251°), and *ψ-3-bromo-5-pentabromo*iso*propyl*-o-*cresol* (*ψ-hexabromo*-5-iso*propyl*-o-*cresol*), $OH \cdot C{<}{\overset{CBr-CH}{\underset{CMe:CH}{}}}{>}C \cdot CBr(CHBr_2)_2$, m. p. 169—170° (decomp.), colourless, monoclinic prisms, which is insoluble in aqueous sodium hydroxide. The hexabromo-ψ-bromide resembles ψ-heptabromo-*p*-*iso*propylphenol (Zincke and Grüters, *loc. cit.*) in its behaviour, and since the latter has the constitution $OH \cdot C_6H_2Br_2 \cdot CBr(CHBr_2)_2$ (Zincke, A., 1912, i, 443), ψ-hexabromo-5-*iso*propyl-*o*-cresol probably has the constitution recorded above; it certainly contains only one bromine atom in the benzene nucleus. It readily yields an *acetyl* derivative, $C_{12}H_{10}O_2Br_6$, m. p. 135—136°, stout plates, by treatment with acetic anhydride and concentrated sulphuric acid. By the action of alcohol and 2*N*-sodium hydroxide at the ordinary temperature, the acetyl derivative is converted into 3-*bromo*-5-*tetrabromo*iso*propenyl*-o-*cresol*, $OH \cdot C{<}{\overset{CBr-CH}{\underset{CMe:CH}{}}}{>}C \cdot C(CHBr_2):CBr_2$, m. p. 94—95°, which forms an *acetyl* derivative, $C_{12}H_9O_2Br_5$, m. p. 114—115°, and *methyl ether*, $C_{11}H_9OBr_5$, m. p. 110—111°. By oxidation with boiling dilute nitric acid and silver nitrate, the methyl ether is converted into 3-*bromo*-2-*methoxy*-m-*toluic acid*, $C_9H_9O_3Br$, m. p. 206—207°, the formation of which proves the presence of only one bromine atom in the benzene nucleus of the methyl ether and, therefore, also in that of the hexabromo-ψ-bromide.

ψ-3-Bromo-5-pentabromo*iso*propyl-*o*-cresol, dissolved in acetone, is

converted by careful treatment with water at the ordinary temperature into *3-bromo-5-tetrabromo*iso*propylidenetoluquinone*,

$$\mathrm{CO}{<}{\mathrm{CBr{:}CH} \atop \mathrm{CMe{:}CH}}{>}\mathrm{C{:}C(CHBr_2)_2},$$

m. p. 180—181°, golden-yellow prisms, which is quite stable. It is reconverted into the hexabromo-ψ-bromide by hydrogen bromide in glacial acetic acid, yields a *diacetate*,

$$\mathrm{OAc{\cdot}C}{<}{\mathrm{CBr{-}CH} \atop \mathrm{CMe{:}CH}}{>}\mathrm{C{\cdot}C(CHBr_2)_2{\cdot}OAc},$$

m. p. 160—161°, colourless needles, by treatment with acetic anhydride and concentrated sulphuric acid, and is converted into *3-bromo-5-tetrabromomethoxy*iso*propyl*-o-*cresol*,

$$\mathrm{OH{\cdot}C}{<}{\mathrm{CBr{-}CH} \atop \mathrm{CMe{:}CH}}{>}\mathrm{C{\cdot}C(CHBr_2)_2{\cdot}OMe},$$

m. p. 100—101°, colourless prisms (*acetyl* derivative, $C_{13}H_{13}O_3Br_5$, m. p. 163°), by boiling methyl alcohol and a few drops of concentrated sulphuric acid.

The *phenol-alcohol*, $\mathrm{OH{\cdot}C}{<}{\mathrm{CBr{-}CH} \atop \mathrm{CMe{:}CH}}{>}\mathrm{C{\cdot}C(CHBr_2)_2{\cdot}OH}$, m. p. 126°, colourless needles or prisms, corresponding with the preceding diacetate, cannot be prepared from the hexabromo-ψ-bromide or from the toluquinone by the addition of water, but is obtained from the latter in a curious manner by the action of glacial acetic acid and fuming sulphuric acid (20% SO_3) on the water-bath, water being subsequently added to the solution.

3-Bromo-5-tribromo*iso*propenyl-o-cresol is produced by the reduction of 3-bromo-5-tetrabromo*iso*propylidenetoluquinone by stannous chloride solution and hot glacial acetic acid, but has only been identified in the form of its *acetate*,

$$\mathrm{OAc{\cdot}C}{<}{\mathrm{CBr{-}CH} \atop \mathrm{CMe{:}CH}}{>}\mathrm{C{\cdot}C(CHBr_2){:}CHBr},$$

m. p. 90—91°, rhombic prisms or plates.

By shaking with aniline and glacial acetic acid, the hexabromo-ψ-bromide or the toluquinone is converted into *pentabromo*iso*propyl*-o-*cresol-ψ-anilide*, $C_{16}H_{14}ONBr_5$, m. p. 128—129°, which is given the quinonoid constitution, $\mathrm{CO}{<}{\mathrm{CBr{:}CH} \atop \mathrm{CMe{:}CH}}{>}\mathrm{CH{\cdot}C(CHBr_2)_2{\cdot}NHPh}$, on account of its insolubility in alkalis. It forms colourless crystals which easily become yellow, and dissolves in boiling methyl or ethyl alcohol or glacial acetic acid; the yellow solutions deposit a *substance*, m. p. 223—224° (decomp.), intensely yellow prisms, which forms an orange-yellow *sodium* salt. The nature of the yellow substance has not yet been ascertained.

C. S.

[Preparation of Compounds containing Selenium.] AUGUST VON WASSERMANN and ERNST WASSERMANN (D.R.-P. 261793).—When a solution of *p*-nitrosodimethylaniline in concentrated hydrochloric acid solution is treated with hydrogen selenide a bluish-red scum is formed; when this *leuco*-derivative (which was not isolated) is oxidised and subsequently treated with an aqueous solution of zinc chloride, a double

compound with zinc chloride is precipitated; this "selenoazine blue" is an analogue of methylene-blue, and can be employed as a dye and for the introduction of selenium into animal tissues; it forms a glistening, dark green bronze powder, readily soluble in water, sparingly so in alcohol. F. M. G. M.

Action of Methyl Iodide on Aromatic Tellurides. Karl Lederer (*Annalen*, 1913, **399**, 260—271).—Aromatic tellurides, unlike aromatic sulphides and selenides, readily react additively with methyl iodide, forming diarylmethyltelluronium iodides. From these, other salts can be prepared, specially characteristic being the sparingly soluble picrates, chromates, dichromates, and platinichlorides; the chlorides form double salts with the chlorides of mercury, gold, zinc, and copper.

The diarylmethyltelluronium hydroxides, prepared from the iodides by means of moist silver oxide, are extremely hygroscopic, oily liquids which have a strong alkaline reaction, liberate ammonia from its salts, precipitate the heavy metals in the form of their hydroxides, but do not combine with carbon dioxide. Aryl tellurides react with ethyl iodide only to a very small extent.

Phenyl telluride and methyl iodide, after being kept for two days, yield a crystalline *compound*, $TePh_2MeI,MeI$, which is converted by ether into *diphenylmethyltelluronium iodide*, $TePh_2MeI$, m. p. or decomp. 123—124° (bath at 110°), colourless needles (from hot water), which is decomposed by alcohol, as also are the *bromide*, m. p. 137—138°, small prisms, and *chloride*, m. p. 129—130° (decomp.). The *nitrate*, m. p. 168—169°, rhombic plates; *platinichloride*, m. p. 157—158°, microscopic, yellow plates; *chromate*, m. p. 151°, orange-red needles; *dichromate*, decomp. 153°, orange-red, quadratic leaflets; *picrate*, $C_{19}H_{15}O_7N_3Te,H_2O$, m. p. 93—94°, long, yellow needles; *mercurichloride*, $C_{13}H_{13}TeCl,HgCl_2$, m. p. 135—136°, colourless needles, and *zincichloride*, m. p. 149—150°, are described. *Diphenylmethyltelluronium hydroxide* has an odour of piperidine or pyrrolidine, and is decomposed by warm water.

p-Tolyl telluride and methyl iodide, after being kept for five days, yield, after treating the product with ether, *di*-p-*tolylmethyltelluronium iodide*, m. p. 85—86° (decomp.); the *picrate*, m. p. 157—158°, yellow needles; *mercurichloride*, m. p. 149—150° (decomp.); *chloride*, *bromide*, m. p. 73—74°; *dichromate*, m. p. 54—55°; *chromate*, m. p. 51—52°; *platinichloride*, m. p. 104—105°, and *aurichloride*, m. p. 35—36°, have been prepared, but the salts and also the *hydroxide* are not particularly stable, several of the preceding salts certainly being impure.

Di-o-*tolylmethyltelluronium iodide*, m. p. 125—126°, small crystals, is obtained directly from its components after keeping for fourteen days. The *bromide*, m. p. 134—135° (bath at 120°), small prisms; *nitrate*, m. p. 155—157°, hexagonal plates; *picrate*, m. p. 143—144°; *platinichloride*, m. p. 186°, microscopic, yellow prisms; *dichromate*, m. p. 171—172° (decomp.), orange-red needles; *chromate*, m. p. 161—162°, small, yellow prisms; *mercurichloride*, m. p. 134—135° (decomp.), felted needles, and basic *zincichloride*, $TeMe(C_7H_7)_2Cl,ZnCl\cdot OH$, micro-

scopic prisms, have been prepared; the *hydroxide* is not hygroscopic, and is comparatively stable, not being decomposed by boiling water.

C. S.

Oxonium Compounds. GEORGE L. STADNIKOFF (*Ber.*, 1913, **46**, 2496—2503. Compare A., 1912, i, 109, 971).—In connexion with the conclusion drawn by the author from the occurrence of tetraphenylethane and *aa*-diphenylbutane after the action of water on the reaction product of diphenylmethyl butyl ether and magnesium propyl iodide, that the additive compound of the latter two substances is of the structure $\frac{C_4H_9}{CHPh_2}>O<\frac{Pr}{MgI}$, it may be objected that the formation of the tetraphenylethane and *aa*-diphenylbutane possibly preceded the addition of water.

To meet this objection, diphenylmethyl butyl ether has been allowed to react with various magnesium alkyl haloids in solution in ether (which does not prevent the formation of such additive compounds) for considerable periods. The procedure was to add the diphenylmethyl butyl ether to the cooled ethereal solution of the magnesium alkyl haloid and to find the quantities of any gaseous products evolved on boiling, and of the total organic products obtained on subsequently treating the cooled reaction product with water.

There are three main directions of decomposition of the ether additive compound which is believed to be the primary product on the addition of water: (1) the regeneration of diphenylmethyl butyl ether; (2) the formation of tetraphenylethane, and (3) the production of a *aa*-diphenyl-substituted paraffin hydrocarbon.

With diphenylmethyl butyl ether and magnesium propyl iodide all the above reactions occur, although the relative amounts of the different products vary from those obtained earlier (A., 1912, i, 971) with the same Grignard reagent in the absence of ethyl ether. The results, however, confirm the author's views.

Diphenylmethyl butyl ether was allowed to form additive compounds also with magnesium ethyl iodide and magnesium methyl iodide; the former gave similar results to the propyl compound; the latter gave as hydrocarbon products only methane and tetraphenylethane.

Magnesium propyl iodide either in benzene or in ethereal solution when treated with diphenylmethyl *iso*amyl ether, and subsequently with water, gave propane and unaltered diphenylmethyl *iso*amyl ether.

In each case, except with the methyl Grignard reagent, a quantity of the corresponding ethylenic hydrocarbon was evolved during the heating after the addition of the "mixed" ether. D. F. T.

The Isomerism of Tri-α-naphthylcarbinol. ALEXEI E. TSCHITSCHIBABIN (*Ber.*, 1913, **46**, 2554—2556).—The author is of opinion that of the so-called isomeric forms of tri-α-naphthylcarbinol described by Schmidlin and Bergmann (this vol., i, 46), the more stable is in reality merely the ether-free carbinol described earlier by himself (A., 1911, i, 969), and is not identical with the stable "isomeride" obtained by Schmidlin and Massini (A., 1909, i, 563), which he has

shown to be an oxidation product, namely, α-naphthyldi-αα-naphthafluoryl alcohol. This view receives further confirmation from the fact that the free tri-α-naphthylcarbinol when dissolved in amyl acetate and treated with much ether is slowly deposited in needles or prisms of the easily oxidisable substance containing ether of crystallisation. The ether-free carbinol has a higher m. p., namely, 160—180° (decomp.), than that recorded hitherto.

There is consequently here no case of isomerism unless the compound containing ether of crystallisation is regarded as a distinct isomeride of the ether-free substance. D. F. T.

Aromatic Selenium Compounds. II. RUDOLF LESSER and R. WEISS (*Ber.*, 1913, **46**, 2640—2658. Compare A., 1912, i, 642).—An extended account of the results of attempts to prepare compounds containing a selenium atom in place of a sulphur atom, a preliminary note of which has previously appeared (*loc. cit.*).

Diphenyldiselinide-di-*o*-carboxylic acid, $Se_2(C_6H_4{\cdot}CO_2H)_2$, is more conveniently prepared by the addition of a diazotised solution of anthranilic acid to a solution of potassium or sodium diselinide in an atmosphere of carbon dioxide. After decomposition of the diazo-compound by heat, the acids are liberated by addition of mineral acid to the hot solution. The crude diphenyldiselinide-di-*o*-carboxylic acid is freed from diphenylselinide-di-*o*-carboxylic acid by digestion with glacial acetic acid, which leaves the former undissolved.

o-*Methylselenolbenzoic acid*, $SeMe{\cdot}C_6H_4{\cdot}CO_2H$, long needles, m. p. 180—181°, is obtained in practically quantitative yield when an alkaline solution of sodium *o*-selenolbenzoate is shaken with methyl sulphate. The corresponding *methyl* ester, m. p. 64—66°, is best obtained by the action of methyl iodide on the *silver* salt, and, in contrast with methyl *o*-methylthiolbenzoate, is odourless. o-*Benzoylselenolbenzoic acid*, $SeBz{\cdot}C_6H_4{\cdot}CO_2H$, has m. p. 163—164°.

o-Selenonbenzoic acid, $SeO_3H{\cdot}C_6H_4{\cdot}CO_2H$, is a very strong acid, the salts of which are not decomposed by dilute nitric acid. It has not been obtained in the crystalline state, but yields a *barium* salt, $C_7H_4O_5SeBa$, which separates from water in colourless, anhydrous needles. An aqueous solution of the acid is transformed by hydrochloric acid into o-*seleninbenzoic acid*, m. p. 228—229° (decomp.), which is also obtained by the oxidation of diphenyldiselenide-di-*o*-carboxylic acid by nitric acid, or a mixture of nitric and sulphuric acids. When heated at 130—140° until constant in weight, it is transformed into the *anhydride*, $O(SeO{\cdot}C_6H_4{\cdot}CO_2H)_2$, without change in m. p.

When diphenyldiselenide-di-*o*-carboxylic acid is warmed with thionyl chloride and excess of the latter removed, a crystalline residue is obtained which can be separated by means of light petroleum into two portions. The smaller of these, m. p. 173—174°, is the normal chloride, $C_{14}H_8O_2Cl_2Se_2$, whilst the larger, m. p. 65—66°, consists of a *compound* of this substance and hydrogen chloride, and has the composition $C_{14}H_{10}O_2Cl_4Se_2$. When the latter is boiled with methyl alcohol, the *hydrochloride* of *methyldiphenyl-diselenide-di-*o*-dicarboxylate*, $C_{16}H_{16}O_4Cl_2Se_2$, yellow needles, m. p. 74—75°, is obtained, which, when treated with warm sodium hydroxide, is converted into the corresponding *ester*, m. p. 143—144°. The *hydrochloride* of the *ethyl*

ester, m. p. 91—92°, is similarly formed and converted in the same manner into the *ethyl* ester, m. p. 129—130°. The normal esters can also be prepared by the action of the requisite alcohol on the normal chloride or on the free acid in the presence of hydrogen chloride.

Phosphorus pentachloride resembles thionyl chloride in its action on the free acid, yielding, however, a less pure product which contains a rather greater proportion of the normal chloride.

Pure diphenylselenide-di-*o*-carboxylic acid has m. p. 234—235° (instead of 228—229° as previously given). Thionyl chloride converts it into the corresponding normal *chloride*, lemon-yellow crystals, m. p. 107—108°, which gradually decomposes when preserved without, however, yielding a uniform product. Boiling methyl and ethyl alcohols transform the chloride into the *methyl* ester, m. p. 70—71°, and the *ethyl* ester, m. p. 64—65°, respectively. The *amide* forms colourless plates, m. p. 212—213°.

When warmed with concentrated sulphuric acid on the water-bath, diphenylselenide-di-*o*-carboxylic acid yields two products which can be separated by means of sodium hydroxide. The soluble portion consists of *selenoxanthone-*o*-carboxylic acid*, $C_6H_4<\genfrac{}{}{0pt}{}{CO}{Se}>C_6H_3\cdot CO_2H$, which sublimes from 250° in yellow needles and decomposes at 290—300°. In the dry state it is stable, but, when dissolved, readily eliminates carbon dioxide, for example, when a hot solution of its alkali salt is acidified. Attempts to transform it into the corresponding selenoxanthone by loss of carbon dioxide were, however, unsuccessful, benzophenone-selenone, $C_6H_4<\genfrac{}{}{0pt}{}{CO}{SeO_2}>C_6H_4$, being invariably produced. This substance also constitutes the portion obtained in the above action which is insoluble in alkali and is obtained as by-product of the action of thionyl chloride on diphenylselenide-di-*o*-carboxylic acid. It forms large, glassy prisms, m. p. 317—318° (decomp.), and sublimes partly undecomposed from about 260°. It thus differs remarkably from the benzophenoneselenone described by Doughty and Elder (this vol., i, 962) for which the m. p. 183° is given.

Acetic anhydride is without action on diphenylselenide-di-*o*-carboxylic acid, whilst potassium permanganate, in neutral or alkaline solution, converts it into the selenone.

o-Carboxyphenylselenolacetic acid is readily converted into its *methyl* ester, leaflets, m. p. 62—63°, by means of methyl alcohol and hydrogen chloride. The ethyl ester is oily.

When a diazotised solution of *m*-aminobenzoic acid is added to a solution of potassium hydrogen selenide or of potassium diselenide under the conditions described for anthranilic acid, *diphenylselenide-di-*m*-carboxylic acid* is produced, the diselenide acid being apparently not formed. It has m. p. 296—297°, and sublimes from about 260°. Concentrated sulphuric acid dissolves it with a yellow colour; fuming sulphuric acid with an intense bluish-green colour. Potassium permanganate oxidises it in the form of its salts to *diphenylselenon-di-*m*-carboxylic acid*, colourless prisms, which becomes yellow at about 255°, and has m. p. 262—263° (decomp.).

p-Aminobenzoic acid, when similarly treated, yields a difficultly separable mixture of the *p*-diselenide and selenide acids. *Diphenyl-*

diselenide-di-p-carboxylic acid is a pale yellow, crystalline powder, m. p. 314—315°. *Diphenylselenide-di-p-carboxylic acid*, two preparations of which had m. p. 312—313° and 315—316°, resembles the above acid so closely that it can only be distinguished from it by ultimate analysis.

Hydroxyselenonaphthen reacts with 5-bromoisatin in alcoholic solution in the presence of piperidine to form "*2-selenonaphthen-[5-bromo-3-indole]-indigo*" (*3'-bromoindoxyl-2-selenonaphthen-3-one*),

$$C_6H_4<{CO \atop Se}>C:C<{CO \atop C_6H_3Br}>NH,$$

red, silky needles, which sublime at about 260°, have m. p. about 355°, and are soluble in fuming sulphuric acid, yielding a sulphonic acid which is soluble in water. Similarly, *3'-methylindoxyl-2-selenonaphthen-3-one* (red needles which sublime at about 250°, and have m. p. approximately 325—330°) is obtained from methylisatin, whilst by heating molecular quantities of isatin chloride and hydroxyselenonaphthen in benzene solution, "*2-selenonaphthen-2-indole-indigo*" [*2'-indoxyl-2-selenonaphthen-3-one*], $C_6H_4<{CO \atop NH}>C:C<{CO \atop Se}>C_6H_4$, is formed. It consists of blackish-violet needles, which sublime undecomposed at approximately 250°, and have m. p. about 335°.

A series of condensation products of hydroxyselenonaphthen with aldehydes and fluorenone has been prepared by boiling molecular quantities of their components in methyl- or ethyl-alcoholic or glacial acetic acid solution in the presence of a few drops of concentrated hydrochloric acid. In general, the compounds are rapidly precipitated in good yield. They dissolve unchanged in concentrated sulphuric acid, but are converted by the fuming acid into sulphonic acids which dissolve in water. The following compounds have been prepared: Glyoxal yields the *substance*,

$$C_6H_4<{CO \atop Se}>C:CH\cdot CH:C<{CO \atop Se}>C_6H_4,$$

violet needles, m. p. 299—300°. Heptaldehyde and citral give oily products. *Furylidene-2-selenonaphthen-3-one*,

$$C_6H_4<{CO \atop Se}>C:CH\cdot C_4H_3O,$$

orange needles, m. p. 145—147°, *p-nitrobenzylidene-2-selenonaphthen-3-one*, reddish-golden needles or rods, m. p. 243—244°; *2:4-dinitrobenzylidene-2-selenonaphthen-3-one*, which exists in two modifications, red or orange needles, both having m. p 226—227° (decomp.); *o-hydroxybenzylidene-2-selenonaphthen-3-one*, brownish-yellow rods, m. p. 206—207° (decomp.); *o-carboxybenzylidene-2-selenonaphthen-3-one*, $C_6H_4<{CO \atop Se}>C:CH\cdot C_6H_4\cdot CO_2H$, yellow plates, m. p. 226—227°; *4-hydroxynaphthylidene-2-selenonaphthen-3-one*, red needles, m. p. 244—248°; *2-methoxynaphthylidene-2-selenonaphthen-3-one*, yellow crystals, m. p. 127—128°; 2-hydroxynaphthaldehyde yields a *compound*, $C_{27}H_{16}O_2Se_2$, pale red crystals, m. p. 210—211° after previous darkening, which does not dissolve in sodium hydroxide, and appears to be derived from two molecules of hydroxyselenonaphthen and one of the aldehyde. Terephthalaldehyde yields the *substance*, $C_6H_4<{CO \atop Se}>C:CH\cdot C_6H_4\cdot CH:C<{CO \atop Se}>C_6H_4$, orange needles, which sub-

lime at about 296°, and have m. p. approximately 330°, whilst β-anthraquinonealdehyde gives the *compound*, $C_6H_4<{CO \atop Se}>C:CH\cdot C_{14}H_7O_2$, orange-red needles, subliming at about 270°, and having m. p. 348—349°. Prolonged warming with fluorenone in alcohlic solution yields the *substance*, $C_6H_4<{CO \atop Se}>C:C<{C_6H_4 \atop C_6H_4}$, deep red crystals, m. p. 169—171°.

p-*Nitrobenzeneazo-3-hydroxyselenonaphthen*,

$$C_6H_4<{C(OH) \atop Se}>C\cdot N:N\cdot C_6H_4\cdot NO_2,$$

reddish-brown crystals, m. p. 239—241° (decomp.), is obtained by the addition of *p*-nitrobenzene diazonium chloride to a solution of the sodium salt of hydroxyselenonaphthen in the presence of sodium acetate. H. W.

Diphenyleneacetic Acid [Fluorene-9-carboxylic Acid]. WILHELM WISLICENUS and ALEXANDER RUTHING (*Ber.*, 1913, **46**, 2770—2771).—An aqueous solution of fluorene-9-carboxylic acid and sodium hydroxide (1 mol.) remains clear when kept in an atmosphere of hydrogen. In the presence of oxygen, it rapidly becomes turbid and deposits fluorenone; the yield of the latter is about 20% of the theoretical, and is increased to about 50% when another mol. of sodium hydroxide is present. At higher temperatures the decomposition proceeds differently, an aqueous solution of sodium fluorene-9-carboxylate at the b. p. yielding fluorene and sodium carbonate, most readily when sodium hydroxide has been added. C. S.

Syntheses by means of Ethyl Diphenyleneacetate [Fluorene 9-carboxylate]. WILHELM WISLICENUS and WILLY MOCKER (*Ber.*, 1913, **46**, 2772—2793).—The *potassium* derivative of ethyl fluorene-9-carboxylate is best obtained by adding rather more than the theoretical quantity of alcohol to ethyl fluorene-9-carboxylate and potassium (1 atom) in dry ether, a current of hydrogen being passed through the apparatus. It is thus obtained as a yellow, microcrystalline powder containing EtOH, which decomposes rapidly in moist air, and is converted in dry air into the additive *compound*,

$$\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}>C(OK)\cdot CO_2Et,EtOH,$$

from which ethyl 9-hydroxyfluorene-9-carboxylate, m. p. 93°, is obtained by the action of sulphuric acid. The *sodium* derivative,

$$C_{16}H_{13}O_2Na,EtOH,$$

of ethyl fluorene-9-carboxylate is prepared in a similar manner and reacts in the same manner with atmospheric oxygen. In consequence of the easy oxidisability of the alkali derivatives of ethyl fluorene-9-carboxylate, syntheses with these reagents must be effected in an atmosphere of hydrogen, otherwise 9-hydroxyfluorene-9-carboxylic acid is the final product.

The following syntheses have been performed. By treatment with the calculated amount of iodine, a solution of the alkali derivative, prepared as above, readily yields ethyl bisdiphenylenesuccinate [9 : 9′-difluorene-9 : 9′-dicarboxylate] (Staudinger, A.,

1906, i, 824), which cannot be hydrolysed to the corresponding acid. The solution of the potassium derivative and methyl iodide gives a nearly quantitative yield of *ethyl α-diphenylene-propionate* [*9-methylfluorene-9-carboxylate*], $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>\!CMe\cdot CO_2Et$, b. p. 188—190°/14 mm., m. p. 33°, which, however, is not obtained quite pure by this method. 9-*Methylfluorene*-9-*carboxylic acid* yields 9-methylfluorene at 250°; the latter has b. p. 154—156°/15 mm. and m. p. 45°. *α-Diphenylenebutyric* [*9-ethylfluorene-9-carboxylic*] *acid*,

$$\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>\!CEt\cdot CO_2H,$$

obtained in a similar manner by means of ethyl iodide, forms an *ethyl* ester, b. p. 200—205°/14—15 mm., and decomposes at 230—240° into carbon dioxide and 9-ethylfluorene. The latter is a liquid, b. p. 169—171°/14 mm., not a solid as stated by Wislicenus and Densch, and does not react with potassium even at 250°. 9-*Allylfluorene*-9-*carboxylic acid*, $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>\!C(CO_2H)\cdot CH_2\cdot CH\colon CH$, colourless prisms containing $\frac{1}{2}C_6H_6$ (*ethyl* ester, b. p. 200—203°/14 mm.), yields 9-*allyl-fluorene*, b. p. 174—176°/15 mm., at 240—250°. 9-*Benzylfluorene*-9-*carboxylic acid*, $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>\!C(CO_2H)\cdot CH_2Ph$, m. p. 201—202°, colourless leaflets (*ethyl* ester, m. p. 90—91°), yields 9-benzylfluorene at 240—250°; the latter is also produced by boiling the ester with alcoholic potassium hydroxide.

Ethyl αα-bisdiphenyleneadipate [9 : 9′-*ethylenedifluorene*-9 : 9′-*dicarboxylate*], $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>\!C\!<\!\begin{matrix}CH_2\text{——}CH_2\\CO_2Et\ \ CO_2Et\end{matrix}\!>\!C\!<\!\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}$, m. p. 179—180°, colourless needles, prepared by the aid of ethylene dibromide, yields, by hydrolysis with alcoholic sodium hydroxide at the ordinary temperature and subsequent acidification, 9 : 9′-*ethylenedifluorene*-9 : 9′-*dicarboxylic acid*, m. p. about 260° (decomp.), *αδ-bisdiphenylenebutane* [9 : 9′-*ethylenedifluorene*], $C_2H_4(C_{13}H_9)_2$, colourless needles, being produced when the hydrolysis is effected on the water-bath.

Iodobenzene does not react with the solution of the potassium derivative of ethyl fluorene-9-carboxylate even at 150—180°. 1-Bromo-2 : 4-dinitrobenzene, however, yields ethyl 9-op-*dinitrophenylfluorene-carboxylate*, $C_{13}H_9(CO_2Et)\cdot C_6H_3(NO_2)_2$, m. p. 130—131°, faintly yellow crystals, which cannot be hydrolysed to the corresponding acid. In a similar manner, ethyl chloroacetate yields *ethyl diphenylene-succinate* [*9-carboxyfluorene-9-acetate*],

$$CO_2Et\cdot C_{13}H_8\cdot CH_2\cdot CO_2Et,$$

m. p. 73—75°, colourless crystals; by hydrolysis at the ordinary temperature, the ester yields the corresponding *acid*, $C_{16}H_{12}O_4$, m. p. 195—196° (decomp.), which is converted at its m. p. into its *anhydride*, $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>\!C\!<\!\begin{matrix}CO\text{--}O\\ \quad\ \ |\\CH_2\cdot CO\end{matrix}$, m. p. 158—159°, b. p. about 255°/16 mm.

Ethyl β-iodopropionate reacts with the solution of the sodium or potassium derivative of ethyl fluorene-9-carboxylate to form, after hydrolysis of the impure ester, *α-diphenyleneglutaric* [*9-carboxyfluorene-*

9-*propionic*] *acid*, $CO_2H\cdot C_{13}H_8\cdot CH_2\cdot CH_2\cdot CO_2H$, m. p. 195—196°, colourless prisms or needles. The acid forms an *ethyl* ester, $C_{21}H_{22}O_4$, b. p. 235—240°/14 mm., yields the *anhydride*,

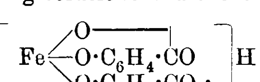
$$\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!\!>C<\!\!\begin{matrix}CH_2\cdot CH_2\\ CO\text{——}O\end{matrix}\!\!>CO,$$

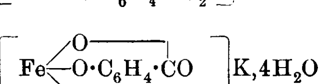
m. p. 175—176°, colourless prisms, by boiling with acetyl chloride, and is converted into γ-*diphenylenebutyric* [*fluorene*-9-*propionic*] *acid*, $C_{16}H_{14}O_2$, m p. 148—149° (*ethyl* ester, b. p. 224—226°/17 mm.), by heating at about 260°.

Ethyl β-benzoyl-α-diphenylenepropionate [9-*phenacylfluorene*-9-*carboxylate*], $CO_2Et\cdot C_{13}H_9\cdot CH_2\cdot COPh$, m. p. 123—124°, obtained by means of ω-bromoacetophenone at about 80°, is converted by the action of aqueous alcoholic sodium hydroxide into *phenyl β-diphenylene-ethyl ketone* [9-*phenacylfluorene*], $C_{12}H_8\cdot CH\cdot CH_2\cdot COPh$, m. p. 96—97°, colourless needles. C. S.

Solubility of Salicylic Acid and of Some Other Substances. EGLIE SAVARRO (*Atti R. Accad. Sci. Torino*, 1913, **48**, 948—959).—Tables are given showing the solubility of salicylic acid at various temperatures, the figures obtained by previous observers being discordant. Some experiments have also been made on isomeric substances (compare Carnelley and Thompson, T, 1888, **53**, 782). The solubilities of the three hydroxybenzoic acids in water at 15° and at 50° increase in the order: ortho, para, meta, whilst those in methyl alcohol follow the order of the melting points: ortho, meta, para. According to the law of Carnelley and Thompson the order of solubilities should be para, meta, ortho. The solubilities in methyl alcohol of four pairs of isomeric pyridine derivatives prepared by Guareschi (*Atti R. Accad. Sci. Torino*, 1900–01, **50**) have also been determined; here the law already mentioned is followed with some exceptions. R. V. S.

Iron Compounds of Phenols. V. Iron Compounds of Salicylic Acid. RUDOLF F. WEINLAND and ALFRED HERZ (*Annalen*, 1913, **400**, 219—268. Compare this vol., i, 458).—The reaction between alkali salicylates and ferric salts in aqueous or alcoholic solution gives rise to very complex iron derivatives of salicylic acid. Their formation is due to the fact that salicylic acid forms, by virtue of its phenolic hydroxyl group, di- and tri-salicylatoferric acids analogous to the catecholferric acids (A., 1912, i, 445), and, by virtue of its carboxyl group, a hexasalicylatotriferric hydroxide analogous to hexabenzoatotriferric hydroxide (A., 1912, i, 854); this complex base can then react with the complex acids to form still more complex salts. In the preparation of the following substances, the concentrations of the reacting solutions and the order of their addition are matters of great importance. All quantities mentioned below are in atomic or molecular proportions.

(I.) 

(II.) 

Salts of Disalicylatoferric Acid (I).—*Potassium disalicylatoferrate* (II), dark copper-red powder, is obtained by adding aqueous ferric chloride to aqueous salicylic acid and potassium hydroxide ($Fe : C_7H_6O_3 : KOH = 1 : 4 : 7$).

Rubidium disalicylatoferrate, dark copper-red powder, is obtained in a similar manner ($Fe : C_7H_6O_3 : RbOH = 1 : 3 : 6$). These two salts form blood-red aqueous solutions, which change to violet by the addition of hydrochloric acid or of ferric chloride, and yield hexasalicylatotriferric monosalicylate (see below) by treatment with dilute acetic acid.

Salts of Trisalicylatoferric Acid, $\left[Fe\overset{O}{\underset{(C_6H_4\cdot CO_2)_3}{}}\right]H_3$.—The gradual addition of very dilute aqueous ferric chloride to concentrated aqueous sodium salicylate produces successively a reddish-yellow, blood-red, and finally violet solution. The blood-red solution contains sodium disalicylatoferrate, and the violet solution a ferric salt of this acid (see below). The reddish-yellow solution contains *sodium trisalicylatoferrate*, which, however, cannot be isolated from aqueous solution. *Potassium trisalicylatoferrate*, $[Fe(C_7H_4O_3)_3]K_3,1\frac{1}{2}H_2O$, brick-red, crystalline powder, is obtained from ferric acetate [of the composition $Fe_6(OAc)_{15}(OH)_3,3H_2O$], potassium salicylate, and potassium hydroxide in 96% alcohol ($Fe : C_7H_6O_3 : KOH = 1 : 4 : 7$). The *rubidium* salt, orange-red, crystalline powder containing $2H_2O$, is obtained in a similar manner. These salts are easily soluble in water, but the solutions rapidly decompose; however, if the alkali salicylate is also present, the solutions can be boiled without decomposition.

The free di- and tri-salicylatoferric acids have not been isolated. The union of the iron with the phenolic oxygen of the acid complex is proved by the fact that ferric acetate, methyl salicylate, and potassium hydroxide ($Fe : C_8H_8O_3 : KOH = 1 : 15 : 3$) in alcoholic solution yield *potassium tetramethylsalicylatoferrate*, $[Fe(C_7H_4O_3Me)_4]K$, reddish-brown, crystalline powder.

Salts of Hexasalicylatotriferric Hydroxide,

$$[Fe_3(O\cdot CO\cdot C_6H_4\cdot OH)_6](OH)_3.$$

—The reddish-yellow, blood-red, and violet solutions obtained, according to the quantities of the reagents used, by the addition of aqueous ferric chloride (at least 1 mol.) to a not too dilute aqueous solution of sodium salicylate (4 mols.) soon yield reddish-brown precipitates. By keeping in the mother liquor, these precipitates soon change to a black, crystalline substance (compare Hopfgartner, A., 1908, i, 891). The reddish-brown substance can be isolated unchanged if ether is added to either solution before the solutions of ferric chloride and sodium salicylate ($Fe : Na = 1 : 3$) are mixed; by shaking, the salicylic acid liberated in the reaction is removed from the aqueous phase, and the precipitate then remains unchanged. The same substance is also obtained unchanged when hot solutions of ferric chloride and sodium salicylate are mixed. It has been isolated as a brown powder containing $3H_2O$, and also as a reddish-brown, crystalline powder containing $2EtOH,2H_2O$. Since the ratio of iron to salicylic acid is 3 : 7 and the substance behaves like hexabenzoatotriferric monobenzoate (A., 1912, i, 854), it is regarded as *hexasalicylatotriferric monosalicylate*, $\left[Fe_3{(O\cdot CO\cdot C_6H_4\cdot OH)_6 \atop (OH)_2}\right]\cdot O\cdot CO\cdot C_6H_4\cdot OH$. A *sesquisalicylate*,

$$\left[Fe_3{(O\cdot CO\cdot C_6H_4\cdot OH)_6 \atop (OH)_2}\right]C_7H_5O_3,\left[Fe_3{(C_7H_5O_3)_6 \atop (OH)}\right](C_7H_5O_3)_2,7H_2O,$$

of the base is obtained as a red, crystalline powder (which rapidly becomes almost black) by treating the preceding substance with a

warm saturated solution of salicylic acid in acetone; chloroform or ethyl alcohol may also be used as the solvent, in the latter case the sesquisalicylate being obtained as a reddish-brown, crystalline powder containing 3EtOH and $9H_2O$.

The ferrisalicylic acid described by Hantzsch and Desch (A., 1902, i, 708) contains acetic acid and is in reality *hexasalicylatotriferric diacetate*, $\left[Fe_3{(O\cdot CO\cdot C_6H_4\cdot OH)_6 \atop (OH)}\right](OAc)_2,3Et_2O$, garnet-red prisms (from ether); by heating at 100°, it changes to the *monoacetate*, $\left[Fe_3{(O\cdot CO\cdot C_6H_4\cdot OH)_6 \atop (OH)_2}\right]\cdot OAc$. Other salts of hexasalicylatotriferric hydroxide have been obtained by the reaction between lithium salicylate and ferric chloride, bromide, or nitrate in alcoholic solution; in some of these reactions a little water must be added. None of these salts contains iron and salicylic acid in a ratio less than 3 : 6; therefore, they are regarded as complex derivatives of the hexasalicylatotriferric base. Thus lithium salicylate and ferric chloride yield, according to the proportions of the reagents, a *chloride salicylate*, $\left[Fe_3{(O\cdot CO\cdot C_6H_4\cdot OH)_6 \atop (OH)}\right]{O\cdot CO\cdot C_6H_4\cdot OH \atop Cl},4\frac{1}{2}H_2O$, red, crystalline powder, or a double *salt* of the chloride and the chloride salicylate,

$$\left[Fe_2{(C_7H_5O_3)_6 \atop (OH)_2}\right]Cl,\left[Fe_3{(C_7H_5O_3)_6 \atop (OH)}\right]{C_7H_5O_3 \atop Cl},H_2O,$$

red, amorphous powder (which becomes crystalline after two days), or a double *salt* of the salicylate and the chloride salicylate,

$$\left[Fe_3{(C_7H_5O_3)_6 \atop (OH)_2}\right]C_7H_5O_3,2\left[Fe_3{(C_7H_5O_3)_6 \atop (OH)}\right]{C_7H_5O_3 \atop Cl},11H_2O,$$

brownish-red, crystalline powder. Ferric bromide ($Fe_3Br_8,6H_2O$, see below) forms a double *salt*,

$$\left[Fe_3{(C_7H_5O_3)_6 \atop (OH)_2}\right]C_7H_5O_3,2\left[Fe_3{(C_7H_5O_3)_6 \atop (OH)}\right]{C_7H_5O_3 \atop Br},11H_2O,$$

carmine, crystalline powder, and ferric nitrate yields a double *salt*,

$$\left[Fe_3{(C_7H_5O_3)_6 \atop (OH)_2}\right]C_7H_5O_3,\left[Fe_3{(C_7H_5O_3)_6 \atop (OH)}\right]{C_7H_5O_3 \atop NO_3},2H_2O,$$

reddish-yellow, crystalline powder.

The great similarity between the salts of hexabenzoatotriferric hydroxide and hexasalicylatotriferric hydroxide indicates that in the latter the iron is attached to the carboxyl group of the salicylic acid, as represented in the preceding formulæ. This is also proved by the fact that salts of a similar base, *hexa-o-methoxybenzoatotriferric hydroxide*, can be obtained from *o*-methoxybenzoic acid. Thus by treating aqueous ferric chloride with aqueous sodium *o*-methoxybenzoate (Fe : Na = 1 : 3) or with warm aqueous *o*-methoxybenzoic acid (Fe : acid = 1 : 3), *hexa-o-methoxybenzoatotriferric mono-o-methoxybenzoate*,

$$\left[Fe_3{(O\cdot CO\cdot C_6H_4\cdot OMe)_6 \atop (OH)_2}\right]\cdot O\cdot CO\cdot C_6H_4\cdot OMe,7\frac{1}{2}H_2O,$$

is obtained as a yellow, crystalline substance; its alcoholic solution reacts with 20% perchloric acid to form the *perchlorate*,

$$\left[Fe_3{(O\cdot CO\cdot C_6H_4\cdot OMe)_6 \atop (OH)_2}\right]ClO_4,H_2O,$$

orange-yellow leaflets.

In a similar manner, by treating aqueous ferric chloride with sodium *m*- or *p*-hydroxybenzoate ($Fe:Na = 1:3$), *hexa*-m-*hydroxybenzoatotriferric mono*-m-*hydroxybenzoate*

$$\left[Fe_3\begin{matrix}(O\cdot CO\cdot C_6H_4\cdot OH)_6\\(OH)_2\end{matrix}\right]\cdot O\cdot CO\cdot C_6H_4\cdot OH,5H_2O,$$

dark brown powder, and the corresponding para-*isomeride*, brown, prismatic crystals, are obtained. The latter reacts with 5% aqueous ferric chloride in excess to form *p*-hydroxybenzoic acid and a very soluble *substance*, garnet-red prisms, which contains $Fe:Cl:C_7H_5O_3 = 1:1:1$, and is regarded as having the constitution

$$\left[Fe_3(O\cdot CO\cdot C_6H_4\cdot OH)_6\right]\left[Fe\begin{matrix}Cl_2\\(OH)_2\end{matrix}\right]_3, 10H_2O.$$

Hexa-p-*hydroxybenzoatotriferric chloride* p-*hydroxybenzoate*,

$$\left[Fe_3\begin{matrix}(O\cdot CO\cdot C_6H_4\cdot OH)_6\\(OH)\end{matrix}\right]\begin{matrix}Cl\\O\cdot CO\cdot C_6H_4\cdot OH\end{matrix}, 1\tfrac{1}{2}H_2O,$$

brown, crystalline powder, is obtained by the reaction of ferric chloride and lithium *p*-hydroxybenzoate ($Fe:Li = 1:1{\cdot}5$) in alcohol containing a little water.

Compounds of Hexasalicylatotriferric Hydroxide and the Salicylatoferric Acids or a Salicylatoferrous Acid.—The reddish-brown precipitate obtained from aqueous ferric chloride and sodium salicylate ($Fe:Na = 1:3$) changes by keeping in the mother liquor for about a day to a black, crystalline *substance* (the streak is violet), which contains $Fe:C_7H_5O_3 = 4:9$, not $1:2$ (compare Hopfgartner, *loc. cit.*), and is regarded as *hexasalicylatotriferric salicylate disalicylatoferrate* (annexed formula).

$$\left[Fe_3\begin{matrix}(O\cdot CO\cdot C_6H_4\cdot OH)_6\\(OH)\end{matrix}\;\begin{matrix}\cdot O\cdot CO\cdot C_6H_4\cdot OH\\ \left[Fe\begin{cases}O\text{------}\\O\cdot C_6H_4\cdot CO\\O\cdot C_6H_4\cdot CO_2\end{cases}\right]\end{matrix}\right], 8\tfrac{1}{2}H_2O.$$

In a similar manner, by keeping the initial reddish-brown precipitates in the mother liquors, ferric nitrate and sodium salicylate ($Fe:Na = 1:3$) yield a double *compound* of the preceding salt and hexasalicylatotriferric monosalicylate,

$$\left[Fe_3\begin{matrix}(C_7H_5O_3)_6\\(OH)\end{matrix}\;\begin{matrix}C_7H_5O_3\\ \left[Fe\begin{cases}O\text{------}\\O\cdot C_6H_4\cdot CO\\O\cdot C_6H_4\cdot CO_2\end{cases}\right]\end{matrix}\right], \left[Fe_3\begin{matrix}(C_7H_5O_3)_6\\(OH)_2\end{matrix}\right]C_7H_5O_3, 15H_2O,$$

black, crystalline powder, ferric sulphate and sodium salicylate ($Fe:Na = 1:1{\cdot}5$) yield a double *salt* of the bisdisalicylatoferrate and the salicylatedisalicylatoferrate of the hexa-base,

$$\left[Fe_3\begin{matrix}(C_7H_5O_3)_6\\(OH)\end{matrix}\right][Fe(C_7H_4O_3)_2]_2, \left[Fe_3\begin{matrix}(C_7H_5O_3)_6\\(OH)\end{matrix}\right]\begin{matrix}O\cdot CO\cdot C_6H_4\cdot OH\\ [Fe(C_7H_4O_3)_2]\end{matrix}, 23H_2O,$$

violet-black, crystalline powder, and ferric acetate and sodium salicylate ($Fe:Na = 1:3$ and $1:4$ respectively) yield *substances*,

$$\left[Fe_3\begin{matrix}(C_7H_5O_3)_6\\(OH)_2\end{matrix}\right][Fe(C_7H_4O_3)_2], 8\tfrac{1}{2}H_2O$$

and

$$\left[Fe_3\begin{matrix}(C_7H_5O_3)_6\\(OH)_2\end{matrix}\right][Fe(C_7H_4O_3)_2], \left[Fe_3\begin{matrix}(C_7H_5O_3)_6\\(OH)_2\end{matrix}\right]\cdot O\cdot CO\cdot C_6H_4\cdot OH, 14H_2O,$$

violet, crystalline powders; the former of the last two substances is

also obtained from the reddish-brown precipitate resulting from the addition of dilute acetic acid to cold saturated aqueous potassium disalicylatoferrate (see above).

The compositions of the preceding complex salts are deduced from the ratio of the iron to the salicylic acid in them, and are most simply explained by assuming that the violet and black substances are salts of hexasalicylatotriferric hydroxide and salicylic or di- or tri-salicylatoferric acid. Thus the violet substance, two methods of preparing which are mentioned above, contains iron and salicylic acid in the ratio 4 : 8 (1 : 2), and is therefore hexasalicylatotriferric disalicylatoferrate. Again, the reddish-yellow, aqueous solution obtained from ferric chloride, salicylic acid, and potassium hydroxide

$$(Fe : C_7H_6O_3 : KOH = 1 : 3 : 5)$$

deposits a reddish-brown precipitate which changes to a *substance*, black, crystalline powder (violet streak), which contains

$$Fe : C_7H_6O_3 : K = 12 : 27 : 2 ;$$

since reddish-yellow solutions are indicative of the alkali salt of trisalicylatoferric acid, the black substance is regarded as

$$2\left[Fe_3{(C_7H_5O_3)_6 \atop (OH)}\right]K[Fe(C_7H_4O_3)_3],[Fe_3(C_7H_5O_3)_6][Fe(C_7H_4O_3)_3],25H_2O.$$

The preceding complex salts of the hexa-base differ from the simpler salts of the base mentioned under the third section in their black or violet colour, and in their insolubility in alcohol, acetone, and ether. Hexasalicylatotriferric monosalicylate changes to the violet and black salts of the hexa-base in the presence of water, and, conversely, the violet and black salts are converted into hexasalicylatotriferric monosalicylate by alcoholic salicylic acid; hence the changes hexa-base $\underset{\text{alcohol and } C_7H_6O_3}{\overset{H_2O}{\rightleftarrows}}$ disalicylatoferric acid are partly the cause of the large number of the iron compounds of salicylic acid.

The violet and black salts are very sparingly soluble in water, forming faintly violet solutions. Possibly the intensely violet coloration developed in the usual ferric chloride test for salicylic acid is due to the formation of a salt of disalicylatoferric acid containing a complex iron cation such as $[Fe(H_2O)_6]$ (salts of disalicylatoferric acid containing a simple cation such as potassium or sodium are red); such a salt would be more soluble than the violet or black salts described above, and would, therefore, produce a more intensely violet coloration. The authors have been unable to isolate such a salt; they have prepared, however, a *salt* of the hexasalicylatotriferric and hexa-acetotriferric hydroxides with disalicylatoferric acid, $\left[Fe_3{(C_7H_5O_3)_6 \atop (OH)_2}\right][Fe(C_7H_4O_3)_2],[Fe_3(OAc)_6](OH)_3,4H_2O$, which is much more soluble in water than the violet and black salts, forming a reddish-violet solution changing to violet by the addition of hydrochloric acid, owing to the decomposition of the hexa-aceto-base.

Intensely violet solutions are obtained from aqueous sodium salicylate and an excess of ferric chloride, from aqueous salicylic acid and ferric chloride, and from all the salts of hexasalicylatotriferric hydroxide by warming them with very dilute hydrochloric acid; in all

these cases, disalicylatoferric acid and (complex) iron cations, that is, the two components necessary for the production of the intensely violet ferric disalicylatoferrate, are formed. Conversely, the addition of soium sal icylate or of sodium carbonate to solutions of salts of hexasalicylatotriferric hydroxide produces, according to the relative quantities of the reagents, red solutions of sodium disalicylatoferrate or reddish-yellow solutions of sodium trisalicylatoferrate. Similarly, the addition of aqueous calcium hydrogen carbonate to the violet solution produces a red solution of calcium disalicylatoferrate.

The residue obtained by the evaporation of aqueous ferric bromide has the composition $Fe_3Br_8,6H_2O$, and contains ferrous iron. In alcoholic solution it reacts with lithium salicylate (Fe : Li = 1 : 3) to form a *substance*, olive-brown crystals, which contains

$$Fe^{III} : Fe^{II} : C_7H_6O_3 = 3 : 1 : 9,$$

and is therefore regarded as *hexasalicylatotriferric salicylate disalicylatoferrite*, $\left[Fe_3^{III}(C_7H_5O_3)_6\right]^{O\cdot CO\cdot C_6H_4\cdot OH}_{[Fe^{II}(C_7H_4O_3)_2]},6H_2O$. The same substance is obtained from lithium salicylate and alcoholic ferric chloride which has been partly reduced by the addition of iron. An alcoholic solution of $Fe_3Br_8,6H_2O$, which has been still further reduced by iron, reacts with lithium salicylate (Fe : Li = 1 : 3) to form *hexasalicylatotriferric hydrogen trisdisalicylatoferrite*,

$$[Fe_3^{III}(C_7H_5O_3)_6]H_2[Fe^{II}(C_7H_4O_3)_2]_3,5\tfrac{1}{2}H_2O,$$

blackish-brown, crystalline powder. C. S.

Methylcarbonato-derivatives of Hydroxy-acids. Emil Fischer and Hermann O. L. Fischer (*Ber.*, 1913, **46**, 2659—2664).—Hydroxy-acids either do not react with methyl chloroformate in aqueous alkaline solution or give very poor yields of methylcarbonato-derivatives. The latter, however, are readily obtained by the combined action of methyl chloroformate and tertiary bases on hydroxy-acids dissolved in anhydrous solvents (compare Fischer, A., 1909, i, 161).

r-*Methylcarbonatomandelic acid*, $CO_2Me\cdot O\cdot CHPh\cdot CO_2H$, is obtained by the addition of methyl chloroformate to a well cooled solution of had *r*-mandelic acid in a mixture of chloroform and dimethylaniline. It m. p. 118—119° (corr.), after slight softening, and begins to decompose at about 140°. Alkalis readily transform it into *r*-mandelic acid, for which the authors give m. p. 120·5° (corr.) after previous softening, instead of 118° as recorded in the text books. r-*Methylcarbonatomandelyl chloride*, colourless prisms, m. p. 39—40°, is obtained by the action of phosphorus pentachloride at the ordinary temperature on a solution of the acid in chloroform, and is converted by cold methyl alcohol into *methyl* r-*methylcarbonatomandelate*, $CO_2Me\cdot O\cdot CHPh\cdot CO_2Me$, prisms, m. p. 51—52°. This ester is rapidly saponified by sodium hydroxide when dissolved in aqueous acetone; when two and a-half molecules of alkali are used, mandelic acid is formed, but when only one molecule is employed, methylcarbonatomandelic acid is the main product.

When mixed with an excess of aniline in ethereal solution, methylcarbonatomandelyl chloride yields a *compound*, $C_{16}H_{15}O_4N$, needles,

m. p. about 142° (corr. decomp.), which is converted by prolonged contact with $2N$-sodium hydroxide (2 mols.) into an acid which melts with decomposition, and has not been completely investigated. In any case, normal formation of the anilide of mandelic acid does not occur, and the authors therefore do not assign a definite structure to the aniline compound.

Glycollic acid reacts with methyl chlorocarbonate in a manner similar to mandelic acid, but yielding a product which is difficult to purify.

The authors have also prepared a compound from *r*-mandelic acid and acetylcarbimide in the expectation that the latter group would be readily eliminated, and that the product could thus be used in place of the methylcarbonato-derivatives. This is, however, not the case, since the re-conversion into mandelic acid does not occur with sufficient ease.

r-*Acetylaminocarboylmandelic acid*, $NHAc\cdot CO\cdot O\cdot CHPh\cdot CO_2H$, colourless needles, m. p. about 168—169° (decomp.), is obtained by the gradual addition of acetylcarbimide to a solution of well dried *r*-mandelic acid in anhydrous ether. It is converted by $2N$-sodium hydroxide at the ordinary temperature into the *urethane* of *mandelic acid*, $NH_2\cdot CO\cdot O\cdot CHPh\cdot CO_2H$, m. p. 172—173° (corr. decomp.), when quickly heated. H. W.

Hydrogenation of Santonin. HEINRICH WIENHAUS (*Ber.*, 1913, **46**, 2836—2839).—Polemical. The author assumes the presence of two conjugated double bonds in santonin based on the fact that at the ordinary temperature and without increased pressure in neutral solution it takes up four atoms of hydrogen (compare Weinhaus and Oettingen, this vol., i, 474; Wedekind and Beniers, this vol., i, 476; Angeli, this vol., i, 864).

Chromosantonin gives the same products on hydrogenation in presence of colloidal palladium chloride as santonin. E. F. A.

Hydrogenation of Santonic Acid. Dihydrosantonin. GUIDO CUSMANO (*Annalen*, 1913, **400**, 332—337).—Results already recorded (this vol., i, 864). C. S.

Action of Sodium Hypochlorite on Amides of Unsaturated Acids. RUDOLF A. WEERMAN (*Annalen*, 1913, **401**, 1—20. Compare A., 1906, i, 665; 1907, i, 132; 1908, i, 22; 1909, i, 589).—Freundler, van Linge, Jeffreys, and Baucke have attempted unsuccessfully to apply Hofmann's reaction to the production of amines from unsaturated acid amides.

Finely-powdered cinnamamide, by shaking with amyl alcohol and aqueous sodium hypochlorite, is converted into the *chloroamide*, $CHPh{:}CH\cdot CO\cdot NHCl$, m. p. 125° (decomp.), white plates, which yields *barium styrylcarbamate*, $Ba(C_9H_8O_2N)_2$, by treatment with aqueous barium hydroxide. The salt yields only a trace of phenylacetaldehyde by treatment with even the weakest acids; however, by decomposition with sodium hydrogen sulphite or hydroxylamine hydrochloride, the aldehyde is obtained in the form of its sodium hydrogen sulphite compound or oxime respectively.

The following substances are obtained by reactions similar to the preceding.

o-*Nitrocinnamchloroamide*, m. p. 142° (decomp.), colourless needles, is converted into *barium* o-*nitrostyrylcarbamate* by 0·3*N*-barium hydroxide on the water-bath; the latter yields o-*nitrophenylacetaldoxime*, m. p. 110°, colourless needles, with aqueous hydroxylamine hydrochloride.

m-*Nitrocinnamide*, m. p. 195—196°, prepared from the acid chloride and gaseous ammonia in benzene, is converted into *methyl* m-*nitrostyrylcarbamate*, m. p. 140°, yellow needles, from which m-*nitrophenylacetaldehyde*, $C_8H_7O_3N,H_2O$, m. p. 78—79°, can be prepared. m-*Nitrocinnamchloroamide*, m. p. 178° (decomp.), is converted as above into *barium* m-*nitrostyrylcarbamate*, yellow leaflets, from which m-*nitrophenylacetaldoxime*, m. p. 105—106°, colourless leaflets, can be obtained.

p-Nitrocinnamamide, m. p. 217° (not 155—160°, as stated by Chiozza in 1853), is converted by methyl alcohol and aqueous sodium hypochlorite into *methyl* p-*nitrostyrylcarbamate*, m. p. 188°, yellow needles, from which *p*-nitrophenylacetaldehyde, m. p. 85°, can be prepared. p-*Nitrocinnamchloroamide*, m. p. 169° (decomp.), colourless needles, is converted into *barium* p-*nitrostyrylcarbamate*, yellow needles, from which p-*nitrophenylacetaldoxime*, m. p. 155°, can be prepared. C. S.

Camphenecarboxylamide and Hydrocamphenecarboxylamide. Josef Houben and Ernst Willfroth (*Ber.*, 1913, **46**, 2530—2537).—The authors have recently shown (this vol., i, 970) that the action of methyl-alcoholic potash on methyl chloro*allo*camphanecarboxylate yields two isomeric unsaturated acids, the occurrence of which may be attributed to the unsymmetrical nature of chloro*allo*camphanecarboxylic acid or to the disturbing effect of the alkali on the single course of the reaction. The latter view receives support from the fact that chloro*allo*camphanecarboxylamide passes into a crystalline unsaturated amide, m. p. 210°, when merely boiled with water (*loc. cit.*), and the product appears to be free from any isomeride. Reduction of the unsaturated amide in acetic acid by platinum black and hydrogen causes a quantitative conversion into a saturated amide, *hydrocamphenecarboxylamide*, leaflets, m. p. 189°, which is quite distinct from *allo*camphanecarboxylamide. If the difference is not due to stereoisomerism, the above elimination of hydrogen chloride must therefore be accompanied by a change from the bornylene to the camphene group.

The mixture of unsaturated esters from methyl chloro*allo*camphanecarboxylate was then converted into the corresponding mixture of acids and treated with thionyl chloride; the resulting acid chlorides, when submitted together in ethereal solution to the action of ammonia, yielded two isomeric unsaturated amides, m. p. 209° and 98° respectively. The former, which preponderated, was identical with the amide (above) obtained by the action of water on the chlorine-substituted amide, and must be related to the camphenecarboxylic acid of m. p. 105°, whilst the latter amide, m. p. 98°, must be related to the second camphenecarboxylic acid.

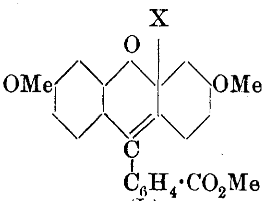
The action of sodium nitrite and hydrochloric acid on the saturated amide, m. p. 189° (see above), gave a saturated acid, *hydrocamphenecarboxylic acid*, hexagonal leaflets, m. p. 126°, which is also obtainable by hydrolysis with hot concentrated hydrochloric acid. D. F. T.

Preparation of Purpurin-3-carboxylic Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 260765. Compare Perkin and Cope, T., 1894, **65**, 848).—Purpurin-3-carboxylic acid, a red powder, m. p. 222—224° (with loss of carbon dioxide), is obtained when 1 : 2-dihydroxyanthraquinone-3-carboxylic acid dissolved in 20 parts of concentrated sulphuric acid is slowly treated at 15—20° with manganese dioxide (0·3—0·4 part); it is identical with the "ψ-purpurin" (purpurincarboxylic acid) present in madder. F. M. G. M.

Preparation of 1 : 4-Diaminoanthraquinone-2-carboxylic Acid and of 1 : 4-Diaminosulphoanthraquinone-2-carboxylic Acid. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 261885. Compare this vol., i, 1206).—1 : 4-*Diaminoanthraquinone*-2-*carboxylic acid*, dark blue, glistening, bronze needles, m. p. 350° (about), is obtained from 2-amino-5-acetylamino-4-carboxybenzoyl-*o*-benzoic acid (this vol., i, 621); the *sulphate* forms brownish-red needles; when heated with anhydrous boric acid (1 part) and 6 parts of fuming sulphuric acid (5% SO_3) at 190° and subsequently at 130—140° with the addition of 1 part of sulphuric acid (50% SO_3), it gives rise to 1 : 4-*diaminosulphoanthraquinone*-2-*carboxylic acid sulphate* as a brownish-red, crystalline precipitate. F. M. G. M

Oxonium and Alkali Salts of Fluorones. HANS VON LIEBIG (*Ber.*, 1913, **46**, 2736—2745).—The composition of the chloride of fluorescein trimethyl ether-ester [Kehrmann and Scheunert's (A., 1910, i, 407) methyl 3 : 6-dimethoxy-9-phenylxanthonium-2′-carboxylate] varies according to the treatment to which it is subjected. When prepared by the author's method (this vol., i, 865) and kept for five days at the ordinary temperature, a methyl-alcoholic solution of the chloride deposits fluorescein dimethyl ether of m. p. 198°; after removal of the latter compound, the addition of ether precipitates a *chloride*, $2C_{23}H_{20}O_6,3HCl,MeOH,2H_2O$, which has m. p. 110—125° (decomp.), and on crystallisation from water has the composition $C_{23}H_{20}O_6,HCl,MeOH,2H_2O$. The above chlorides resemble those previously described in yielding with 33% aqueous potassium hydroxide a blue *o*-quinonoid potassium salt. The hydrate, $C_{23}H_{20}O_6,H_2O$, obtained by acidifying an aqueous solution of the potassium salt with acetic acid, probably has the constitution represented in formula II. (*loc. cit.*, 867). On treatment with water the potassium salt yields a substance, $C_{23}H_{20}O_6$, which was previously considered to be a trimethyl ether-ester of fluorescein. The same substance is obtained by treating the potassium salt with methyl alcohol. It crystallises from cold methyl alcohol in slender, white needles, which sinter at 105—110° and gives off vapour at 126°, and again at a temperature a little above

180°; by warm methyl alcohol it is transformed into fluorescein dimethyl ether. It does not yield blue salts with alkalis, and therefore must contain the pyrone ring. It probably has the annexed constitution (I, where X = OMe).

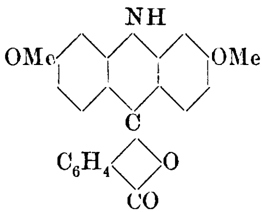


(I.)

Solutions of the preceding methoxy-compound and the hydrate mentioned above, in 10—15% hydrochloric acid, deposit a *chloride*, which melts with evolution of gas at 150°, then solidifies, and has m. p. 205°. This chloride differs from the chlorides of fluorescein trimethyl ether-ester already described in being practically insoluble in water. It yields blue salts with alkalis and probably has the formula I (X = Cl).

By heating the disodium salt of fluorescein with methyl sulphate and shaking the product with ether and ammonia, the author has obtained a substance, m. p. 255°, which he considered to be a dimethyl ether of fluorescein (A., 1912, i, 381). The same substance is formed by treating the chloride of fluorescein trimethyl ether ester with strong aqueous ammonia. When pure it has m. p. 256—257°, and is stable towards boiling alcoholic hydrogen chloride and potassium hydroxide. Its constitution is now represented by formula II.

(II.)



By the action of ammonia on a methyl-alcoholic solution of the chloride of fluorescein trimethyl ether-ester, Loth (*Diss.*, Lausanne, 1913) has obtained a substance, m. p. 257°, which he considers to be identical with the compound, just mentioned, and to have the following structure:

$$NH\left[CO\cdot C_6H_4\cdot C(OMe)<\begin{matrix}C_6H_3(OMe)\\C_6H_3(OMe)\end{matrix}>O\right]_2.$$

The stability of the author's compound towards alcoholic hydrogen chloride and potassium hydroxide is, however, not in agreement with this formula. It is possible that both substances are formed in the action of ammonia on the chloride, but that the particular compound isolated depends on the conditions under which the reaction is carried out and the method of working up the product.

In agreement with this view, the author finds that the action of ammonia on the product formed from ethyl sulphate and the disodium salt of fluorescein gives rise to two substances of m. p. 234° and 221°. The former compound has been described previously (this vol., i, 80) as a diethyl ether of fluorescein, but is now considered to have a similar structure to that of the methyl compound represented in II, whilst the second *compound*, m. p. 221°, is presumably the ethyl analogue of Loth's compound.

When heated with acetic anhydride and sodium acetate, and the product treated with water, the chloride of fluorescein trimethyl ether-ester is partly converted into fluorescein dimethyl ether, of m. p. 198°. The dichloride of resorcinolbenzein dimethyl ether, when subjected to

same treatment, yields an *acetyl* derivative, $OAc\cdot CPh{<}{\begin{smallmatrix}C_6H_3(OMe)\\ C_6H_3(OMe)\end{smallmatrix}}{>}O$, crystallising with benzene (1 mol.) in slender, colourless leaflets, which melt and lose their benzene at 110°, then solidify, and have m. p. 178°. This is converted by prolonged boiling with ethyl alcohol into the ethyl ether of m. p. 158°, the acetyl group being replaced by ethyl.

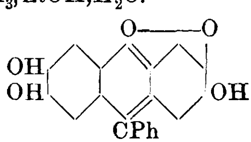
When shaken with ether and ammonia, the dichloride of resorcinol-benzein dimethyl ether yields a *substance*, which forms pale yellow crystals, m. p. 112—113°, and has the following structure:

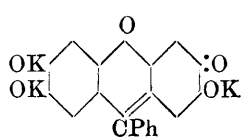
$$OH\cdot CPh{<}{\begin{smallmatrix}C_6H_3(OMe)\\ C_6H_3(OMe)\end{smallmatrix}}{>}NH.$$

Evidence of the existence of eosin in various forms, corresponding with those of fluorescein (A., 1912, i, 379), has been obtained as follows: The chloride, formed by treating fluorescein with a hot mixture of alcohol and hydrochloric acid, is brominated in alcoholic solution and the resulting eosin fractionally extracted with methyl alcohol. The first extractions deposit a dark red eosin, the later fractions a reddish-white or flesh-coloured modification, whilst the residue is either reddish-white or orange. When heated, the eosin from the later fractions acquires a red colour at 200°, then becomes almost white at a temperature below 300°, and finally turns red again and melt at 304—305°. On crystallisation from benzene, the light-coloured eosin separates as a mixture of colourless, yellow and red prisms. The red variety probably corresponds with the red multi-molecular modification of fluorescein, the light-coloured form to the yellow unimolecular fluorescein, and the colourless variety to the lactone-form.

When boiled with aqueous alcoholic potassium hydroxide, the light-coloured eosin yields intensely violet or blue solutions. The addition of sulphuric acid to these solutions precipitates a brown substance, which on extraction with boiling chloroform leaves an eosin of the composition $2C_{20}H_8O_5Br_4,CHCl_3$ as a reddish or bluish-white, crystalline residue. The latter compound differs from ordinary eosin in giving a deep violet coloration with strong sulphuric acid, and in yielding with aqueous alkalis deep blue solutions having a green fluorescence; when kept, the blue solutions slowly become violet and finally red. It loses its chloroform at 185—186°, and then dissolves in alkalis with a red colour. Attempts to isolate the blue salt formed by warming the compound with 33% aqueous potassium hydroxide were unsuccessful; instead of the blue salt a brownish-red *tripotassium* salt, $C_{20}H_5O_5Br_4K_3$, was obtained.

Hydroxyquinolbenzein, to which Kehrmann has assigned formula III, yields with aqueous alcoholic potassium hydroxide a *tripotassium* salt IV, which separates in brownish-red crystals of the composition $C_{19}H_{19}O_5K_3,EtOH,H_2O$.

(III.) 

(IV.) 

The author considers that the constitution of hydroxyquinolbenzein is best represented by a quinonoid structure, similar to that given above for the potassium salt, and thus avoids the assumption that the betaine-linking is stable towards alkalis, or that transformation into the quinonoid form occurs. F. B.

Oxidation with Oxygen in Presence of Metallic Osmium. I. RICHARD WILLSTÄTTER and EUGEN SONNENFELD (*Ber.*, 1913, **46**, 2952—2958).—Unsaturated substances alone or diluted with acetone are agitated in special flasks with a small quantity of metallic osmium, prepared by igniting osmium ammonium chloride in a current of hydrogen, in an atmosphere of oxygen. The other metals of the platinum group do not act as oxygen-carriers under these conditions, but tellurium is active, although less so than osmium. A detailed account of the oxidation of *cyclo*hexene by this method is given; the products are Δ^2-*cyclo*hexenol, Δ^1-*cyclo*pentenealdehyde, much adipic acid, and a little adipoin (*cyclo*hexan-2-ol-1-one).

The first two were separated by converting the *cyclo*hexenol into the *naphthylurethane*, m. p. 156°, which crystallises in needles from alcohol or ethyl acetate on cooling its solution in either. Adipoin gives a p-*nitrophenylhydrazone*, m. p. 146° (decomp.), which crystallises from boiling alcohol in orange-red, hexagonal leaflets. T. A. H.

Action of Light on the Colour Changes of Aldehyde Phenylhydrazone Solutions. HANS STOBBE and ROBERT NOWAK (*Ber.*, 1913, **46**, 2887—2902).—The change of colour of solutions of the phenylhydrazones of benzaldehyde, cuminaldehyde, anisaldehyde, piperonaldehyde, and acetaldehyde on exposure to light has been investigated. In all cases the change is extremely sensitive to the action of light. Acid solutions are much more quickly affected than neutral solutions. The change is not due, as supposed by Baly and Tuck (T., 1907, **91**, 1572), to photo-isomerisation of the hydrazones to azo-compounds, but it is an oxidation process which takes place slowly in the dark and is greatly accelerated by light. The colour changes of other hydrazones and of osazones is likewise attributed to oxidation.

Benzaldehydephenylhydrazone is oxidised to dibenzylidenediphenylhydrotetrazone, whilst in no case were azo-compounds formed. E. F. A.

Halogenated Alicyclic Ketones. II. Monohalogenides of Penta-, Hexa-, and Hepta-cyclic Ketones. ARTHUR KÖTZ, K. BLENDERMANN, E. KÁRPÁTI, and RICHARD ROSENBUSCH (*Annalen*, 1913, **400**, 47—54. Compare Kötz and Steinhorst, A., 1911, i, 210).—When *cyclo*pentanone, 1 : 4-dimethyl*cyclo*hexan-3-one, and *cyclo*heptanone are halogenated by Kötz and Götz's method (A., 1908, i, 173), chlorine or bromine is substituted most easily in dimethyl*cyclo*hexanone and least readily in *cyclo*pentanone. The chloro-ketones are stable in the absence of light, but the bromo-ketones decompose very easily. 2-*Chloro*cyclo*pentanone*, b. p. 76—77°, 2-*bromo*cyclo*pentanone*, b. p. 79—82°/15 mm., 2-*chloro*cyclo*heptanone*, b. p. 95°/13 mm., 2-*bromo*cyclo*heptanone*, b. p. 103°/13 mm., and 2-*chloro*-1 : 4-*dimethyl*cyclo*hexan*-3-*one*, b. p. 108—109°/15 mm., are described. C. S.

α-Hydroxy-ketones of the *cyclo*Hexanone and *cyclo*Heptanone Series. Arthur Kötz, K. Blendermann, Richard Rosenbusch, and E. Sirringhaus (*Annalen*, 1913, **400**, 55—72).—Comparative experiments on the hydrolysis of 2-chloro*cyclo*pentanone, 2-chloro*cyclo*hexanone, and 2-chloro*cyclo*heptanone by aqueous alkali carbonates or hydrogen carbonates show that *cyclo*pentan-2-olone cannot be thus obtained, that 2-chloro*cyclo*hexanone is readily hydrolysed by aqueous potassium carbonate in the cold, and that the formation of *cyclo*heptan-2-olone in satisfactory yield requires the action of boiling concentrated potassium carbonate for six hours. *cyclo*Hexan-2-ol-1-one, m. p. 98°, forms a *benzoyl* derivative, m. p. 122—123°, *semicarbazone*, m. p. 238°, *oxime*, m. p. 102—103°, *methyl ether*, m. p. 162°, and *ethyl ether*, m. p. 137° (which is converted into the methyl ether by warm methyl alcohol). cyclo*Heptan-2-ol-1-one*, m. p. 28°, unlike *cyclo*hexan-2-ol-1-one, possesses acidic properties and forms a *potassium* derivative. It forms a *methyl ether*, b. p. 65—66°/12 mm., but not a semicarbazone or oxime. The ethers of *cyclo*hexan-2-olone also do not form oximes or semicarbazones, and 2-hydroxy*cyclo*hexanoneoxime cannot be etherified; the group

OR·CH·C:NOH,

therefore, apparently cannot be formed.

2-Methoxy*cyclo*hexanone does not react with magnesium methyl iodide. *cyclo*Hexan-2-olone reacts only with difficulty, and yields ultimately *cyclo*hexanone (compare Sabatier and Mailhe, A., 1905, i, 706), whilst 1-methyl*cyclo*hexan-3-ol-2-one is similarly converted into 1 : *2-dimethyl*cyclo*hexan-3-one*, b. p. 178—179°.

*cyclo*Hexan-2-olone and its methyl and ethyl ethers react with phenylhydrazine in glacial acetic acid to form the same *osazone*, $C_{18}H_{20}N_4$, m. p. 150—151°, red crystals. *cyclo*Hexan-2-olone and its methyl ether are oxidised to adipic acid by alkaline potassium permanganate, and to glutaric acid by boiling nitric acid, D 1·22; the oxidation of the methyl ether is effected much less readily in both cases.

It is well known that hydroaromatic cyclic ketones condense with aldehydes except when a methyl group is present in the ortho-position to the carbonyl group. Hydroxyl and methoxy-groups apparently exert a similar inhibiting influence, because *cyclo*hexanolone or its methyl ether does not condense with benzaldehyde or cinnamaldehyde in the presence of alcoholic sodium hydroxide. 2-Methoxy-*cyclo*hexanone, however, reacts with sodium and amyl formate in ether to form, after acidification of the product, *2-methoxy-6-hydroxymethylene*cyclo*hexanone*, $C_8H_{12}O_3$, b. p. 98—100°/11 mm. (*semicarbazone*, m. p. 212—215°).

1 : *4-Dimethyl*cyclo*hexan-2-ol-3-one*, $C_8H_{14}O_2$, b. p. 91°/13 mm. (*benzoyl* derivative, m. p. 162°), is obtained by boiling 2-chloro-1 : 4-dimethyl*cyclo*hexan-3-one with saturated aqueous potassium carbonate, or, in a similar manner, from ethyl 2-chloro-1 : 4-dimethyl*cyclo*hexan-3-one-4-carboxylate. Since the last compound, being produced by the chlorination of ethyl 1:4-dimethyl*cyclo*hexan-3-one-4-carboxylate by Kötz and Götz's method, must contain the chlorine atom in position 2 (compare Kötz and Steinhorst, A., 1911, i, 210), it follows, from the

production of 1 : 4-dimethyl*cyclo*hexan-2-ol-3-one by the hydrolysis of both chlorinated substances, that 2-chloro-1 : 4-dimethyl*cyclo*hexan-3-one (preceding abstract) must have this constitution, not that of the 4-chloro-isomeride. The chlorination of ethyl 1-methyl-4-*iso*propyl*cyclo*hexan-3-one-4-carboxylate yields *ethyl* 2-*chloro*-1-*methyl*-4-iso*propyl*-cyclo*hexan*-3-*one*-4-*carboxylate*, by the hydrolysis of which 2-*hydroxy*-1-*methyl*-4-iso*propyl*cyclo*hexan*-3-*one*, b. p. 139°/17 mm., is obtained.

C. S.

Unsaturated Cyclic Ketones. Δ^2-*cyclo*Hexenone and Δ^2-*cyclo*-Heptenone (Tropilene). ARTHUR KÖTZ, K. BLENDERMANN, F. MÄHNERT, and RICHARD ROSENBUSCH (*Annalen*, 1913, **400**, 72—86).—Comparative experiments on the production of unsaturated cyclic ketones from the α-halogenated saturated ketones prove that hydrogen iodide is most readily, and hydrogen chloride is least readily, eliminated, and that the difficulty of eliminating hydrogen haloid increases from halogen-*cyclo*pentanones to halogen-*cyclo*heptanones. Aniline or trimethylamine is the most suitable eliminating reagent; to avoid the formation of hydroxy-ketones, water must not be present.

Willstätter's tropilene is identical with Δ^2-*cyclo*heptenone, obtained by the action of aniline on 2-bromo*cyclo*heptanone; it forms an *oxime*, m. p. 80—88°, and yields *cyclo*heptanone by reduction by Paal's method.

1 : 4-*Dimethyl*-Δ^1-cyclo*hexen*-3-*one*, $C_8H_{12}O$, b. p. 75°/19 mm., is obtained by heating 2-hydroxy-1 : 4-dimethyl*cyclo*hexan-3-one with anhydrous oxalic acid at 110°. *Ethyl* 1 : 2-*dimethyl*-Δ^1-cyclo*hexen*-3-*one*-6-*carboxylate*, $C_{11}H_{16}O_3$, b. p. 144—146°/13 mm. (*semicarbazone*, m. p. 202°; *oxime*, m. p. 109—110°), obtained by the action of methyl iodide and sodium ethoxide on ethyl 1-methyl-Δ^1-*cyclo*hexen-3-one-6-carboxylate, yields *ethyl* 1 : 2-*dimethyl*cyclo*hexan*-3-*one*-6-*carboxylate*, b. p. 256—258° (*semicarbazone*, m. p. 210—211° [decomp.]), by reduction by Paal's method, and is converted into 1 : 2-*dimethyl*-Δ^1-cyclo-*hexen*-3-*one*, b. p. 118—119°/12 mm. (*semicarbazone*, m. p. 225° [decomp.]), by hydrolysis by alcoholic potassium hydroxide and distillation in a vacuum of the resulting acid. 1 : 2-Dimethyl-Δ^1-*cyclo*hexen-3-one is reduced to the corresponding saturated *ketone*, b. p. 84°/11 mm. (*semicarbazone*, m. p. 203—204°), by Paal's method, and yields γ-acetyl-butyric acid by oxidation by aqueous potassium permanganate at 0—6°.

C. S.

Zinc Chloride as a Condensing Agent. III. Auto-condensation of Anils. G. REDDELIEN (*Ber.*, 1913, **46**, 2712—2717).—The author has shown previously (A., 1910, i, 118, 746) that acetophenone condenses with aniline in the presence of aniline zincichloride as a catalyst, yielding acetophenoneanil, together with a small quantity of a yellow substance, m. p. 98—99°. The by-product is now found to be dypnoneanil, and is formed by the auto-condensation of acetophenone anil. If the condensation is carried out at 180—190° a better yield of the substance is obtained. It was observed that in all cases in which dypnoneanil was formed as a by-product, the aniline zincichloride used as a catalyst underwent slight decomposition into zinc hydroxide, and

this suggested the possibility that the aniline hydrochloride, simultaneously produced by this decomposition, was the prime factor in the further condensation of acetophenoneanil to dypnoneanil. This view has been confirmed by heating acetophenoneanil for a few minutes with aniline hydrochloride, when a 60% yield of dypnoneanil was obtained; under the same conditions, using aniline zincichloride, the acetophenoneanil remains unchanged.

If the heating is more prolonged and the temperature higher, 1 : 3 : 5-triphenylbenzene is formed. Exposure to air at the ordinary temperature also causes the transformation of acetophenoneanil into dypnoneanil, the condensation in this case being probably due to traces of hydrochloric acid in the air, for in closed vessels the acetophenoneanil may be kept for a long time without undergoing change.

Miller and Plöchl (A., 1896, i, 609) have already pointed out that there exists a very close resemblance in the reactions of aldehydes and ketones on the one hand, and of their anils on the other. In emphasising this analogy, the author refers to the similarity in the autocondensation products of acetophenone and its anil, and to the similar behaviour of aldehydes and their anils towards organo-magnesium compounds (Busch, A., 1904, i, 663; 1905, i, 519).

Further, anils closely resemble ketones and aldehydes in their behaviour toward phenylhydrazine and semicarbazide: thus, benzophenoneanil and acetophenoneanil readily react with these compounds in alcoholic solution to form the semicarbazones and phenylhydrazones of the corresponding aldehydes.

Finally, the ability of unsaturated and aromatic aldehydes to form coloured additive compounds with strong acids is shared by anils; fluoroneanil and dypnoneanil yield additive compounds with hydrogen chloride which are coloured respectively red and reddish-yellow, and are rapidly resolved by water into their components.

Dypnoneanil, CMePh:CH·CPh:NPh, forms lustrous, light yellow, glassy prisms, m. p. 98—99°, and gives an intensely yellow coloration with sulphuric acid. It has also been obtained, together with acetophenoneanil, by heating dypnone and aniline in the presence of aniline zincichloride; if aniline hydrochloride is used as a condensing agent, triphenylbenzene is produced.

Dypnone-p-*tolil*, prepared from dypnone and aniline, using *p*-toluidine zincichloride as a catalyst, has m. p. 110°. It is accompanied by acetophenone-*p*-tolil, which crystallises from alcohol in yellowish-white needles, m. p. 31°. F. B.

Catalytic Action of Hydrogen Haloids in Condensations. I. Preparation of Ketoneanils. G. Reddelien (*Ber.*, 1913, **46**, 2718—2723. Compare preceding abstract).—In the preparation of ketoneanils by the condensation of aromatic ketones with amines, hydrogen haloids or their salts with aromatic amines may often be employed as catalysts in place of zinc chloride or amine zincichlorides previously used. Thus, benzophenoneanil is readily obtained by heating benzophenone and aniline at 170° in the presence of one drop of hydrochloric acid.

The reaction proceeds more rapidly than when the zinc salts are

employed, but is not so general in its application. Methyl ketones, such as acetophenone and $\alpha\beta$-unsaturated ketones, do not yield anils by this method, although the latter are readily obtained when aniline zincichloride is employed.

With respect to the mechanism of the reaction the author considers that the ketones first combine with the amines in the presence of hydrochloric acid to form compounds of the type OH·CRR·NHR,HCl, which lose water when heated, yielding hydrochlorides of the anils, CRR:NR,HCl; the anils, however, are very feeble bases in comparison with the amines, and, therefore, are liberated from their hydrochlorides by the action of the unchanged amines, the hydrochlorides of the latter compounds thus being regenerated.

It is pointed out that the hydrogen haloids may act as catalysts in opposite directions accordingly as they ionised or not. Whilst un-ionised hydrogen haloids act as catalysts in the condensation of ketones with amines, in the ionised state they accelerate the decomposition of the anils into their components and thus exert a catalytic action in the opposite direction.

In addition to benzophenoneanil, the following anils were obtained by heating the necessary ketones and amines in the presence of a little hydrochloric acid: phenyl α-naphthyl-ketoneanil, m. p. 93—94° (compare Busch and Falco, A., 1910, i, 747); benzildianil, m. p. 142°; benzophenone-*p*-tolil, crystallising from alcohol in long, stout, lustrous prisms, m p. 48° (compare Reddelien, A., 1910, i, 118); benzophenone-α-naphthil (Pauly, this Journ., 1877, ii, 614), which has m. p. 137·5°, and gives a blood-red coloration with strong sulphuric acid; fluorenone-anil (A., 1910, i, 746), the *hydrochloride* of which is precipitated in blood-red needles by passing hydrogen chloride into a benzene solution of the anil. F. B.

Certain Substituted Benzalacetophenones [Phenyl Styryl Ketones]. FRANZ KUNCKELL and MARTIN HAMMERSCHMIDT (*Ber.*, 1913, **46**, 2676—2680. Compare Kunckell and Fürstenberg, A., 1912, i, 118).—2-*Hydroxy*-5-*acetylaminophenyl* 2-*nitrostyryl ketone*, golden-brown needles, m. p. 205° (decomp.), is obtained when aqueous sodium hydroxide is gradually added to an alcoholic solution of 2-hydroxy-5-acetylaminoacetophenone and *o*-nitrobenzaldehyde and the mixture neutralised after some time with dilute sulphuric acid, the temperature being maintained at about 20° during the whole operation. It is somewhat unstable, and decomposes when preserved for a short time. The preparation of the corresponding dibromide and flavone could not be effected.

2-*Hydroxy*-5-*acetylaminophenyl* 4-*nitrostyryl ketone*,

$$OH\cdot C_6H_3(NHAc)\cdot CO\cdot CH{:}CH\cdot C_6H_4\cdot NO_2,$$

red, microcrystalline powder, m. p. 204°, is prepared in a similar manner from 2-hydroxy-5-acetylaminoacetophenone and *p*-nitrobenzaldehyde. It absorbs bromine in chloroform solution, yielding the corresponding *dibromide*, yellow needles, m. p. 125°, after previous softening, from which the flavone could not be obtained by the action of alcoholic potassium hydroxide.

2-*Hydroxy*-5-*acetylaminophenyl* 4-*chlorostyryl ketone*, golden needles,

m. p. 174°, and *2-hydroxy-5-acetylaminophenyl 2-hydroxystyryl ketone*, yellow crystals, m. p. 134°, are similarly formed from their components. In these cases, complete condensation can only be effected by heating the mixture on the water-bath. In neither case could the corresponding dibromide be obtained.

2-Hydroxy-5-acetylaminophenyl 4-methylstyryl ketone forms yellowish-white needles, m. p. 185°. It combines with bromine in chloroform solution to yield *2-hydroxy-5-acetylaminophenyl αβ-dibromo-β-p-tolylethyl ketone*, m. p. 162°.

Terephthalaldehyde condenses with *2-hydroxy-5-acetylaminoacetophenone*, yielding a yellow *substance*, m. p. 217°, the constitution of which has not been definitely determined. H. W.

Metal Ketyls, a Large Class of Substances with Tervalent Carbon. WILHELM SCHLENK and ALEXANDER THAL (*Ber.*, 1913, **46**, 2840—2854. Compare A., 1911, i, 545).—Phenyl diphenylyl ketone was dissolved in dry ether in an atmosphere of nitrogen, and the boiling point of the solution determined. This remained unchanged on the addition of a piece of bright potassium, indicating that potassium phenyl diphenylyl ketone has the formula

$$Ph\cdot C_6H_4\cdot CPh(OK)-.$$

When a suspension of benzpinacone in benzene is mixed with a concentrated, alcoholic sodium ethoxide solution, sodiobenzophenone is formed, as indicated by the unstable, dark blue coloration. The sodium salt of the benzpinacone at first formed is dissociated immediately into the free radicles with a tervalent carbon atom, $CPh_2(ONa)-$. The name metal ketylen is proposed for such compounds containing tervalent carbon.

Special apparatus is described for their filtration, isolation, and for drying them in a current of nitrogen.

The sparingly soluble ketyls cannot be prepared in the manner described, since the surface of the metal becomes coated with a film of insoluble ketyl which prevents further action.

In such cases the ketone (dimethylpyrone) is mixed with the very soluble potassium phenyl diphenylyl ketone, when the insoluble ketyl (red potassiodimethylpyrone) separates out. Ether, benzene or pyridine may be used as solvents, but the two latter are more difficult to remove from the ketyl. Potassium, sodium, and lithium react equally well; magnesium in the form of amalgam also reacts with diaryl ketones.

Potassiodimethylpyrone forms a bright red powder, which oxidises so readily that it glows on exposure to the air.

Potassiochromone yields a deep orange-red product, and contains a further molecule of chromone. It chars on exposure.

Potassioxanthone separates together with a molecule of xanthone as deep blue needles.

Potassio β-benzpinacolin, $CPh_3\cdot CPh\cdot OK-$, forms dark cubic crystals with a brown surface reflex.

Potassiophthalophenone is dark red.

Potassio-N-methylisatin separates in deep blue flakes.

Potassio-O-methylisatin forms a deep violet precipitate.

Potassio-m-*dibenzoylbenzene*, $COPh\cdot C_6H_4\cdot CPh\cdot OK-$, forms a dark red powder.

Potassio-p-*dibenzoylbenzene* forms a additive compound with two molecules of potassium per molecule; a deep red precipitate is formed, and the solution becomes deep red. The alternative ketyl (I) and quinonoid (II) formulæ are considered, but the latter is rejected,

$$\underset{\text{(I.)}}{-CPh(OK)\cdot C_6H_4\cdot CPh(OK)-} \qquad \underset{\text{(II.)}}{CPh(OK):C_6H_4:CPh(OK)}$$

since the compound behaves like the other ketyls and glows on exposure to the air.

Potassiobenzil, $-CPh(OK)\cdot CPh:O$, is obtained as a violet-coloured precipitate.

Potassiofuril is a black or bluish-black substance.

Potassiophenanthraquinone, $C_6H_4<\begin{matrix}CO-\\C_6H_4\end{matrix}>C(OK)-$, is dark brown.

Potassio-p-*benzoquinone* possesses a quinhydrone structure combining with a molecule of quinone; it forms a deep bluish-green compound.

When *o*-benzoquinone is mixed with potassium phenyl diphenylyl ketyl, a dark green precipitate is formed, which soon becomes colourless, and is then potassiocatechol. When the ketyl solution is added slowly to the quinone, a precipitate is formed, and the solution becomes an intense reddish-violet; this is attributed to the formation of the metal ketyl.

On adding diphenyl ketone to the potassium phenyl diphenylyl ketyl an intense violet-red coloration is produced. Excess of the ketyl causes a separation of a compound containing 1 atom of potassium to 2 molecules of diphenyl ketone. The red compound could not be isolated; it possibly has the composition $CPh_2:C(OK)-$.

The atomic groups OK, ONa are considered to exhaust practically the entire valency force of the atoms to which they are attached.

E. F. A.

Preparation of Arylidoquinones. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 262180).—*Di*-p-*chloroanilinobenzoquinone*, a yellowish-brown powder, m. p. over 300°, is obtained by heating together quinol and *p*-chloroaniline in the presence of ammoniacal copper oxide.

Bromoanilinonaphthaquinone is prepared in a similar manner from *p*-bromoaniline and *α*-naphthaquinone. F. M. G. M.

Preparation of 1 : 4-Diaminoanthraquinone and its Derivatives, or of Sulphonic Acids of these Compounds. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 260899. Compare A., 1904, i, 512; 1905, i, 447; 1909, i, 243).—The preparation of aminoanthraquinones from aminobenzoyl-*o*-benzoic acids has previously been recorded, and that of 1 : 4-diaminoanthraquinones from 2-amino-5-acetylaminobenzoyl-*o*-benzoic acid, or its lactam (this vol., i, 621), is now described; the operation is carried out at 190—200° with either 95% or fuming sulphuric acid; under the latter conditions, especially in the presence of boric acid, sulphonated products are also formed. 2 : 5-*Diaminobenzoyl*-o-*benzoic acid*, yellow

crusts, which melt at 185° with conversion into the *lactam*, can also be employed in this reaction.

1 : 4-*Diamino-2-methylanthraquinone*, dark violet, glistening, bronze needles, m. p. 252°, is obtained from 2 : 5-diamino-*p*-toluoyl-*o*-benzoic acid, whilst 4-chloro-2-amino-5-acetylaminobenzoylbenzoic acid gives rise to 2-*chloro*-1 : 4-*diaminoanthraquinone*, dark violet needles, m. p. 234°. F. M. G. M.

Replacement of the Sulphonic Acid Group by Halogens in Hydroxyanthraquinonesulphonic Acids. GUSTAV HELLER [with SIEGFRIED SKRAUP (*Ber.*, 1913, **46**, 2703—2711).—Kelbe's method (A., 1883, 806; compare also Ullmann and Ochsner, A., 1911, i, 489, and Schilling, this vol., i, 493) of replacing the sulphonic acid group by chlorine or bromine, by the action of these elements on sulphonic acids in aqueous solution, has been applied by the author to the preparation of halogen derivatives of alizarin and anthrachrysone from the corresponding sulphonic acids.

3-Bromo-1 : 2-dihydroxyanthraquinone (D.R.-P. 77179 and 78643) is obtained in a pure condition by the addition of an aqueous solution of potassium bromide and bromate to sodium alizarin-3-sulphonate, acidified with sulphuric acid, and maintained at 95°. It crystallises in rosettes of brownish-red needles, m. p. 260—261°, yields a pale yellow *diacetyl* derivative, m. p. 204—205°, and dissolves in dilute aqueous alkali hydroxides, yielding bluish-violet solutions; concentrated solutions of the hydroxides precipitate the corresponding alkali salts.

3-Chloro-1 : 2-dihydroxyanthraquinone, prepared by passing chlorine into a hot aqueous solution of alizarin-3-sulphonic acid, has m. p. 270—271°, and on benzoylation in pyridine solution yields a *dibenzoyl* derivative, m. p. 184°, together with a red *substance*, m. p. above 300°.

When dissolved in an ice-cold mixture of sulphuric and nitric acids, it is oxidised to 3-*chloro*-1 : 2 : 4-*trihydroxyanthraquinone*, m. p. 242—244°.

Nitration in glacial acetic acid solution yields 3-*chloro*-4-*nitro*-1 : 2-*dihydroxyanthraquinone*. This crystallises in orange-yellow needles, which become dark red and decompose slightly at 220°, then acquire a lighter colour, and finally melt at 285°.

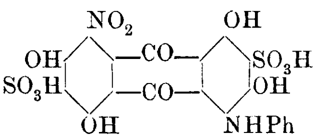
3-*Chloro*-4-*anilino*-1 : 2-*dihydroxyanthraquinone*, prepared by heating the preceding nitro-compound in aqueous sodium carbonate solution with aniline, crystallises in black needles or plates, m. p. 223—224°.

A solution of anthrachrysone in 33% aqueous sodium hydroxide deposits a lustrous, vivid red *sodium* salt, which is converted by ammonium chloride into the *ammonium* salt.

1 : 3 : 5 : 7-Tetrahydroxyanthraquinone-2 : 6-disulphonic acid, prepared by heating anthrachrysone with an excess of fuming sulphuric acid, forms a *sodium* salt, $C_{14}H_6O_6(SO_3Na)_2$, crystallising in glistening, coppery platelets (compare D.R.-P. 70803). On treatment with bromine in dilute acetic acid solution, the sodium salt is converted into 2 : 4 : 6 : 8-tetrabromo-1 : 3 : 5 : 7-tetrahydroxyanthraquinone, which forms lustrous, dark red needles, m. p. above 300°, and yields a sparingly soluble *ammonium* salt.

2 : 6-*Dibromo*-1 : 3 : 5 : 7-*tetrahydroxyanthraquinone*, prepared by brominating anthrachrysone in glacial acetic acid solution, crystallises in orange-red needles, m. p. above 290°, and also forms a sparingly soluble *ammonium* salt.

2 : 6-*Dichloro*-1 : 3 : 5 : 7-*tetrahydroxyanthraquinone* is obtained in lustrous, orange, silky needles by the addition of sodium hypochlorite to an aqueous solution of the sodium salt of anthrachrysone. The action of chlorine on 1 : 3 : 5 : 7-tetrahydroxyanthraquinone-2 : 6-disulphonic acid yields 4 : 8-*dichloro*-1 : 3 : 5 : 7-*tetrahydroxyanthraquinone*-2 : 6-*disulphonic acid.*



8-*Nitro*-4-*anilino*-1 : 3 : 5 : 7-*tetrahydroxyanthraquinone*-2 : 6-*disulphonic acid* (annexed formula) is obtained in the form of its *trisodium* salt (dark bluish-violet crystals of a coppery lustre) by heating a solution of 4 : 8-dinitro-1 : 3 : 5 : 7-tetrahydroxyanthraquinone in aqueous sodium carbonate with aniline.

A similar replacement of the nitro-group by the aniline residue occurs when 4 : 8-dinitro-1 : 3 : 5 : 7-tetrahydroxyanthraquinone (D.R.-P. 71964) is heated with aqueous sodium carbonate and aniline. The 8-*nitro*-4-*anilino*-1 : 3 : 5 : 7-*tetrahydroxyanthraquinone* thus formed crystallises in blackish-blue needles of a coppery lustre.

An account of the tinctorial properties of the above dyes is given.

F. B.

Preparation of a Menthol Ester. ROBERT MEYER (D.R.-P. 261228).—*Menthylglycine hydrochloride*, slender needles, is obtained when a fused suspension of glycine (20 parts) in menthol (70 parts) is treated with continual agitation at about 100° with dry hydrogen chloride and the product purified by crystallisation from water; the free *base*, an oil, is decomposed by warm alkaline hydroxides, and with mercuric chloride furnishes a sparingly soluble *mercury* derivative.

F. M. G. M.

Scission of Racemic Amino-acids by means of Active Acids. I. AMEDEO COLOMBANO and GIUSEPPE SANNA (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 234—237).—A solution containing equimolecular quantities of *d*-camphorsulphonic acid and glycine deposits a salt, $C_{12}H_{21}O_6NS$, which forms long, hygroscopic prisms, m. p. 165—173°, $[\alpha]_D$ + 14·69° (in 10·664% aqueous solution). Alanine similarly yields a camphorsulphonate, m. p. 105—110°, $[\alpha]_D^{18}$ + 14·33° (in 12·153% aqueous solution). These salts, however, yield racemic products when they are decomposed. Similar results were obtained under many different conditions, and no better success was obtained by substituting *d*-bromocamphorsulphonic acid.

Racemic salts were also produced from leucine and tyrosine in the same way.

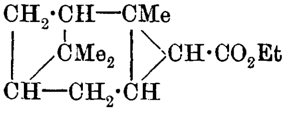
R. V. S.

***dl*-α-Pinene and Ethyl Diazoacetate.** EDUARD BUCHNER and KURT REHORST (*Ber.*, 1913, **46**, 2680, 2687. Compare Buchner and Weigand, this vol., i, 376—887).—The application of ethyl diazo-

acetate to the study of the constitution of *dl*-pinene leads the authors to the conclusion that the latter contains an endocyclic double bond and a methyl group directly attached to a carbon atom having a double bond. This is in conformity with Wagner's formula for pinene.

Pure *dl*-pinene was prepared from American turpentine by subjecting the latter to the action of nitrosyl chloride, the product formed being subsequently decomposed by boiling aniline.

A solution of ethyl diazoacetate in a little *dl*-pinene is slowly added to a mixture of the latter substance and copper powder at 160—165°; nitrogen is violently evolved, and, on distillation, *ethyl* 1:6:6-*trimethyl*-[0,1,4$^{5\cdot7}$,1]-tricyclo*octane*-2-*carboxylate* (annexed formula), b. p. 135°/12·5 mm., is obtained. Since, however, when suspended in alkali it immediately decolorises permanganate, it is probably contaminated with ethyl fumarate.



When saponified with methyl-alcoholic potassium hydroxide, it yields 1 : 6 : 6-*trimethyl*-[0,1,4,$^{5\cdot7}$,1]-tricyclo*octane*-2-*carboxylic acid*, crystalline powder, m. p. 165°, which is stable towards permanganate. The *silver* and *barium* salts were prepared, the latter being readily soluble in water. The *amide*, colourless leaflets, has m. p. 181°. Oxidation by potassium permanganate in hot acid solution converts the acid into a mixture of products from which terebic acid, m. p. 175°, separates after some time. Two other acids can be separated from the residue by converting them into their methyl esters. One of these crystallises in large prisms, whereas the other remains liquid. The latter, when saponified, yields an *acid*, m. p. 211—212°, which could not be further identified on account of its small amount. The former gives methyl*cyclo*propane-1 : 2 : 3-tricarboxylic acid, which has m. p. 192°, and does not evolve carbon dioxide at 220°. The identity of this substance is further established by comparison of its methyl ester, m. p. 76·5°, with a synthetically prepared specimen of the same substance (Buchner and Dessauer, A., 1894, i, 347).

The action of ethyl diazoacetate on pinene in the presence of copper powder has been previously investigated by Loose (A., 1909, i, 463), who obtained an oily product which, on saponification, yielded a non-crystallisable substance. This result is attributed to lack of uniformity in the pinene.

The authors have also studied the action of ethyl diazoacetate on *d*-pinene (α_D + 39·8° in 1-dcm. tube) and have obtained a product which, when saponified, yields an acid, colourless needles, m. p. 123°, together with very small quantities of an isomeric acid, m. p. about 165°. With *l*-pinene (α_D − 31·1° in 1-dcm. tube), on the other hand, the main product is the acid, m. p. about 165°, whilst only small amounts of the substance, m. p. about 123°, are obtained. The complete separation of the two acids is difficult, and it is suggested that the acid, $C_{12}H_{18}O_2$, m. p. 123°, is derived from nopinene present in crude optically-active oil of turpentine. H. W.

Bornylene Ozonide. CARL HARRIES and REINHOLD HAARMANN (*Ber.*, 1913, **46**, 2595—2596).—By the action of washed, 8% ozone on

bornylene in hexane solution, the *ozonide*, $C_{10}H_{16}O_3$, was obtained as a white precipitate, which gradually decomposed after some time, but was fairly stable towards boiling water. In order to hydrolyse the product, bornylene was saturated with ozone in glacial acetic acid and the solution heated for thirty minutes. The solvent was then evaporated under reduced pressure and the residue distilled, when a pale yellow oil, containing a dialdehyde, b. p. 90—110°/16 mm., and a solid, b. p. 125—150°/18 mm., containing in all probability an aldehydic acid, were obtained. J. C. W.

Research on the Eucalypts of Tasmania and their Essential Oils. RICHARD T. BAKER and HENRY G. SMITH (*Reprint* from the *Proc. Roy. Soc. Tasmania*).—Oils distilled from leaves of the various species of eucalyptus occurring in Tasmania have been examined with a view to ascertain their composition and economic value, and of using some of the data thus obtained as a guide in deciding certain outstanding taxonomic problems in connexion with the genus. The results show that the twenty-one species found in Tasmania may be divided into groups as follows:

I. Eight species yielding oils containing over 50% cineole, much pinene, but no phellandrene or piperitone. The characters of the oils from these species are as follows: ***Eucalyptus cordata***, D_{15}^{15} 0·9138, α_D +9·3°, n_D^{16} 1·4965, saponification number 14·8, soluble in 1·25 vols. of 70% alcohol; contains cineole 62%, *d*-pinene, and esters. *E. Muelleri*, D_{15}^{15} 0·9096, α_D +10·4°, n_D^{24} 1·4629, saponification number 15·3, soluble in 4 vols. of 70% alcohol; contains cineole 60%, *d*-pinene, and esters. *E. Perriniana*, D_{15}^{15} 0·9119, α_D +8·9°, n_D^{15} 1·4651, saponification number 10·3, soluble in 2 vols. of 70% alcohol; contains cineole 68%, *d*-pinene, esters, and sesquiterpene. *E. Rodwayi*, D_{15}^{15} 0·9075, α_D +10·6°, n_D^{24} 1·4653, saponification number 3·9, soluble in 6 vols. of 70% alcohol; contains cineole 64%, *d*-pinene, and sesquiterpene. *E. unialata*, D_{15}^{15} 0·9179, α_D +3·1°, n_D^{18} 1·4690, saponification number 11·1, soluble in 1·75 vols. of 70% alcohol; contains cineole 62%, *d*-pinene, esters, and sesquiterpene. ***E. urnigera***, D_{15}^{15} 0·9088, α_D +11·8°, n_D^{23} 1·4638, soluble in 5 vols. of 70% alcohol; contains cineole 63%, *d*-pinene, and esters. ***E. vernicosa***, D_{15}^{15} 0·9038, α_D +11·3°, n_D^{18} 1·4651, saponification number 5·9, soluble in 1 vol. of 80% alcohol; contains cineole 59%, and *d*-pinene. *E. globulus*, as already frequently recorded.

II. Two species yielding oils containing cineole from 25—50%, as well as pinene and phellandrene. *E. Gunnii*, D_{15}^{15} 0 9014, α_D +1·5°, n_D^{18} 1·4752, saponification number 6·7, soluble in 4 vols. of 80% alcohol; contains cineole 41%, *d*-pinene, phellandrene, esters, and sesquiterpene. *E. viminalis*, D_{15}^{15} 0·9154, α_D +4·2°, n_D^{19} 1·4711, saponification number 9·5, soluble in 1 vol. of 80% alcohol; contains 50% cineole, *d*-pinene, phellandrene, esters, and sesquiterpene.

III. Two species yielding oils with over 50% cineole, phellandrene largely replacing pinene, and piperitone being present. *E. linearis*, D_{15}^{15} 0·9096, α_D −10·2°, n_D^{24} 1·4659, saponification number 5·8, soluble in 6 vols. of 70% alcohol; contains cineole 52%, with phellandrene, piperitone, and sesquiterpene. *E. Risdoni*, D_{15}^{15} 0·9045—0·9145, α_D −0·3° to 14·6°, n_D 1·4660 (at 19°) to 1·4733 (at 16°), saponification

number 21·3—27, soluble in 1·25—5 vols. of 70% alcohol; contains cineole 56—58%, phellandrene, piperitone, and esters.

IV. Seven species yielding oils containing much phellandrene, less than 25% of cineole, and having piperitone present. *E. amygdalina*, D_{15}^{15} 0·8668—0·8848, a_D − 59·1° to − 75·1°, n_D^{18} 1·4761—1·4790, saponification number 2·9—3·2, soluble in 7 vols. of 70% alcohol; contains cineole 12—24%, phellandrene, piperitone and sesquiterpene. *E. coccifera*, D_{15}^{15} 0·8810, a_D − 35·8°, n_D^{24} 1·4831, saponification number 4·9, insoluble in 10 vols. of 80% alcohol; contains cineole less than 5%, phellandrene, piperitone and eudesmol. *E. Delegatensis*, D_{15}^{15} 0·8664, a_D − 48·4°, n_D^{24} 1·4828, saponification number 3·1, insoluble in 10 vols. of 80% alcohol; contains traces of cineole, and is chiefly composed of phellandrene with some piperitone and sesquiterpene. *E. regnans*, D_{15}^{15} 0·8802—0·8879, a_D − 28·4° to 31·1°, n_D^{20} 1·4882—1·4901, saponification number 13·2—15·4, soluble in 5vols. of 80% alcohol; contains phellandrene, eudesmol, piperitone, esters, sesquiterpene and traces of cineole. *E. taeniola*, D_{15}^{15} 0·8864, a_D − 27·6°, n_D^{17} 1·4872, saponification number 3·2, soluble in 5 vols. of 80% alcohol; contains cineole 7%, phellandrene, piperitone, eudesmol and sesquiterpene. *E. virgata*, D_{15}^{15} 0·8883, a_D − 20·9°, n_D^{18} 1·4819, saponification number 3·3, soluble in 3 vols. of 80% alcohol; contains cineole 21%, phellandrene, piperitone, eudesmol and sesquiterpene. *E. obliqua*, D_{15}^{15} 0·8836—0·8845, a_D − 24·2° to 28·8°, n_D 1·4839 (at 19°) to 1·4852 (at 24°), saponification number 7·2—8·1, soluble in 3—4 vols. of 70% alcohol; contains phellandrene, aromadendral, less than 5% of cineole and no piperitone.

The two remaining species do not fall readily into any of the above groups. *E. acervula*, D_{15}^{15} 0·8956, a_D − 1·1°, n_D^{18} 1·4756, saponification number 32·8, soluble in 1 vol. of 80% alcohol; contains cineole 21%, *d*-pinene, phellandrene, geraniol, geranyl acetate, liquid and solid paraffins, sesquiterpene. *E. phlebophylla*, D_{15}^{15} 0·8925, a_D − 22·4°, n_D^{18} 1·4761, saponification number 3·2, insoluble in 10 vols. of 80% alcohol; contains cineole 9%, *l*-pinene, phellandrene and eudesmol.

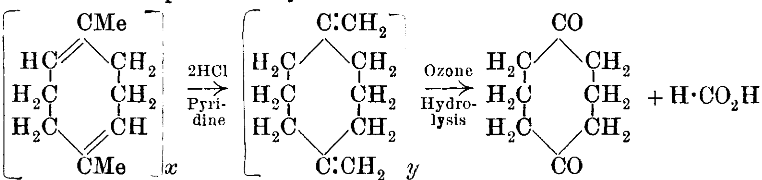
The cineole was determined by the resorcinol method. T. A. H.

The Presence of the 8-Carbon Ring in Normal Caoutchoucs.

CARL HARRIES (*Ber.*, 1913, **46**, 2590—2595. Compare this vol., i, 286).—The author has succeeded in degrading Para caoutchouc to *cyclo*octane-1 : 5-dione. The caoutchouc regenerated by heating the dihydrochloride with pyridine (this vol., i, 380) was converted into the diozonide in ethyl acetate solution, and the residue, after removing the solvent under reduced pressure, was heated for an hour with water at 125°. The filtrate was then neutralised with calcium carbonate, filtered, evaporated in a vacuum, and extracted twenty times with ether. The extract was distilled, and the fraction b. p. 60—90°/14 mm. contained chiefly lævulinaldehyde, the fraction b. p. 100—125°/14 mm. partly solidified and contained *cyclo*octane-1 : 5-dione, and the fraction b. p. 180—200°/14 mm. deposited non-aldehydic crystals, m. p. 88°. The syrup of calcium salts was acidified and extracted with ether, and the extract distilled. The products included much formic and lævulic acids and an oily ketonic acid, b. p. 160—180°/14 mm.

The fraction containing *cyclo*octane-1 : 5-dione was redistilled, and the pale yellowish-green distillate, b. p. 107—110°/14 mm., was found to solidify in ice to large, colourless leaflets. It was difficult to remove the last traces of lævulinaldehyde, so the *disemicarbazone*, $C_{10}H_{18}O_2N_6$, was prepared. It forms a white, crystalline mass, m. p. 186·5°.

The variety of products shows that the regenerated caoutchouc consists of a mixture of at least three forms, due to the displacement of the double linkings in the 8-ring, but the formation of so much lævulinaldehyde and acid indicates that a large part of the caoutchouc is regenerated in its natural form. The degradation into *cyclo*butane-1 : 5-dione is represented by the scheme:



J. C. W.

Estimation of Free Sulphur in Vulcanised Caoutchouc. PAUL BARY (*Rev. gen. Chim. pure appl.*, 1913, **16**, 142—145).—Polemical against Alexander (this vol., i, 67), and in agreement with Hinrichsen and Kindischer (A., 1912, i, 706). F. M. G. M.

New Glucosamine Compound and the Constitution of Chitin. YASHIRO KOTAKE and YOSHITA SERA (*Zeitsch. physiol. Chem.*, 1913, **88**, 56—72).—α- and β-Modifications of *lycoperdin*,

$$C_{13}H_{24}O_9N_2,$$

are obtained from the fungus *Lycoperdon gemmatum*. Both show the biuret and iodine reactions and reduce Fehling's solution: they occupy a mean position between the polypeptides and polysaccharides.

α-Lycoperdin is insoluble in water and crystallises in characteristic, granular crystals, $[\alpha]_D$ − 6·7°, changing to − 5·28°. It becomes black at 240°. β-Lycoperdin forms a soluble sulphate crystallising in needles.

On hydrolysis, 90% of glucosamine and 14% of formic acid are obtained, equivalent to the formation of two molecules of glucosamine and one molecule of formic acid. Constitutional formulæ are assigned to lycoperdin and to chitin, which is assumed to contain four glucosamine molecules, in all of which the NH_2 group is acetylated. The carbon to which the amino-group is attached is supposed to be directly joined to the potentially aldehydic carbon in the next molecule. E. F. A.

Application of the Bio-chemical Method to Gentiana acaulis, L. Isolation of a New Glucoside; Gentiacaulin. MARC BRIDEL (*J. Pharm. Chim.*, 1913, [vii], **8**, 241—250).—Investigation of a purified alcoholic extract of *Gentiana acaulis* showed that it contained products hydrolysable by both invertase and emulsin, and in addition a new glucoside, which is not attacked by emulsin, which was isolated and characterised. No gentiopicrin was present.

The new glucoside, *gentiacaulin*, $C_{47}H_{60}O_{29}$, crystallises from hot alcoholic extracts of the plant in transparent, golden-yellow needles, has no definite melting point, but decomposes from 145° to 160°, and is lævorotatory, $[\alpha]_D$ −63·84° in water. It is precipitated by lead subacetate solution, gives an unstable green coloration with ferric chloride, and reduces Fehling's solution on boiling. It is hydrolysed by boiling dilute sulphuric acid, yielding xylose and *gentiacaulein*, m. p. 177°, crystallising in bright yellow needles, soluble in alcohol or ether, and dissolving in alkalis to give solutions which rapidly become dark brown on exposure to air. T. A. H.

Gitonin, a New Digitalis Glucoside. ADOLF WINDAUS and A. SCHNECKENBURGER (*Ber.*, 1913, **46**, 2628—2633).—Merck's "digitonin" (compare Kiliani, A., 1911, i, 139) is not an individual substance, but contains another glucoside to which the name gitonin is applied. The solubilities of the two substances in alcohol vary considerably with the strength of the solvent. *Gitonin*, $C_{49}H_{80}O_{23}$, is less soluble in 95% alcohol, but more soluble in 85% alcohol, than digitonin, and was obtained in white, amorphous granules when a solution of 100 grams of crude material in 3 litres of 95% alcohol was left for some weeks. It decomposes at 272°, has $[\alpha]_D^{20}$ −50·69°, and gives a rose-red to wine-red coloration on boiling with concentrated hydrochloric acid. It forms an *additive* compound, $C_{76}H_{126}O_{24}$, with cholesterol, in sparingly soluble, small, slender needles, and a similar *compound*, $C_{79}H_{130}O_{24}$, with stigmasterol (compare digitonin compounds, A., 1909, i, 172).

After hydrolysis with alcoholic hydrochloric acid, water caused the crystallisation of *gitogenin*, $C_{26}H_{42}O_4$, which was obtained pure after many recrystallisations, in the form of white, narrow leaflets, m. p. 271—272°. It is indifferent towards hydroxylamine, but forms a *diacetyl* derivative, long needles, m. p. 243—244°, a *dipropionyl* derivative, long, narrow leaflets, 195—196°, and yields on oxidation with chromic acid, a dibasic *acid*, $C_{26}H_{40}O_6$, m. p. 242—243°, the *methyl* ester of which crystallises in leaflets, m. p. 145—146°. The sugar syrup did not readily crystallise, although it contained much galactose. The presence, in addition, of 21% of pentoses agrees with the equation: $C_{49}H_{80}O_{23} + 4H_2O = C_{26}H_{42}O_4 + 3C_6H_{12}O_6 + C_5H_{10}O_5$.
J. C. W.

Mustard Oil Glucosides. II. Glucocheirolin. WILHELM SCHNEIDER and LUDWIG A. SCHÜTZ (*Ber.*, 1913, **46**, 2634—2640. Compare A., 1912, i, 1007).—The isolation of the glucoside, glucocheirolin, from wallflower seeds is described. The crude substance was obtained from the dry, fat-free seeds by extraction with several large portions of alcohol which had been dried over sodium. The different fractions contained products in which the proportion, K : S : N, varied, but approached more and more to the expected value 1 : 3 : 1. The very hygroscopic glucoside was then dissolved in water, clarified by shaking with litharge, then quickly treated with lead acetate, and filtered. After precipitating the dissolved lead and exactly neutralising, the solution was concentrated in a vacuum and stirred into absolute alcohol. The precipitate

was then recrystallised a few times from much 90% alcohol, and finally obtained in small, colourless needles, m. p. 158—160°.

Glucocheirolin, $C_{11}H_{20}O_{11}NS_3K,H_2O$, only parts with water after some days in a hot exhausted desiccator over phosphoric oxide. It is tasteless, has $[\alpha]_D^{27}$ $-21\cdot56°$ to $-21\cdot09°$, and gives up one molecule of sulphuric acid on boiling with acidified barium chloride. When silver nitrate is added to the dilute solution, the cheirolin silver sulphate separates after a time as a jelly, in which crystal-centres slowly appear, and finally small, feathery needles, $C_5H_9O_2NS_2,Ag_2SO_4,H_2O$, decomp. 154°, are deposited. The behaviour of glucocheirolin is similar to that of sinigrin and accords with the constitution:

$$SO_2Me\cdot CH_2\cdot CH_2\cdot CH_2\cdot N(O\cdot SO_3K)\cdot S\cdot C_6H_{11}O_5.$$

J. C. W.

Derivatives of α- and β-Bromopicrotoxinins. PAUL HORRMANN (*Ber.*, 1913, **46**, 2793—2801).—The author now finds that picrotoxinin really has the old formula, $C_{15}H_{16}O_6$, not $C_{14}H_{16}O_6$ (A., 1912, i, 709).

By treatment with boiling aqueous potassium hydroxide and subsequent acidification, α-bromopicrotoxinin yields an *acid*,

$$C_{15}H_{17}O_7Br,$$

m. p. 248° (decomp.), needles containing H_2O or prisms, $[\alpha]_D^{17\cdot5}$ $-28°51'$ in alcohol ($c = 2\cdot889$) (*methyl* ester, m. p. 218°, $[\alpha]_D^{17\cdot5}$ $-29°21'$; *ethyl* ester, crystals, $[\alpha]_D^{17\cdot5}$ $-31°59'$), a boiling alcoholic solution of which is reduced by zinc dust and aqueous ammonium chloride to *α-picrotoxininic acid*, $C_{15}H_{18}O_7$, m. p. 209° (decomp.), $[\alpha]_D^{17\cdot5}$ $-4°53'$ in alcohol ($c = 5\cdot981$). α-Picrotoxininic acid reacts additively with bromine, reduces alkaline potassium permanganate in the cold and Fehling's solution and ammoniacal silver oxide solution by heating, and neutralises 1 mol. of sodium hydroxide at the ordinary temperature and 2 mols. on the water-bath. It forms a *methyl* ester, m. p. 182°, $[\alpha]_D^{17\cdot5}$ $-9°44'$ in alcohol ($c = 1\cdot970$), and *ethyl* ester, m. p. 159°, $[\alpha]_D^{17\cdot5}$ $-8°4'$ ($c = 4\cdot238$); its potassium salt reacts with aqueous bromine to form an *acid*, $C_{15}H_{17}O_7Br,H_2O$, m. p. 236° (decomp.), $[\alpha]_D^{17\cdot5}$ $-58°2'$ in alcohol ($c = 3\cdot532$). By reduction with palladous chloride and hydrogen at 2 atmospheres, α-picrotoxininic acid yields *α-dihydropicrotoxininic acid*, $C_{15}H_{20}O_7$, m. p. 232° (decomp.), $[\alpha]_D^{17\cdot5}$ $-4°10'$ in alcohol ($c = 2\cdot006$), which is also a lactonic acid, since it neutralises one mol. of alkali in the cold and 2 mol. on the water-bath. By boiling with $2N$-sulphuric acid, α-picrotoxininic acid is converted into an isomeride, *β-picrotoxininic acid*, $C_{15}H_{18}O_7$, m. p. 235° (decomp.), $[\alpha]_D^{17\cdot5}$ $-48°$ in alcohol ($c = 9\cdot254$) (*methyl* ester, m. p. 204°, $[\alpha]_D^{17\cdot5}$ $-50°3'$ in alcohol [$c = 1\cdot049$]; *ethyl* ester, m. p. 198°, $[\alpha]_D^{17\cdot5}$ $-49°57'$ in alcohol [$c = 2\cdot436$]), which is stable to aqueous bromine, does not reduce Fehling's solution or ammoniacal silver oxide solution, and neutralises only 1 mol. of alkali on the water-bath. C. S.

Chlorophyll. XXII. Degradation of the two Components of Chlorophyll by Alkalis. RICHARD WILLSTÄTTER, MAX FISCHER, and LENNART FORSÉN (*Annalen*, 1913, **400**, 147—181. Compare A., 1908, i, 198; 1910, i, 126; 1911, i, 392).—The monocarboxylic acids,

phyllophyllin and pyrrophyllin, obtained as the final products of the action of alcoholic potassium hydroxide on chlorophyll, are produced, not one from each component of the chlorophyll as might be expected, but both from each component. An explanation of this is to be found in Willstätter and Utzinger's lactam theory of the brown phase (A., 1911, i, 392). The first action of the alkali on, for example, chlorophyll-*a*, indicated in the colour phase, is rupture of the lactam group and its closure in another direction, yielding chlorophyllin-*a* (lactam group, $\cdot CO_{\gamma} \cdot NH_{\delta} \cdot$, closed and the α- and β-carboxyl groups free) and *iso*chlorophyllin *a* (lactam group, $\cdot CO_{\alpha} \cdot NH_{\delta} \cdot$, closed and β- and γ-carboxyl groups free); in the subsequent changes caused by the alkali, the lactam groups disappear and the β-carboxyl group is destroyed, so that the difference between phyllophyllin and pyrrophyllin is due probably to the different positions of the carboxyl groups α and γ.

Rapid hydrolysis of chlorophyll by hot alkalis yields mainly *iso*chlorophyllins *a* and *b* (from which phytochlorin-*e* and phytorhodin-*g* respectively are obtained by eliminating the magnesium by acids); in the cold, the chief products are chlorophyllin-*a* and -*b*, from which phytochlorin-*g* and the feebly basic phytorhodins-*k* and -*i* are respectively obtained by the action of acids. In the *a* series, every change shown in the diagram has been accomplished.

Chlorophyll-*a*

↙ ↘

Phytochlorin-*g* (→ Pyrroporphyrin)	← Chlorophyllin-*a*	*iso*Chlorophyllin-*a* →	Phytochlorin-*e* (→ Phylloporphyrin)
	↓	↓	
Glaucoporphyrin	← Glaucophyllin	Cyanophyllin →	Cyanoporphyrin
	↓	↓	
Rhodoporphyrin	← Rhodophyllin	Erythrophyllin →	Erythroporphyrin
	↓	↓	
Pyrroporphyrin	← Pyrrophyllin	Phyllophyllin →	Phylloporphyrin

The degradation of chlorophyll-*b* is more difficult, because the second oxygen atom must be reduced without any elimination of carbon dioxide occurring; this has been effected by means of concentrated methyl-alcoholic potassium hydroxide in the presence of pyridine, whereby even the very unstable phytorhodin-*g* has been degraded to phylloporphyrin.

Chlorophyll-*b*

↙ ↘

Phytorhodin-*k* and -*i*	← Chlorophyllin-*b*	*iso*Chlorophyllin-*b* →	Phytorhodin-*g* (→ Phylloporphyrin)
↓	↓	↓	
		Rubiphyllin →	Rubiporphyrin
		↓	
Pyrroporphyrin	← Pyrrophyllin	Phyllophyllin →	Phylloporphyrin

The differentiation and identification of the preceding porphyrins have been effected by the partition method (between hydrochloric acid and ether).

Potassium iso*chlorophyllin*-a, $C_{34}H_{31}O_6N_4MgK_3$, a dark blue powder with a pale green streak, is obtained by boiling gently methylchlorophyllide-*a* with concentrated methyl-alcoholic potassium hydroxide for five minutes and, after further suitable treatment of the solution and dilution with water, adding potassium chloride. Its solutions, in contrast to those of chlorophyllin-*a*, are intensely fluorescent. By heating with pyridine (3 parts) and methyl-alcoholic potassium hydroxide (10 parts) at 150—155° in a silver autoclave for four or five hours, it yields the easily soluble *potassium* salt of the very unstable *cyanophyllin*, $C_{33}H_{34}O_4N_4Mg$. Cyanophyllin is a weaker acid than the isomeric glaucophyllin and is not extracted from ether by 0·003% aqueous ammonia. Its solutions are splendidly blue and intensely fluorescent. By treatment with strong hydrochloric acid it is converted into *cyanoporphyrin*, $C_{33}H_{36}O_4N_4$, reddish-brown needles.

Erythrophyllin, $C_{33}H_{34}O_4N_4Mg$, is prepared from chlorophyll-*a* by boiling with pyridine and methyl alcoholic potassium hydroxide and, after the hydrolysis, heating the alkaline mass in an autoclave at exactly 175—180°; the *potassium* salt, obtained by diluting with water, is then decomposed by sodium dihydrogen phosphate. Erythrophyllin crystallises in pointed rhombic plates, forms a *dimethyl* ester, $C_{35}H_{38}O_4N_4Mg$, long, red prisms, and has weaker acidic properties than rhodophyllin. It is converted into phyllophyllin by methyl-alcoholic potassium hydroxide at 200—210°. Mixtures of cyanophyllin, erythrophyllin, and phyllophyllin can be separated by treating the ethereal solution with 0·2% disodium hydrogen phosphate which extracts the strongest acid, cyanophyllin; somewhat concentrated disodium hydrogen phosphate or not too dilute aqueous ammonia then removes erythrophyllin, the phyllophyllin remaining in the ethereal solution.

Erythroporphyrin, $C_{33}H_{36}O_4N_4$, red, silky prisms, obtained by treating erythrophyllin with concentrated hydrochloric acid and a little ether, forms a *hydrochloride*, pale red needles (insoluble in dilute hydrochloric acid), and a *dimethyl* ester, $C_{35}H_{40}O_4N_4$, brown or reddish-brown prisms, the *hydrochloride* of which is easily soluble in hydrochloric acid.

Di- and mono-basic phyllins derived from the *b* component of chlorophyll are most readily obtained from methylchlorophyllide-*b*. This substance, dissolved in pyridine, is completely hydrolysed by gentle boiling for five minutes with methyl-alcoholic potassium hydroxide, and the blood-red, fluorescent, alkaline solution is heated at 150—155° (whereby an unstable *phyllin* is obtained, the solution of which in ether is green and in alcoholic alkali blue and fluorescent), and finally at 165—170° after dilution with more alcoholic potassium hydroxide. The product is now the *potassium* salt, bluish-violet crystals, of rubiphyllin, from which *rubiphyllin*, $C_{33}H_{34}O_4N_4Mg$, is obtained by treatment with sodium dihydrogen phosphate. Rubiphyllin, which is more easily obtained by hydrolysing methylphæophorbide-*b* or phytorhodin-*g* with methyl-alcoholic potassium hydroxide and heating the resulting solution with magnesium oxide at 170°, crystallises usually in triangular leaflets; its crystalline powder is bluish-black. Rubiphyllin, unlike erythrophyllin and rhodophyllin, is not extracted

from its ethereal solution by 0·5% disodium hydrogen phosphate, but is at once removed by a 1% solution; the *dipotassium* salt,

$$C_{33}H_{32}O_4N_4MgK_2,$$

is a violet powder, which reacts with methyl sulphate to form *rubiphyllin dimethyl* ester, $C_{35}H_{38}O_4N_4Mg$, olive-brown prisms. *Rubiporphyrin*, $C_{33}H_{36}O_4N_4$, obtained by dissolving the preceding potassium salt in 20% hydrochloric acid, crystallises in rhombic leaflets which are olive-brown, in transmitted light, and forms a *hydrochloride*, olive-brown prisms, and *dimethyl* ester, $C_{35}H_{40}O_4N_4$, violet prisms.

By heating with methyl-alcoholic potassium hydroxide above 170°, rubiphyllin is converted into phyllophyllin, which is identified as the characteristic calcium salt.

By hydrolysing a pyridine solution of methylchlorophyllide-*b* with methyl-alcoholic potassium hydroxide in the cold, chlorophyllin-*b* is obtained, but always accompanied with *iso*chlorophyllin-*b*; consequently, the degradation products of the former are always contaminated with the phyllins of the *iso*-series, the final products at 205—210° being pyrrophyllin and phyllophyllin. Pure pyrrophyllin can be obtained by hydrolysing methylphæophorbide-*b* by methyl-alcoholic potassium hydroxide in the cold, and heating the resulting alkaline solution with magnesium oxide in a silver autoclave; up to 200°, several still unknown phyllins are formed, but after heating for five hours at 220°, the product is pyrrophyllin, which is identified by conversion into pyrroporphyrin. The latter is obtained directly when phytorhodins-*i* and -*k* are heated at 205—210° with methyl-alcoholic potassium hydroxide alone.

Phytorhodins-i and -k, the latter usually predominating, are obtained together by several methods; the hydrochloric acid number of *k* is 14—14·5, of *i* 15—16, so that their separation requires very careful fractionation with 14% hydrochloric acid. The best method of preparing them is as follows. Chlorophyll (from stinging-nettle leaves) is kept in petroleum for a few weeks until allomerisation is complete. The solution is shaken with concentrated methyl-alcoholic potassium hydroxide until the hydrolysis of the chlorophyll is complete, and then with hydrochloric acid to remove the magnesium. The products are dissolved in ether, the more basic constituents are removed by repeated extraction with 13% hydrochloric acid, and finally the brown ethereal solution is treated with 14—14·5% hydrochloric acid to remove phytorhodin-*k*, and with 17% hydrochloric acid to separate phytorhodin-*i*; the substances require still further purification.

Phytorhodin-k, $C_{34}H_{34}O_6N_4$, black, metallic leaflets, and *phytorhodin*-i, $C_{34}H_{34}O_6N_4$, black, metallic leaflets, resemble one another in their solubilities, but give different colour reactions with potassium hydroxide, cæsium hydroxide, formic acid, and concentrated nitric acid.

By the term "hydrochloric acid" number of a chlorophyll derivative, the author denotes the percentage strength of the hydrochloric acid which is required to extract about 2/3 of the solute from the solution of the derivative in a volume of ether equal to that of the hydrochloric acid. A more rigidly defined number, however, is required for the differentiation of substances which have very nearly equal basicities. This is found in the "partition" number, which

represents the percentage amount of a substance extracted under definite conditions from ethereal solution by hydrochloric acid of a definite strength; the conditions are, 3 milligrams of substance, 1 litre of ether, and 100 c.c. of hydrochloric acid, the extraction lasting one minute. The concentration of the acid is either that denoted by the hydrochloric acid number, or, in the comparison of substances of different basicity, any other concentration suitable for the extraction.

The value of the partition number is illustrated by the comparison of phylloporphyrin and pyrroporphyrin; both have hydrochloric acid number 0·5, but the partition number of the former is about 35 and of the latter about 4. C. S.

Chlorophyll. XXIII. Parent Substances of the Phyllins and Porphyrins. RICHARD WILLSTÄTTER and MAX FISCHER (*Annalen*, 1913, **400**, 182—194).—Since the degradation of hæmin and of chlorophyll yields similar, but not identical, porphyrins, which, however, give identical products by oxidation (A., 1910, i, 499) and by reduction (A., 1912, i, 41), and since the dissimilarity of the porphyrins is possibly conditioned by differences in the position of the carboxyl groups, the elimination of the latter becomes a matter of prime importance. This has been accomplished with the phyllins and porphyrins derived from chlorophyll. The decarboxylation of chlorophyll derivatives by heating with methyl-alcoholic potassium hydroxide in a sealed tube proceeds only as far as the monocarboxylic acid, decomposition then beginning at 250° with the formation of hæmopyrrole and amorphous, brown products. Complete removal of carbon dioxide from the carboxyl groups, however, is effected by heating rapidly and carefully with soda-lime; the yields are small because the product decomposes at temperatures below the temperature of formation. Potassium rhodophyllin is mixed with soda-lime (free from iron), and is heated in small quantities rapidly and carefully by a naked flame until the colour changes suddenly from pale grey to brown. The mass is rapidly cooled, moistened with water, and extracted with warm ether. The ethereal solution is well washed with potassium hydroxide and with 5% hydrochloric acid. After washing finally with dilute ammonia and concentrating the ethereal solution, a *substance*, $C_{31}H_{34}N_4Mg$, m. p. about 205°, bluish-violet crystals, is obtained, which is called *aetiophyllin*, and is the parent of the phyllins. Aetiophyllin forms violet-red, intensely fluorescent solutions, and in ether is remarkably stable to 4—7% hydrochloric acid; in petroleum, however, even 0·05% hydrochloric acid changes the colour of the solution to that of aetioporphyrin.

Porphyrins lose carbon dioxide much less readily than phyllins, so that the best method of preparing aetioporphyrin, the parent of the porphyrins, is by treating an ethereal solution of aetiophyllin with 20% hydrochloric acid, whereby the magnesium is at once replaced by hydrogen. *Aetioporphyrin*, $C_{31}H_{36}N_4$, m. p. about 280°, hydrochloric acid number 3, partition number for 3% hydrochloric acid 40 (compare preceding abstract), is obtained in violet, crystalline crusts, and forms a *styphnate*, $C_{31}H_{36}N_4,C_6H_3O_8N_3$, m. p. 170°, red prisms, by which it is best purified. It also forms a *hydrochloride*, olive-brown needles,

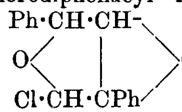
picrate, red prisms, *aurichloride* and *platinichloride*, and yields characteristic complex compounds with salts of the heavy metals.

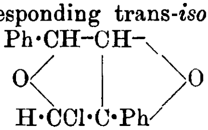
Phylloporphyrin, pyrroporphyrin, and rhodoporphyrin when heated with soda-lime each yields aetioporphyrin, thus confirming Willstätter's theory that the two former are different because of the difference in the position of the carboxyl group.

Aetiophyllin can be obtained from aetioporphyrin by treating a concentrated ethereal solution of the latter with magnesium methyl iodide (Willstätter and Forsén, this vol., i, 499), and subsequently with sodium dihydrogen phosphate.

The absorption spectrum of aetiophyllin is very similar to that of pyrrophyllin, and that of aetioporphyrin to that of pyrroporphyrin, but contains much stronger bands. C. S.

The Quantitative Dyeing of Silk with Basic Dyes. H. SALVATERRA (*J. pr. Chem.*, 1913, [ii], **88**, 502—504. Compare this vol., ii, 258).—Quantitative experiments on the dyeing of silk with a number of magenta-dyes show that the amount of these dyes taken up by the silk is proportional to their molecular weights, and thus supports the view that the dyeing of silk is a chemical process analogous to salt-formation. F. B.

Constitution of the So-called α- and β-Halogendiphenacyls. OSKAR WIDMAN [with G. KARL ALMSTRÖM] (*Annalen*, 1913, **400**, 86—130).—The constitutions previously ascribed to the α- and β-halogendiphenacyls (A., 1909, i, 822) are withdrawn and are to be replaced by the following: α-chlorodiphenacyl is cis-2-*chloro*-3:4-*oxido*-3:5-*diphenyltetrahydrofuran*,  and β-chlorodiphenylacyl is the corresponding trans-*isomeride*,



The evidence on which these constitutions are based is given below the most important proofs being furnished by the reactions of the α- and β-halogendiphenacyls with aniline and with hydrazine hydrate.

Paal and Demeler's statements, that only α-bromodiphenacyl results from the interaction of alcoholic sodium ethoxide and ω-bromoacetophenone and that the α-compound is changed to the β-isomeride by boiling alcohol, are incorrect. The authors show that α-chloro(or bromo-)-diphenacyl is unchanged by boiling alcohol, but that in the presence of sodium chloride and a little sodium hydroxide, it is converted almost quantitatively into the β-isomeride in twenty-four to forty-eight hours at the ordinary temperature. In the preparation of the halogendiphenacyls, therefore, both isomerides are formed, the amount of the β-compound being greater the longer the substances are kept in contact with the alcoholic, alkaline mother liquor. Since β-halogendiphenacyl can be converted indirectly into the α-compound (*loc. cit.*), the two compounds are most probably stereoisomeric.

β-Chlorodiphenacyl (*trans*-2-chloro-3 : 4-oxido 3 : 5-diphenyltetrahydrofuran) has m. p. 147—148°, not 154—155°, as stated in the literature.

The course of the reaction whereby ω-halogenacetophenones and alcoholic sodium ethoxide yield oxido-tetrahydrofurans is, in its first stage, probably analogous to those described by Darzens (A., 1905, i, 116) and by Claisen (A., 1905, i, 286), in which ketones or aldehydes condense with esters of halogenated fatty acids in the presence of sodium ethoxide or of sodamide to form esters of substituted glycidic acids: $2CH_2Cl{\cdot}COPh + NaOH = O{<}\begin{matrix}CH{\cdot}COPh\\ |\\ CPh{\cdot}CH_2Cl\end{matrix} + NaCl + H_2O$. The intermediate product then does not yield a four-membered ring by loss of hydrogen chloride, but is converted into a furan derivative, $O{<}\begin{matrix}CH{-}CHPh\\ |\\ CPh{\cdot}CHCl\end{matrix}{>}O$. The two suppositions in this explanation are supported by experimental evidence. With regard to the formation of the oxido-group, the authors find that ω-chloro- or bromo-acetophenone and benzaldehyde in the presence of alcoholic sodium ethoxide, in accordance with Darzen's statement that esters of halogenated fatty acids condense preferentially with aldehydes rather than with ketones, yield not a trace of a furan derivative, but a *substance*, m. p. 89—90°, which proves to be *α-benzoyl-β-phenylethylene oxide*, $O{<}\begin{matrix}CHPh\\ |\\ CH{\cdot}COPh\end{matrix}$. The second supposition, that a ketone containing a halogen atom in the γ-position to the carbonyl group is capable of yielding a furan derivative, is supported by the behaviour of a substance described by Perkin (T., 1885, **47**, 842) as phenyl ω-bromopropyl ketone; this substance, however, does not exhibit the properties of a ketone, and is most probably 2-bromo-5-phenyltetrahydrofuran.

By heating with a large excess of 99% hydrazine hydrate, α-chlorodiphenacyl (*cis*-2-chloro-3 : 4-oxido-3 : 5-diphenyltetrahydrofuran) is converted into a *substance*, $C_{16}H_{12}N_2$, m. p. 139—140°, faintly yellow, rhombic plates, which proves to be 3 : 5-diphenylpyridazine (Almström, this vol., i, 1240).

By treatment with boiling aniline, α-chlorodiphenacyl yields a *substance* (I.), $C_{22}H_{16}NCl$, m. p. 146—147°, faintly yellow plates, whilst β-chlorodiphenacyl (*trans*-2-chloro-3 : 4-oxido-3 : 5-diphenyltetrahydrofuran) yields a *substance* (II.), $C_{22}H_{17}ON$, m. p. 150°, citron-yellow needles, which forms yellow solutions with bluish-green fluorescence. The constitutions of the substances I. and II. were elucidated after the discovery (compare Almström, *loc. cit.*) that 1 : 3 : 5-triphenylpyrrol-2-one (which is isomeric with II.) is converted by phosphorus trichloride into 2-chloro-1 : 3 : 5-triphenylpyrrole (which is isomeric with I.), and by phosphorus pentachloride into 2 : 4-dichloro-1 : 3 : 5-triphenylpyrrole. Since the last substance is also formed by the action of phosphoric and phosphoryl chlorides on I., it follows that I. must be 4-*chloro*-1 : 3 : 5-*triphenylpyrrole*. Substance II. is then easily proved to be 4-*hydroxy*-1 : 3 : 5-*triphenylpyrrole*, since it forms an *acetyl* derivative, m. p. 132—133°, colourless needles, by treatment with aqueous sodium hydroxide and acetyl chloride in acetone at 0°, and is converted into I. (4-chloro-1 : 3 : 5-triphenylpyrrole) by phosphorus trichloride at 170—190°.

By treatment with warm acetic anhydride and a little concentrated sulphuric acid, 4-hydroxy-1 : 3 : 5-triphenylpyrrole or its acetyl derivative yields 4-*acetoxy*-2-*acetyl*-1 : 3 : 5-*triphenylpyrrole*,

$$\left.\begin{array}{l}OAc\cdot C\text{——}CPh\\ \quad\ \|\\ \quad CPh\cdot NPh\end{array}\right> C\cdot COMe,$$

m. p. 189—190°, colourless needles, from which 4-*hydroxy*-2-*acetyl*-1 : 3 : 5-*triphenylpyrrole*, m. p. 180—181°, is obtained by hydrolysis with alcoholic sodium ethoxide.

4-Chloro-1 : 3 : 5-triphenylpyrrole is a very stable substance, and is not attacked by sodium amalgam, boiling alcoholic sodium ethoxide, nitrous acid, or boiling alkaline potassium permanganate. By treatment with boiling acetic anhydride and concentrated sulphuric acid, it yields 4-*chloro*-2-*acetyl*-1 : 3 : 5-*triphenylpyrrole*, $C_{24}H_{18}ONCl$, m. p. 136° (*semicarbazone*, m. p. about 236° [decomp.]), which reacts with benzaldehyde (1 mol.), 10% sodium hydroxide, and alcohol at the b. p. to form 4-*chloro*-2-*cinnamoyl*-1 : 3 : 5-*triphenylpyrrole*, $C_{31}H_{22}ONCl$, m. p. 197°, stout, yellow needles. By reduction with hydriodic acid, D 1·22, and amorphous phosphorus at 160°, 4-chloro-1 : 3 : 5-triphenylpyrrole yields 1 : 3 : 5-triphenylpyrrole, m. p. 150—151°, which reacts with boiling acetic anhydride and concentrated sulphuric acid to form 2(?)-*acetyl*-1 : 3 : 5-*triphenylpyrrole*, $C_{24}H_{19}ON$, m. p. 165—166°.

By treatment with methylaniline at 130—140°, α- and β-chlorodiphenacyls yield, not pyrrole derivatives, but phenacylmethylaniline.

Now that the α- and β-halogendiphenacyls have been proved to be *cis*- and *trans*-2-halogen-3 : 4-oxido-3 : 5-diphenyltetrahydrofuran respectively, the nature of their additive compounds with halogen hydrides and acyl haloids (Paal and Stern, A., 1901, i, 154 ; Paal and Schulze, A., 1902, i, 229) is readily understood, and some inaccuracies in the statements of these investigators are easily detected. *trans*-2-Chloro-3 : 4-oxido-3 : 5-diphenyltetrahydrofuran and hydrogen chloride, best in warm glacial acetic acid, yield 2 : 3-*dichloro*-4-*hydroxy*-3 : 5-*diphenyltetrahydrofuran*, $O\left<\begin{array}{l}CHPh\cdot CH\cdot OH\\ CHCl\text{—}CPhCl\end{array}\right.$, m. p. 164° (decomp.), which is converted into 4-hydroxy-1 : 3 : 5-triphenylpyrrole and 4-*hydroxy*-3 : 5-*diphenyl*-1-p-*tolylpyrrole*, m. p. 152°, citron-yellow plates, by aniline and *p*-toluidine respectively on the water-bath. In a similar manner, *trans*-2-chloro-3 : 4-oxido-3 : 5-diphenyltetrahydrofuran and 12% hydrogen bromide in glacial acetic acid at about 30° yield 2-*chloro*-3-*bromo*-4-*hydroxy*-3 : 5-*diphenyltetrahydrofuran*, m. p. 155° (decomp.). The substance is given this constitution, not that of the 4-bromo-3-hydroxy-isomeride, because it loses only hydrogen bromide, not both hydrogen chloride and bromide by treatment with alcoholic sodium ethoxide. Contrary to the statement of Paal and his collaborators (*loc. cit.*), the substance, being a bromohydrin, obviously contains a hydroxyl group ; the acetyl derivative, m. p. 89—90°, is obtained by the action of acetic anhydride and two drops of concentrated sulphuric acid. This acetyl derivative is identical with the additive compound (2-chloro-3-bromo-4-acetoxy-3 : 5-diphenyltetrahydrofuran) of β-chlorodiphenacyl and acetyl bromide described by Paal and his co-workers (*loc. cit.*). In a similar manner, the additive compound of β-bromodiphenacyl and hydrogen chloride (*trans*-3-chloro-2-bromo-4-hydroxy-

3 : 5-diphenyltetrahydrofuran) yields an acetyl derivative, m. p. 89—90°, identical with the additive compound of β-bromodiphenacyl and acetyl chloride. Knowing the constitutions of β-chloro- and bromo-diphenacyls, the author is able to assert that the two preceding acetyl derivatives, in spite of their similarities in appearance and m. p., are not identical, as stated by Paal (*loc. cit.*). The assertion is proved, not only by a comparison of the corresponding propionyl and valeryl derivatives which differ in m. p. (see below), but also by the fact that by treatment with alcoholic sodium ethoxide, *trans*-3-chloro-2-bromo-4-acetoxy-3 : 5-diphenyltetrahydrofuran (that is, the additive compound of β-bromodiphenacyl and acetyl chloride) yields *trans*-3-chloro-2-bromo-4-hydroxy-3 : 5-diphenyltetrahydrofuran, whilst *trans*-2-chloro-3-bromo-4-acetoxy-3 : 5-diphenyltetrahydrofuran (the additive compound of β-chlorodiphenacyl and acetyl bromide) is more extensively changed and yields *cis*-2-chloro-3 : 4-oxido-3 : 5-diphenyltetrahydrofuran (α-chlorodiphenacyl). In a similar manner, *trans*-2 : 3-dichloro-4-acetoxy-3 : 5-diphenyltetrahydrofuran, prepared by the addition of acetyl chloride to β-chlorodiphenacyl or by treating *trans*-2 : 3-dichloro-4-hydroxy-3 : 5-diphenyltetrahydrofuran with acetic anhydride and concentrated sulphuric acid, is converted by alcoholic sodium ethoxide into *trans*-2 : 3-dichloro-4-hydroxy-3 : 5-diphenyltetrahydrofuran or *trans*-2-chloro-3 : 4-oxido-3 : 5-diphenyltetrahydrofuran, according as 1 or 2 molecules of the ethoxide are used.

trans-3-Chloro-2-bromo-4-hydroxy-3 : 5-diphenyltetrahydrofuran (the additive compound of β-bromodiphenacyl and hydrogen chloride) yields the *propionyl* derivative, $C_{19}H_{18}O_3ClBr$, m. p. 106°, and the *valeryl* derivative, m. p. 104—105°, by treatment with propionic anhydride and valeric anhydride respectively in the presence of a little concentrated sulphuric acid. By similar treatment, *trans*-2-chloro-3-bromo-4-hydroxy-3 : 5-diphenyltetrahydrofuran (the additive compound of β-chlorodiphenacyl and hydrogen bromide) yields a *propionyl* derivative, m. p. 69°, and *valeryl* derivative, m. p. 93°.

As stated by Paal and Schulze (*loc. cit.*), *cis*-2-halogen-3 : 4-oxido-3 : 5-diphenyltetrahydrofurans (α-halogendiphenacyls) do not react with halogen hydrides to form additive compounds (*cis*-2 : 3-dihalogen-4-hydroxy-3 : 5-diphenyltetrahydrofurans) ; moreover, these substances cannot be prepared by the action of sodium ethoxide on the *cis*-2 : 3-dihalogen-4-acetoxy-3 : 5-diphenyltetrahydrofurans (additive compounds of α-halogendiphenacyls and acetyl chloride).

Bromodeoxybenzoin, CHBrPh·COPh, and bromopropiophenone, CHBrMe·COPh, by treatment with cold alcoholic sodium ethoxide do not yield analogues of the α- and β-bromophenacyls ; the former is converted into the benzoin, m. p. 131°, and the latter into an oily substance which does not contain bromine. C. S.

Conversion of Quinatoxines into Quinaketones and the Reduction of these to the Alkaloids of Cinchona Bark. ADOLF KAUFMANN and MAX HUBER (*Ber.*, 1913, **46**, 2913—2924). Rabe and collaborators have shown (A., 1910, i, 417) that of the four asymmetric carbon atoms in the chief cinchona alkaloids, that numbered 3 (*loc. cit.*) is the principal source of the isomerism among the alkaloids,

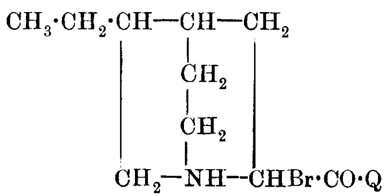
and have explained the apparent formation of a single ketone from each pair of isomerides (A., 1909, i, 252) by assuming that the ketone is tautomeric in each case. They have also shown (Abstr., 1911, i, 742) that cinchotoxine can be converted into cinchoninone and the latter reduced to cinchonine (A., 1908, i, 100), but the yield of the latter is very small, and no proof has been given that it is optically identical with natural cinchonine. The authors now show that in the conversion of cinchotoxine into cinchonine by Rabe's method, the reactions may be regarded as taking place (1) symmetrically, when two pairs of mirror-image isomerides will be formed in equal quantities, or (2) asymmetrically, when 4 optical isomerides will be formed in unequal quantities. They have applied this method to hydrocinchotoxine, and although the results are not conclusive, they indicate that it is the asymmetric direction which the reactions take, whence they conclude that hydrocinchoninone is not an equivalent mixture of two mirror-image isomerides.

Hydrocinchotoxine (hydrocinchonicine), prepared by von Miller and Rohde's method from hydrocinchonine, itself obtained by the reduction of cinchonine by von Skita's process, is an oil having $[\alpha]_D^{23}$ $+8·8°$ in dry alcohol; it yields a *benzoyl* derivative, m. p. 121—122°, which crystallises from light petroleum in colourless needles, and is sparingly soluble in ether. On treatment in hydrobromic acid with bromine vapour, hydrocinchotoxine yields *bromohydrocinchotoxine dihydrobromide*,

$$C_{19}H_{23}ON_2Br,2HBr,$$

m. p. 198° (approx.), yellow crystals, readily soluble in water but sparingly so in alcohol, and this with sodium in an alcoholic solution of sodium ethoxide yields hydrocinchoninone, m. p. 130°, which shows mutarotation (compare Rabe, A., 1909, i, 253), and on reduction with palladium black in presence of hydrogen yields dihydrocinchonine (cinchotine), $[\alpha]_D^{21}$ $+203·4°$, as chief product with a smaller amount of dihydrocinchonidine, m. p. 231°, $[\alpha]_D^{21}$ $-94·6°$.

In like manner, hydroquinotoxine (hydroquinicine) was converted into *bromohydroquinotoxine dihydrobromide*,



$$C_{20}H_{25}O_2N_2Br,2HBr,H_2O,$$

m. p. 178° (annexed formula, in which Q = 6-methoxyquinoline), and this into *hydroquininone*,

$$C_{20}H_{24}O_2N_2,$$

m. p. 98—99°, $[\alpha]_D^{21}$, changing from $+83·08°$ after twenty-four hours to $+73·29°$ as the final value, which forms a mixture of needles, platelets, and crusts of yellow colour, and yields a *picrate*, m. p. 224°.

T. A. H.

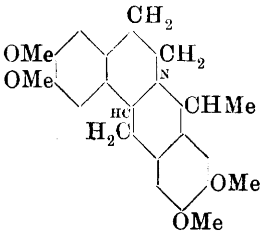
Oxycolchicine. SIMON ZEISEL and A. FRIEDRICH (*Monatsh*, 1913, **34**, 1181—1186).—*Oxycolchicine*, $C_{22}H_{23}(\text{or}_{25})O_7N$, m. p. 266—268°, obtained by oxidising colchicine with potassium pyrochromate and sulphuric acid, crystallises in faintly yellow, microscopic prisms; it is fairly soluble in hot alcohol and readily so in chloroform. Oxycolchicine gives a green colour passing into brown with sulphuric acid,

and with nitric acid a carmine-red changing to violet and brown. With boiling hydrochloric acid it appears to undergo changes quite similar to those given by colchicine. It is insoluble in cold potassium hydroxide solution, but gradually passes into solution on warming, methyl alcohol and acetic acid being split off. Oxycolchicine also reacts with hydroxylamine, but no definite derivative has been obtained. It is probable that in its formation from colchicine a $>CH_2$ group is converted into $>CO$. Formic and acetic acids were found as by-products of the oxidation. Further work on oxycolchicine will be undertaken by Windaus in continuation of his researches on the parent alkaloid (A., 1911, i, 904). T. A. H.

Preparation of Alcoholic Methyl Ethers. J. D. RIEDEL (D.R.-P. 261588).—The following methyl ethers have been prepared from the corresponding alcohols in alkaline solution by means of methyl sulphate: benzyl methyl ether, methyl *iso*amyl ether, and borneol methyl ether; whilst the employment of methyl iodide gave rise to *γ-methylmorphimethine methyl ether*, leaflets, m. p. 259°; *δ-methylmorphimethine methyl ether*, needles, m. p. 277°; *methylcodeine methiodide*, glistening, colourless rods, decomp. 263°; *α-dimethylmorphimethine methiodide*, needles, decomp. 263°; *β-dimethylmorphimethine methiodide*, needles, m. p. 320—330°, and *cinnamyl methyl ether*, b. p. 115°/15 mm. F. M. G. M.

Action of Acetal on Tetrahydropapaverine. AMÉ PICTET and STANISLAS MALINOWSKI (*Ber.*, 1913, **46**, 2688—2697. Compare Pictet and Gams, A., 1911, i, 807).—The authors have studied the condensation of acetal with tetrahydropapaverine, in the hope that it would proceed on similar lines to the action of methylal on veratrylnorhydrohydrastinine, and thus yield one of the optically inactive corydalines. This does not appear to be the case. Two isomeric substances, which the authors name *α*- and *β*-coralydine, are obtained, which have the same composition as the coryladines, but differ from them in their properties.

When acetal is gradually added to a hot solution of tetrahydropapaverine hydrochloride in hydrochloric acid, a mixture of hydrochlorides is obtained, which can be separated by cautious washing with water and subsequent fractional crystallisation from dilute hydrochloric acid. In this manner, *α-coralydine hydrochloride*, m. p. 254°, and *β-coralydine hydrochloride*, m. p. 228—230°, are obtained.



α-Coralydine (annexed formula), prepared by the addition of sodium carbonate to the above hydrochloride, forms colourless, shining leaflets, m. p. 148°. It gives a green coloration with warm, concentrated sulphuric acid. The following salts have been prepared: *sulphate*, m. p. 210°; *nitrate*, m. p. 242°; *picrate*, pale yellow needles, m. p. 134°; *aurichloride*, red crystals, m. p. 154°; *platinichloride*, yellow crystals, m. p. 246—247°. Attempts to resolve the base by quinic acid in alcohol solution and by

o-bromocamphorsulphonic acid in aqueous or alcoholic solution were unsuccessful.

When warmed with alcohol and iodine, α-coralydine yields *dehydrocoralydine.* The *hydriodide,* golden-yellow needles, m. p. 263°; *hydrochloride,* pale yellow needles, m. p. 230°; *nitrate,* yellow needles, m. p. 277—278°, and *aurichloride,* yellowish-brown needles, m. p. 252° (decomp.), of the base have been prepared. These salts differ greatly from the corresponding salts of dehydrocorydaline, from which the conclusion is drawn that the tetrahydro-derivatives, coralydine and corydaline, are structurally isomeric.

Oxidation of α-coralydine by potassium permanganate has been effected according to the directions of Dobbie and Lander for coryladine (T., 1894, **65**, 57; 1895, **67**, 17). The sole product appears to be *m*-hemipinic acid, which was identified by conversion into its ethylimide (Goldschmidt, A., 1889, 167). The latter consists of colourless needles (instead of pale yellow needles described by Goldschmidt), m. p. 229°.

β-Coralydine crystallises in colourless prisms, m. p. 115°. It gives a colourless solution in cold concentrated sulphuric acid, which becomes green when warmed. Oxidation with alcoholic iodine solution converts it into dehydrocoralydine, the identity of which, with the product obtained in a similar manner from α-coralydine, is established by comparison of the hydrochlorides, hydriodides and nitrates obtained from the two substances. From this it follows that α- and β-coralydines must be stereoisomerides, and probably are related to one another in the same manner as the two inactive corydalines. H. W.

1. Polymeric Tetramethylenecarbamide. 2. Some Derivatives of Pyrrole. EMIL FISCHER (*Ber.*, 1913, **46**, 2504—2510).—In attempting to prepare ornithin by the combination of tetramethylenediamine and carbon dioxide, it has been found that the base absorbs carbon dioxide with the formation of a substance which is apparently a carbamate; this, when heated for two days in a sealed tube at 220°, undergoes conversion into a colourless, sparingly soluble compound which commences to decompose at 260°. When heated with lime or in a sealed tube with hydrochloric acid, this substance, which is probably a polymeric form of *tetramethylenecarbamide,*

$$\begin{matrix} CH_2\cdot CH_2\cdot NH \\ | \\ CH_2\cdot CH_2\cdot NH \end{matrix}\!\!>\!CO,$$

regenerates tetramethylenediamine.

Pyrrole-2:5-dicarboxylic acid (Ciamician and Silber, A., 1886, 938) in the form of the sodium salt is easily reduced by sodium amalgam with formation of a *pyrroline-2:5-dicarboxylic acid,* colourless prisms or needles, which becomes pink in the air and when heated commences to decompose at 235°.

2:5-Diacetyl-1-methylpyrrole, m. p. 133—134° (Ciamician and Silber, A., 1887, 843), is more readily obtained by the action of sodium hydroxide and methyl sulphate on 2:5-diacetylpyrrole than by the earlier process starting with 1-methylpyrrole. It can be oxidised by potassium permanganate followed by hydrogen peroxide to *1-methylpyrrole-2:5-dicarboxylic acid,* needles of no definite m. p.; *silver* salt,

colourless needles. This acid is possibly identical with a substance briefly described earlier (Bell, A., 1879, 525).

Pyrrolealdehyde (Bamberger and Djierdjian, A., 1900, i, 309) can be methylated in alkaline solution by methyl sulphate with production of 1-*methylpyrrole-2-aldehyde*, a colourless oil, b. p. 75—76° (corr.) /12—13 mm., which, unlike the inodorous unsubstituted aldehyde, has an odour resembling benzaldehyde; *phenylhydrazone*, an almost colourless, crystalline powder, m. p. 127—128°(corr.). Oxidation by silver oxide converts the aldehyde into 1-methylpyrrole-2-carboxylic acid, agreeing in m. p. with that described by Bell (*loc. cit.*); *silver* salt, sparingly soluble. D. F. T.

Condensation of Ethyl Oxalate with Acetylpyrroles. Oskar Piloty and H. Will (*Ber.*, 1913, **46**, 2607—2612).—Acetylpyrroles condense with ethyl oxalate with elimination of alcohol, giving rise to coloured compounds which are closely related to the phonopyrrolecarboxylic acids and, therefore, to the blood pigments. The substances are very easily converted into blue, red or green dyes.

3-Acetyl-2 : 4-dimethylpyrrole was condensed with ethyl oxalate in presence of sodium ethoxide, and the product, after evaporating the solvent in vacuum, was acidified with acetic acid, when *ethyl* 2 : 4-*dimethylpyrryl*-3-*ethanoneoxalate*, $NH<\begin{matrix}CH{=}CMe\\ CMe{:}C\cdot CO\cdot CH_2\cdot CO\cdot CO_2Et\end{matrix}$, was precipitated. The ester crystallises in lemon-yellow leaflets, m. p. 179·5°, forms a *phenylhydrazone*, $C_{18}H_{21}O_3N_3$, pale yellow, slender needles, m. p. 189°, and yields the *hydrazide* of a *ketazine*, $C_{10}H_{13}ON_5$, in thin, glistening, colourless leaflets, m. p. 235°, when mixed with hydrazine hydrate. When left with 2·5% potassium hydroxide, the ester is hydrolysed to 2 : 4-*dimethylpyrryl*-3-*ethanoneoxalic acid*,

$$C_{10}H_{11}O_4N,$$

which forms short, golden-yellow, prismatic crystals, decomp. 174°. The ester also dissolves in hot concentrated hydrochloric acid, giving a dark blue solution from which water precipitates the dye in greenish-black masses. On boiling the acid solution for some time, however, the dye separates as an indigo-blue powder. It gives a deep red solution in alkalis.

4-Acetyl-2 : 3-dimethylpyrrole (this vol., i, 196) was also condensed with ethyl oxalate, giving a dark red powder which is insoluble in ether, and also *ethyl* 2 : 3-*dimethylpyrryl*-4-*ethanoneoxalate*,

$$NH<\begin{matrix}CMe{:}CMe\\ CH{=}C\cdot CO\cdot CH_2\cdot CO\cdot CO_2Et.\end{matrix}$$

The latter crystallises in long, spindle-like prisms, m. p. 180°, and yields a dark red dye on boiling with concentrated hydrochloric acid. J. C. W.

Electrolytic Oxidation of Cyclic Ammonium Bases. Otto Fischer and K. Neundlinger (*Ber.*, 1913, **46**, 2544—2546).—The authors required a convenient method of preparation for 1-methyl-2-pyridone from which a ready passage through the corresponding 2-chloro-compound to the 2-amino-compound is available.

The aim is achieved by electrolytic oxidation of 1-methylpyridinium sulphate between iron electrodes with a catholyte and anolyte of sodium hydroxide solution, the latter (D approx. 1·17) containing also some potassium ferricyanide as catalyst (compare Decker and Kaufmann, A., 1911, i, 1023). The yield of 1-methylpyridone (*picrate*, needles, m. p. 145°) is good, both from the point of view of the substance oxidised and the current passed.

By a similar process, 1-methylquinolinium sulphate can be almost quantitatively converted into 1-methyl-2-quinolone. D. F. T.

Condensation of Unsaturated Aldehydes with Ammonia and Ethyl Acetoacetate. II. E. GRISCHKEVITSCH-TROCHIMOVSKI and (Mlle.) I. PAVLOVSKAJA (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 935—946. Compare A., 1911, i, 320).—Ethyl 2 : 6-dimethyl-4-allyldihydropyridine-3 : 5-dicarboxylate, which exhibits the normal molecular weight in freezing benzene or boiling ether, is converted by oxidation with nitrogen trioxide into *ethyl* 2 : 6-*dimethyl*-4-*allylpyridine*-3 : 5-*dicarboxylate*, $C_{16}H_{21}O_4N$, a yellow liquid, b. p. 208·2°/21 mm., $D_4^{16·5}$ 1·0762, $n_D^{16·5}$ 1·5065 ; the corresponding *nitrate*, $C_{16}H_{21}O_4N,HNO_3$, m. p. 85·5°, and the *hydriodide*, $C_{16}H_{21}O_4N,HI$, m. p. 137—140° (decomp.), were prepared (see also *loc. cit.*). The free acid, 2 : 6-*dimethyl*-4-*allylpyridine*-3 : 5-*dicarboxylic acid*, $N{<}{\substack{CMe\cdot C(CO_2H)\\ CMe\colon C(CO_2H)}}{>}C\cdot CH\colon CHMe$, decomposes at about 205° ; its *silver* salt, *hydrochloride*, m. p. about 220° (decomp.), and *platinichloride*, m. p. about 225° (decomp.), were prepared and analysed.

In order to explain the mechanism of the formation of 2 : 4 : 6-trimethylpyridine by the dry distillation of potassium 2 : 6-dimethyl-4-allylpyridine-3 : 5-dicarboxylate (*loc. cit.*), experiments are being made on the condensation of acraldehyde with ethyl acetoacetate and ammonia, which yields ethyl 2 : 6-*dimethyl*-4-*vinyldihydropyridine*-3 : 5-*dicarboxylate*, $NH{<}{\substack{CMe\colon C(CO_2Et)\\ CMe\colon C(CO_2Et)}}{>}CH\cdot CH\colon CH_2$, crystallising in needles, m. p. 86—87°. T. H. P.

The Action of 2-Methylindole on Formic Acid. MAX SCHOLTZ (*Ber.*, 1913, **46**, 2539—2542).—Mainly polemical in favour of the views of the author (this vol., i, 895) and König (A., 1911, i, 809) as opposed to those of Ellinger and Flamand (A., 1911, i, 329) concerning the formula of the product of the interaction of 2-methylindole and formic acid.

The *nitrate* of the substance in question has now been prepared in a similar manner to the method recently described (Scholtz, *loc. cit.*); it forms ruby-red octahedra, decomp. above 220°, the composition agreeing with the formula $C_{19}H_{16}N_2,HNO_3$, or with the less probable $(C_{28}H_{23}N_3)_2,3HNO_3$. D. F. T.

Structure of 3-Nitroso-2-phenylindole. I. and II. LUIGI ALESSANDRI (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 150—155, 227—234. Compare Angeli and Morelli, A., 1908, i, 828).—In this preliminary note the author describes some transformations under-

gone by this substance. The production of the *O*-ether described by Angeli and Spica (A., 1899, i, 938) is confirmed. When nitrosophenylindole is heated, small quantities of 2-benzoylaminobenzonitrile are produced. This compound has m. p. 156°, but is readily converted by dilute acids into the corresponding amide, m. p. 216°. The supposed 2-benzoylaminobenzonitrile of Pinnow and Sämann (A., 1896, i, 368) probably consisted of this amide.

By the action of phosphorus pentachloride, 3-nitroso-2-phenylindole is converted into 2-phenyldihydro-4-quinazolone. When 3-nitroso-2-phenylindole is heated with zinc chloride, an apparently isomeric substance, m. p. about 228°, is formed, together with other products. This substance yields the above-mentioned quinazoline derivative when boiled with dilute acids or alkalis, and the same quinazoline derivative is also produced when the amide of m. p. 216° is heated.

The second paper gives experimental details regarding the results recorded in the first paper. 2-Benzoylaminobenzonitrile, prepared either by heating nitrosophenylindole (*loc. cit.*), or from 2-aminobenzonitrile, crystallises in colourless prisms or in long needles, m. p. 156°. R. V. S.

Scission of Decahydroquinoline into the Two Optical Antipodes. Bruno Veneziani (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 155—157).—Synthetical decahydroquinoline can be resolved with the aid of *d*-bromocamphorsulphonic acid. d-*Decahydroquinoline* d-*bromocamphorsulphonate* forms acicular crystals, m. p. about 220°, $[\alpha]_D^{27}$ +64·01° (in 1·117% aqueous solution), and is less soluble than the *l*-salt, which was obtained only in the form of an oil. d-*Decahydroquinoline* has $[\alpha]_D^{27}$ +1·28° (in 4·013% ethereal solution). l-*Decahydroquinoline* has $[\alpha]_D^{27}$ −1·02° (in 14·11% ethereal solution). In consequence of the small quantity of substance available, the author suggests that the rotatory powers of the pure enantiomorphs may be numerically greater than those above recorded. R. V. S.

Arsenic Compounds of the Quinoline Group. Sigmund Fränkel and Paul Löwy (*Ber.*, 1913, **46**, 2546—2550).—The authors have turned their attention to the arsenic compounds of quinoline because both constituents of such molecules would be physiologically active.

Schiff (*Annalen*, 1864, **131**, 116) has already given a brief report on certain compounds from quinoline and arsenic trichloride. It is now found that the action of quinoline and analogous bases with arsenic trichloride is an additive one; the action was effected in ethyl acetate solution with equimolecular quantities of the reagents. *Quinoline arsenotrichloride*, $C_9H_7N,AsCl_3$, is a colourless solid, m. p. 138°; *tetrahydroquinoline arsenotrichloride*, $C_9H_{11}N,AsCl_3$, is a pink solid, m. p. 134°; 8-*hydroxyquinoline arsenotrichloride*, $C_9H_7ON,AsCl_3$, is a bright yellow substance, m. p. 168°. Even under the influence of aluminium chloride the arsenic atom could not be made to enter the quinoline nucleus, and a similar failure was experienced when quinoline and tetrahydroquinoline were heated with arsenic acid at 200° in a sealed

tube, the products being *quinoline arsenate*, bright yellow leaflets, decomp. at 250°, and *tetrahydroquinoline arsenate*, colourless leaflets, m. p. 123°.

Attempts to synthesise the quinoline nucleus from arsanilic acid by Skraup's method gave merely quinoline, whilst Knorr's process with ethyl acetoacetate left the arsanilic acid unaltered. However, arsanilic acid condenses with acetaldehyde when an intimate mixture is treated with hydrobromic acid (D 1·49); the *hydrochloride* of 2-*methylquinolinearsinic acid*, a yellow, crystalline solid, separates, from which the free acid, decomp. at 140°, can be liberated by washing with distilled water. Reduction of this acid in alcohol by sodium yields the tervalent arsenic compound, 2-*methylquinolinearsenoxide*, decomp. at 120°; the *picrate* was prepared. D. F. T.

Synthesis of 2-Cyanoquinoline and 1-Cyano*iso*quinoline. ADOLF KAUFMANN and PAUL DÄNDLIKER (*Ber.*, 1913, **46**, 2924—2929).—2-Cyanoquinoline, already prepared by Pfitzinger (Abstr., 1902, i, 53), was made by treating Reissert's 2-cyano-1-benzoyl-1 : 2-dihydroquinoline, dissolved in chloroform, with phosphorus pentachloride. It is readily hydrolysed to quinaldinic acid, which is also formed as a by-product in the preparation of the cyano-base.

1-*Cyano*iso*quinoline*, similarly obtained from 1-cyano-2-benzoyl-1 : 2-dihydro*iso*quinoline (Reissert, Abstr., 1905, i, 926) has m. p. 74°, crystallises from light petroleum, and is very soluble in ether or alcohol, but sparingly in water. On hydrolysis by acids or alkalis, it yields *iso*quinaldinic acid (*iso*quinoline-1-carboxylic acid). T. A. H.

Preparation of Arylquinolinecarboxylic Acid Esters. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 261028).—*Salicyl 2-phenylquinoline-4-carboxylate*, colourless leaflets, m. p. 188°, is obtained when a benzene solution of 2-phenylquinoline-4-carboxylic acid is warmed during two hours with thionyl chloride and the solid residue (left after evaporating the solvent) mixed with salicylic acid and benzene and heated during three hours at 80°.

o-*Hydroxytoluoyl 2 : 3-diphenylquinoline-4-carboxylate*, colourless needles, m. p. 250°, is prepared in an analogous manner from hydroxytoluic acid and 2 : 3-diphenylquinoline-4-carboxylic acid. *Salicyl* 2-p-*anisylquinoline-4-carboxylate*, colourless needles, has m. p. 132°, and *salicylglycine 2-phenylquinolinecarboxylate*, m. p. 120°. F. M. G. M.

Quinolyl Ketones. III. ADOLF KAUFMANN, PAUL DÄNDLIKER and HANS BURKHARDT (*Ber.*, 1913, **46**, 2929—2935. Compare Abstr., 1912, i, 1017; this vol., i, 294).—It is now shown that in the preparation of these ketones by the use of Grignard reagents with cyanoquinolines, a molecule of the magnesium alkyl iodide is first attached to the cyclic nitrogen and then a second molecule to the cyano-group. The position of the cyano-group has some influence on the reactions; thus 2-cyanoquinoline and 1-cyano*iso*quinoline give good yields of the corresponding alkyl ketones, whilst 5-cyanoquinoline does not react with Grignard reagents.

2-*Quinolyl methyl ketone*, $C_9H_6N\cdot COMe$, m. p. 52°, b. p. 146—148°/

13 mm., forms small needles from dilute alcohol, and has a jasmine-like odour. The *phenylhydrazone*, m. p. 154°, crystallises from alcohol in slender, yellow needles. 2-*Quinolyl ethyl ketone*, m. p. 59—60°, distils in steam, forms colourless needles from alcohol, and has a pleasant ketone-like odour. The *phenylhydrazone*, m. p. 106°, forms short, yellow needles. 2-Quinolyl phenyl ketone was also prepared by this means (compare Besthorn, 1908, i, 681). 2-*Quinolyl benzyl ketone*, m. p. 78°, crystallising in flat needles, was prepared by treating 2-cyanoquinoline with magnesium methyl iodide followed by magnesium benzyl chloride, or by the action of ethyl quinaldinate on the sodium derivative of benzyl cyanide, which gave 2-*quinolyl cyanobenzyl ketone*, m. p. 120—121°, long needles, which was then hydrolysed to the corresponding *acid* and the latter heated at 120—130°.

1-iso*Quinolyl methyl ketone*, m. p. 48°, crystallises in colourless needles, is readily soluble in organic solvents, and has only a slight odour. The *phenylhydrazone* decomposes at 160°. 1-iso*Quinolyl-phenyl ketone*, m. p. 76—77°, b. p. 231°/12 mm., crystallises in highly refractive tablets, is readily soluble in benzene, alcohol or ether, but sparingly in light petroleum. It does not yield a methiodide with methyl iodide at 100° under pressure. T. A. H.

New Synthesis of Carbostyril. HANS MEYER and ROBERT BEER (*Monatsh.*, 1913, **34**, 1173—1179).—When *o*-chlorocinnamic acid is heated with copper and ammonia solution it is partly converted into carbostyril (2-hydroxyquinoline), the reaction being almost complete when the mixture is heated during thirty hours at 160—170°. At 120—130°, on the contrary, more or less *o*-aminocinnamic acid is also formed. A process for the isolation of the latter is described. The *o*-aminocinnamic acid produced in this reaction differs in certain respects from that prepared by reduction of *o*-nitrocinnamic acid, being (1) more soluble in water; (2) not readily convertible into coumarin, and (3) of different melting point, namely, 150°. It seems possible that it may be a new *trans*-form of the acid (compare Stoermer and Heymann, Abstr., 1912, i, 974).

When 2-methoxyquinoline is (1) distilled under atmospheric pressure, (2) heated on a water-bath, or (3) kept for some time in diffused light, it passes into the non-volatile isomeride in which the methyl group is attached to the nitrogen, a change analogous with the conversion of α-methoxypyridine into *N*-methylpyridine (compare Abstr., 1901, i, 343).

o-Chlorophenylpropionic acid when heated at 140—160° with copper and ammonia solution during thirty hours is converted quantitatively into hydrocarbostyril. T. A. H.

Nitro-derivatives of Thiodiphenylamine [Phenthiazine]. FRIEDRICH KEHRMANN and OLGA NOSSENKO (*Ber.*, 1913, **46**, 2809—2820).—The nitrophenthiazinesulphoxides obtained by the action of nitric acid on phenthiazine (Bernthsen, A., 1886, 53) are converted into the corresponding nitrophenthiazines by mineral acids in the presence of alcohol or glacial acetic acid; the most suitable reagent is concentrated hydrochloric and glacial acetic

acids, although it has a tendency to replace nitro-groups by chlorine atoms and to form chlorinated products. Smiles and Barnett (T., 1909, **95**, 1261) and Claasz (A., 1912, i, 513) have examined the action of such reagents on nitrated phenthiazinesulphoxides and have described the products as derivatives of phenazothionium hydroxide. This is incorrect, the products obtained by these investigators being nitrophenthiazines mixed with chlorinated and oxidised by-products.

5-*Nitrophenthiazine*, $C_6H_4{<}{}^{NH}_{S}{>}C_6H_3{\cdot}NO_2$, m. p. 111°, violet-black leaflets, is obtained by condensing *o*-aminophenyl disulphide with 1-chloro-2 : 6-dinitrobenzene (2 mols.) in boiling alcohol in the presence of sodium acetate (2 mols.), and reducing the resulting dinitrodiphenylamine disulphide in boiling alcohol and benzene with concentrated aqueous sodium sulphide; the yield is very unsatisfactory. By reduction with stannous chloride and hydrochloric acid, it is converted into 5-*aminophenthiazine hydrochloride*, colourless needles, which is oxidised by aqueous ferric chloride to 5-*aminophenazothionium chloride*, $C_6H_4{<}{}^{N}_{SCl}{\geqslant}C_6H_3{\cdot}NH_2$, which is isolated as the *platinichloride*, $2C_{12}H_9N_2SPtCl_6$, greyish-green crystals. 5-Aminophenthiazine forms an *acetyl* derivative, m. p. 174°, colourless prisms.

3-*Nitrophenthiazine*, m. p. 218°, violet-black crystals, is obtained by treating an alcoholic suspension of 3-nitrophenthiazinesulphoxide with 30% sulphuric acid, warming finally on the water-bath. The sulphoxide is converted by hydrochloric and acetic acids into 9(?)-*chloro*-3-*nitrophenthiazine*, $C_6H_3Cl{<}{}^{NH}_{S}{>}C_6H_3{\cdot}NO_2$, m. p. about 268°, brownish-black, bronze needles; by reduction, the latter yields the chloroaminophenthiazine by the oxidation of which by ferric chloride the chloroaminophenazothionium chloride is obtained.

The action of hydrochloric and acetic acids on 3 : 9-dinitrophenthiazinesulphoxide yields a mixture of 3 : 9-dinitrothiodiphenylamine and a *tetrachloro*-derivative, m. p. 235°, colourless needles (probably 3 : 5 : 7 : 9-*tetrachlorophenthiazine*), which is separated by extracting the latter with chloroform. 3 : 9-*Dinitrophenthiazine*,

$$NO_2{\cdot}C_6H_3{<}{}^{NH}_{S}{>}C_6H_3{\cdot}NO_2,$$

m. p. 276°, dark brownish-red needles, forms solutions with a characteristic brick-red fluorescence and yields by reduction the leuco-derivative of Lauth's violet. It is also the chief product of the action of solid sodium nitrite on a suspension of phenthiazine in glacial acetic acid.

Smiles and Barnett's tetranitrophenthiazinesulphoxide (*loc. cit.*) is, contrary to their statement, practically unchanged by treatment with alcohol and mineral acids. From the by-products in its preparation a *substance*, $C_{12}H_6O_8N_4S$, m. p. 270°, yellow needles, is obtained, which is probably a *hydroxytrinitrophenthiazinesulphoxide*.

Attention is called to the fact that all nitrophenthiazines containing at least one nitro-group in the para-position to the nuclear nitrogen

atom form intensely blue or green alkali salts, which probably have the quinonoid constitution $C_6H_4<{N \atop S}>C_6H_3{:}NO{\cdot}OM$. C. S.

Preparation of Anthraquinonedithiazoles and their Reduced Derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 260905).—2 : 6-*Diaminoanthraquinone*-1 : 5-*dimercaptol* is obtained by heating 1 : 5-dichloro-2 : 6-diaminoanthraquinone with an aqueous-alcoholic solution of sodium polysulphide under pressure, and it has been employed in the preparation of the following *compounds*: (1) by boiling the foregoing mercaptol (50 parts) with 50 to 100 parts of either benzaldehyde, benzylidene chloride, benzotrichloride, or benzoyl chloride; (2) in a similar manner with *p*-dimethylaminobenzaldehyde; (3) with anthraquinone-2-aldehyde.

The tinctorial properties of these compounds are described, also modifications in methods of preparation, whilst the same reaction with other aldehydes and mercaptols is also discussed. F. M. G. M.

Quinone-benzidine and its Reaction Products. KURT BRASS (*Ber.*, 1913, **46**, 2902—2906).—When the components are brought together in toluene, 2 mols. of benzidine unite with 1 mol. of quinone to form a soluble bluish-black addition product (compare Fecht, A., 1908, ii, 916). On warming in alcohol, an insoluble brown powder is obtained containing benzidine and quinone in molecular proportions.

The bluish-black product crystallises in platelets, m. p. 118°. The brown product does not melt; it dissolves with a blue coloration in concentrated sulphuric acid, and probably represents a polymeride.

Chloranil and benzidine when warmed together in toluene solution condense to an insoluble brown vat dye, which is regarded as a mixture of dibenzidinodichloroquinone with a little monobenzidinotrichloroquinone. E. F. A.

Oxidation of Anilinoquinones to Benzidine Derivatives. II. KURT BRASS (*Ber.*, 1913, **46**, 2907—2912. Compare A., 1912, i, 874).—1-Anilinoanthraquinone is readily oxidised by manganese dioxide and sulphuric acid to N : N′-bis*anthraquinonyl*-1-*benzidine*, a clear violet vat dye, which is composed of microscopic, transparent, violet crystals, m. p. 311°. The solution in concentrated sulphuric acid is olive-green.

In a similar manner, 1-anthra-anilinoanthraquinone may be oxidised to N : N′-*bis*-(*anthraquinonyl*-1)-*benzidine*-o-*dicarboxylic acid*, which forms a mass of violet-red needles, m. p. about 360°. On heating in concentrated sulphuric acid at 100—110°, the green solution becomes orange, and *dianthraquinone*-2 : 1-*acridone*,

$$C_6H_4<{CO \atop CO}>C_6H_2<{CO- \atop NH}>C_6H_3{\cdot}C_6H_3<{CO- \atop NH}>C_6H_2<{CO \atop CO}>C_6H_4$$

is obtained in the form of a mass of pale violet needles. It does not melt or sublime.

Bis-a-naphthoquinonyl-2-benzidine, obtained on oxidation of anilino-α-naphthoquinone, gives a brownish-violet solution in concentrated sulphuric acid. E. F. A.

Phenylhydrazine. I. Anhydrous Phenylhydrazine as a Cryoscopic Solvent. BERNARDO ODDO (*Gazzetta*, 1913, **43**, ii, 263—274).—The cryoscopic constant of phenylhydrazine is 58·59 (from experiments with naphthalene, diphenyl, dibenzyl, veratrole, and safrole). The molecular weight of hydrocarbons (benzene, toluene, *p*-xylene, and *p*-cymene) dissolved in phenylhydrazine increases with the concentration, and the same phenomenon is observed with alcohols (ethyl alcohol, *iso*butyl alcohol, *iso*amyl alcohol, and ethylene glycol); triphenylcarbinol gives a value below the normal at all concentrations. Phenols (phenol, *p*-cresol, and β-naphthol) have molecular weights below the theoretical value, and they diminish slowly when the concentration is increased. Bases (pyridine, piperidine, aniline, dimethylaniline, and quinoline) behave normally. Acetic acid and butyric acid are almost normal, whilst benzoic acid and salicylic acid have molecular weights much below the calculated values. R. V. S.

Phenylhydrazine. II. The System Phenylhydrazine–Water and the Cryoscopic Constant of Hydrated Phenylhydrazine. BERNARDO ODDO (*Gazzetta*, 1913, **43**, ii, 274—281. Compare preceding abstract).—Phenylhydrazine and phenylhydrazine hydrate show an eutectic point at 16°, and there is a maximum corresponding with the formula $(NHPh\cdot NH_2)_2,H_2O$, which agrees with that of the phenylhydrazine hydrate already known. The cryoscopic constant of phenylhydrazine hydrate is 44·15 (from experiments with diphenyl, veratrole, and naphthalene). R. V. S.

Phenylhydrazine. III. Velocity of Reaction of Aldehydes and Ketones with Phenylhydrazine. BERNARDO ODDO (*Gazzetta*, 1913, **43**, ii, 354—362. Compare preceding abstracts).—Comparative cryoscopic experiments show that the reaction of phenylhydrazine with acetone is complete in forty minutes, that with acetophenone in 162 minutes, whilst that with benzophenone has hardly begun after 225 minutes. Tables are also given showing the cryoscopic behaviour of a number of aldehydes and ketones in phenylhydrazine. R. V. S.

Action of Stannic Chloride on Phenylhydrazine. JITENDRA N. RAKSHIT (*J. Proc. Asiatic Soc., Bengal*, 1913, **9**, 131—135, Reprint).—Pure stannic chloride reacts very vigorously with phenylhydrazine, yielding benzene and nitrogen, whilst phenylhydrazine hydrochloride may be isolated from the product by dissolving it in water, precipitating the tin as the sulphide, and concentrating. A quantitative study of the reaction has shown that two molecules of the base give rise to one molecule of benzene, one of phenylhydrazine hydrochloride, and one of nitrogen. The equation:

$$2NHPh\!:\!NH_2 + SnCl_4 = C_6H_6 + N_2 + SnCl_2 + NHPh\!:\!NH_2,2HCl$$

agrees with these results, but introduces the anomaly that phenylhydrazine forms a dihydrochloride. Such an easily decomposable compound would be analogous to the dihydrofluoride described by Thieme (A., 1893, i, 155), and since no double salt of the base with a chloride of tin could be detected, its existence must be taken for granted.

The question whether the benzene is formed through the intervention of benzenediazonium chloride remains to be proved.

J. C. W.

Mutual Replacement of Ammonia and Amines in Carbon Compounds. N. Conev and Pavel Iv. Petrenko-Krittschenko (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1092—1098).—In order to throw light on the results obtained by Schöttle and Petrenko-Krittschenko (A., 1911, i, 1020; 1912, i, 128; this vol., i, 48), the authors have investigated the action of ammonia and amines on acetylphenylmethylpyridonone (compare von Pechmann and Neger, A., 1893, i, 398), which differs from benzoyldehydracetic acid in that the two phenyl side-groups are replaced by methyl groups. The substituents have such a considerable influence on the course of the reaction that the latter is of an entirely different character from that previously observed. The ring is here found to exhibit great stability, substitution of oxygen and mutual replacement of ammonia and amines taking place only in the side-chains. Further, heating of acetylphenylmethylpyridonone with hydrochloric acid results in the separation, not of aniline, but of acetic acid.

The action of ammonia on 5-acetyl-1-phenyl-2-methylpyridonone gives a quantitative yield of the *compound*,

$$CMe{<}{\begin{matrix}CH{-}CO\\NPh{\cdot}CO\end{matrix}}{>}C{:}CMe{\cdot}NH_2,$$

m. p. 247—248°. Similarly, the action of methylamine gives the *compound*, $CMe{<}{\begin{matrix}CH{-}CO\\NPh{\cdot}CO\end{matrix}}{>}C{:}CMe{\cdot}NHMe$, in colourless, thin needles, m. p. 183°, and that of aniline the *compound*, $C_{12}H_9O_2N{:}CMe{\cdot}NHPh$, m. p. 154—155°.

When these derivatives are subjected to suitable conditions, the methylamine or aniline residue may be replaced by the amino-group, the latter by the methylamine or aniline residue, or the aniline by the methylamine group.

1-*Phenyl-2-methylpyridonone*, $NPh{<}{\begin{matrix}CMe{:}CH\\CO{-}CH_2\end{matrix}}{>}CO$, obtained by heating the acetyl compound with excess of concentrated hydrochloric acid in a sealed tube at 150°, forms transparent, lustrous plates, m. p. 270—271°, and yields an *acetyl* derivative, $NPh{<}{\begin{matrix}CMe{:}CH\\CO{-}CH\end{matrix}}{\geqslant}C{\cdot}OAc$, which crystallises in needles, m. p. 146—147°, and is isomeric with von Pechmann and Neger's compound (*vide supra*). With benzaldehyde, it yields 1-*phenyl-5-benzylidene-2-methylpyridonone*,

$$NPh{<}{\begin{matrix}CMe{=\!=}CH\\CO{\cdot}C({:}CHPh)\end{matrix}}{>}CO,$$

m. p. 308—309°, which has the normal molecular weight in freezing phenol.

T. H. P.

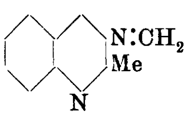
Synthesis of Aminoacetyl-8-methoxyquinoline. Sigmund Fränkel and Oskar Grauer (*Ber.*, 1913, **46**, 2551—2554).—After several fruitless attempts to prepare substances which should constitu-

tionally resemble adrenaline, the authors have obtained the above substance.

8-Methoxyquinoline was prepared by the method of Bedall and Fischer (A., 1882, 412) improved by the replacement of ether by benzene for the purpose of extraction; the base, needles, b. p. 172°/24 mm., gives a *platinichloride*, and a *picrate*, decomp. at 143°. When treated in light petroleum with chloroacetyl chloride and aluminium chloride, the methoxyquinoline is slowly converted into *chloroacetyl-8-methoxyquinoline*, a volatile, colourless solid, m. p. 58°, b. p. 152°/22 mm., which powerfully attacks the skin and eyes. Although the action of ammonia on this substance caused resinification, a mixture with potassium phthalimide in a sealed tube at 160—170° gave rise to *phthaliminoacetyl-8-methoxyquinoline*, a colourless solid, m. p. 219°, which by hydrolysis with concentrated hydrochloric acid in a sealed tube was converted into *aminoacetyl-8-methoxyquinoline hydrochloride*, $OMe\cdot C_9H_5N\cdot CO\cdot CH_2\cdot NH_2,1\frac{1}{2}HCl$, m. p. 198° (decomp.). D. F. T.

Reactivity of the Methyl Group in 3-Amino-2-methylquinoline. OTTO STARK and FELIX HOFFMANN (*Ber.*, 1913, **46**, 2697—2703). —Unsuccessful attempts have been made to involve the methyl group of 2-methyl-3-aminoquinoline in condensations with formaldehyde or carbonyl chloride. Further, ring formation is not observed when 3-amino-2-methylquinoline is diazotised, nor could it be brought about by the elimination of water from 3-acetylamino-2-methylquinoline, although, in the latter case, the basicity of the amino-group is weakened by introduction of the acetyl radicle.

When a solution of 3-amino-2-methylquinoline in hydrochloric acid is warmed with formaldehyde, a salt separates from which sodium hydroxide liberates the *base* (annexed formula), m. p. 204—205°. The *hydrochloride*, yellow, prismatic needles, m. p. 210—211°, and the *platinichloride*, yellow needles, m. p. 234—235°, were analysed. Boiling aqueous hydrochloric acid slowly decomposes the base into aminoquinaldine and formaldehyde.



Di-2-methylquinolinecarbamide, $C_{21}H_{18}ON_4$, m. p. 278°, is obtained when a solution of 3-amino-2-methylquinoline in dry toluene is left in contact with a solution of carbonyl chloride in the same solvent during two days and the product decomposed with 2*N*-sodium hydroxide. The *hydrochloride*, $C_{21}H_{18}ON_4,2HCl$, pale yellow needles, has m. p. 232—233°.

When a diazotised solution of 3-amino-2-methylquinoline is neutralised with sodium hydrogen carbonate and the precipitate dissolved in ether, a red, crystalline *powder* is obtained (after removal of the solvent), which has m. p. 105—115°, from which a definite substance could not be isolated. A solution of aniline hydrochloride, however, yields *2-methylquinolinediazoaminobenzene*, yellow crystals, m. p. 158°, when added to a diazotised solution of 3-amino-2-methylquinoline hydrochloride in the presence of sodium acetate. The corresponding *aminoazo*-compound, reddish-yellow crystals, m. p. 98—99°, is readily obtained by the usual methods. H. W.

Constitution of the Blood and Bile Pigments. II. HANS FISCHER and ERICH BARTHOLOMÄUS (*Zeitsch. physiol. Chem.*, 1913, **87**, 255—269. Compare this vol., i, 209).—Further examples of the coupling of pyrrole nuclei in the 2-position to a carbon atom are described.

Equimolecular quantities of ethyl 2 : 5-dimethylpyrrole-3-carboxylate and ethyl 2 : 4-dimethylpyrrole-3-carboxylate couple with formaldehyde to form *ethyl* 2 : 5 : 2′ : 4′-*tetramethyldipyrrylmethane*-3′ : 4-*dicarboxylate*,
$$\begin{array}{l}CMe\!:\!C(CO_2Et)\\ NH\text{———}CMe\end{array}\!\!>C\cdot CH_2\cdot C<\!\!\begin{array}{l}NH-CMe\\ CMe\cdot C\cdot CO_2Et\end{array}.$$
This forms faintly yellow crystals, m. p. 178—179°. From acetone, it crystallises in long, colourless needles.

Ethyl 2 : 5′ : 2′ : 5-*tetramethyldipyrrylmethane*-3 : 3′-*dicarboxylate*, formed in a similar manner, separates as a colourless, crystalline powder, m. p. 231—232°, after previously sintering.

Ethyl 5-*acetyl*-2 : 4 : 2′ : 4′-*tetramethyldipyrrylmethane*-3′-*carboxylate* crystallises in colourless needles in fan-like aggregates, m. p. 188—189°.

Ethyl 3-*acetyl*-2 : 4 : 2′ : 4′-*tetramethyldipyrrylmethane*-3′-*carboxylate*, crystallises in yellow prisms belonging to the rhombic system, m. p. 231—232°.

Ethyl 3 : 3′-*diacetyl*-2 : 4 : 2′ : 4′-*tetramethyl*-αα-*dipyrrylethane*,
$$CHMe\left(C<\!\!\begin{array}{l}CMe\cdot C\cdot COMe\\ NH-CMe\end{array}\right)_2,$$
obtained on condensing acetyldimethylpyrrole with acetaldehyde, crystallises in colourless, rectangular platelets, m. p. 251—252°.

Ethyl 2 : 4 : 2′ : 4′-*tetramethyl*-αα-*dipyrrylethane*-3 : 3′-*dicarboxylate* separates in well formed, colourless crystals, m. p. 171—172°.

Ethyl 3-*acetyl* 2 : 4 : 2′ : 4′-*tetramethyl*-αα-*dipyrrylethane*-3′-*carboxylate*, crystallises in hexagonal tablets, m. p. 202—203°, but giving a clear flux only at 209°.

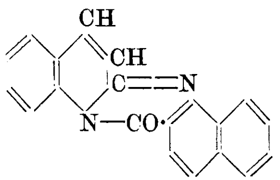
5 : 5′-*Diacetyl*-2 : 4 : 2′ : 4′-*tetramethyl*-αα-*dipyrrylpropylene*,
$$CH_2\!:\!CH\cdot CH\left(C<\!\!\begin{array}{l}CMe\!:\!CAc\\ CMe\cdot NH\end{array}\right)_2,$$
formed on condensing acetyldimethylpyrrole with an alcoholic solution of acraldehyde, was obtained as a yellow, microcrystalline powder.

5-*Bromo*-3-*acetyl*-2 : 4-*dimethylpyrrole*, $NH<\!\!\begin{array}{l}CMe\!:\!CAc\\ CBr\!:\!CMe\end{array}$, obtained on brominating acetyldimethylpyrrole in acetic acid, crystallises in faintly yellow prisms, m. p. 165—166° (decomp.).

Pyrroles couple with diazo-compounds more easily in the 2- than in the 3-position. Accordingly, in a mixture of 2 : 4-dimethylpyrrole and 2 : 4-dimethyl-5-ethylpyrrole on the cautious addition of diazobenzene-sulphonic acid the former is completely precipitated. On adding more of the diazo-compound to the filtrate, the latter (3-position free) is also completely precipitated as azo-dye. E. F. A.

New Class of Quinoline Dyes. III. EMIL BESTHORN (*Ber.*, 1913, **46**, 2762—2770).—The dye, $C_{19}H_{12}ON_2$, obtained by the methods

previously described (Besthorn and Ibele, A., 1904, i, 527; 1905, i, 612), probably has the annexed constitution; it is certainly not 2 : 2′-diquinolyl ketone (Gebhard, A., 1909, ii, 284), since its properties are quite different from those of 2-quinolyl phenyl ketone (A., 1908, i, 681).



The asymmetric structure of the dye is proved as follows. If the dye is 2 : 2′-diquinolyl ketone, it is evident that the substances produced from quinaldinyl chloride and 4-phenylquinoline and from 4-phenylquinaldinyl chloride and quinoline must in each case be be 4-phenyl-2 : 2′-diquinolyl ketone. Actually, the two products are different. 4-*Phenylquinaldinyl chloride*, m. p. 116°, and quinoline in benzene at the ordinary temperature yield a *substance*, $C_{25}H_{16}ON_2$, m. p. above 240°, brownish-red crystals, which is converted into carbostyril and 4-phenylquinaldinic acid by concentrated sulphuric acid at 70—75°. The *substance*, $C_{25}H_{16}ON_2$, produced from quinaldinyl chloride and 4-phenylquinoline has m. p. above 240°, forms brownish-red crystals, and yields quinaldinic acid and 4-phenylcarbostyril by treatment with concentrated sulphuric acid at 70°.

In a similar manner, quinaldinyl chloride and ethyl cinchoninate in benzene yield a *substance*, $\begin{matrix} C_6H_4\text{—}N\text{=\!=}C\text{—}CH \\ CH\!:\!CH\cdot C\cdot CO\cdot N\cdot C_6H_4 \end{matrix}\!\!>\!C\cdot CO_2Et$, m. p. 238°, brownish-red needles with a green reflex, which resembles other dyes of the same type in forming strongly fluorescent solutions.

These quinoline dyes are more sensitive to sunlight than any other class of organic dyes; a change, however, only occurs in the presence of oxygen. Under such conditions in benzene, the preceding dye is rapidly decolorised, ethyl 2-hydroxycinchoninate being formed, whilst the dye from quinaldinyl chloride and 4-phenylquinoline yields 4-phenylcarbostyril; products corresponding with the other halves of the two molecules cannot be isolated. C. S.

Hydantoins. XXV. The Preparation of Hydantoin from Hippuric Acid. TREAT B. JOHNSON and ROBERT BENGIS (*J. Amer. Chem. Soc.*, 1913, **35**, 1605—1606).—When a specimen of hydantoin is required urgently and potassium cyanate is not available, the following method is convenient.

Hippuric acid (or, indeed, any α-acylamino-acid) is first converted into 3-benzoyl-2-thiohydantoin, which is possible with excellent yields (Johnson and Nicolet, A., 1912, i, 53). This substance is then desulphurised by digesting with an aqueous solution of chloroacetic acid when hydrolysis concurrently occurs, the products therefore being benzoic acid and hydantoin. D. F. T.

Hydantoins. XXVI. Syntheses of 4-Hydroxy-3-methoxyphenylalanine and 3 : 4-Dimethoxyphenylalanine. TREAT B. JOHNSON and ROBERT BENGIS (*J. Amer. Chem. Soc.*, 1913, **35**, 1606—1617).—Vanillin condenses with hydantoin when heated

together with anhydrous sodium acetate in acetic acid, the product being 4-p-*hydroxy*-m-*methoxybenzylidenehydantoin*,

$$\begin{matrix} NH-CO \\ | \\ CO\cdot NH \end{matrix}\!\!>C{:}CH\cdot C_6H_3(OMe)\cdot OH,$$

a granular solid, m. p. 264—265°; this was reduced by tin and an alcoholic solution of hydrogen chloride with formation of 4-p *hydroxy*-m-*methoxybenzylhydantoin*, prisms, m. p. 194—195°.

The condensation product of vanillin with 2-thiohydantoin, obtainable under similar conditions to the above, was 2-*thio*-4-p-*hydroxy*-m-*methoxybenzylidenehydantoin*, yellow needles, m. p. 232—233°, which gives a blood-red solution in concentrated sulphuric acid and a yellow one in aqueous sodium hydroxide solution. When digested with an aqueous solution of chloroacetic acid, it undergoes desulphurisation to the above 4-*p*-hydroxy-*m*-methoxybenzylidenehydantoin, and on reduction in aqueous suspension by sodium amalgam becomes converted into 4-*hydroxy*-3-*methoxybenzylthiohydantoic acid*,

$$OH\cdot C_6H_3(OMe)\cdot CH_2\cdot CH(CO_2H)\cdot NH\cdot CS\cdot NH_2,$$

yellow prisms from aqueous solution, m. p. 181—182° (decomp.). Reduction of the thiomethoxyhydroxybenzylidenehydantoin by tin or by stannous chloride in each case with an alcoholic solution of hydrogen chloride gave the 4-*p*-hydroxy-*m*-methoxybenzylhydantoin described above. The last-named substance when submitted to the action of boiling barium hydroxide solution for many hours evolves ammonia and 4-*hydroxy*-3-*methoxyphenylalanine*,

$$OH\cdot C_6H_3(OMe)\cdot CH_2\cdot CH(NH_2)\cdot CO_2H,$$

prisms (with $1H_2O$), m. p. 255—256° (decomp.), is simultaneously produced.

Veratraldehyde condenses with 2-thiohydantoin, under the conditions described above, with formation of 2-*thio*-4-mp-*dimethoxybenzylidenehydantoin*, prisms, m. p. 229—230°, which can be reduced in suspension in water by sodium amalgam to 2-*thio*-4-mp-*dimethoxybenzylhydantoin*, crystals with $1H_2O$, m. p. 102—103°. When desulphurised by aqueous chloroacetic acid, this gives rise to 4-mp-*dimethoxybenzylhydantoin*, a viscous syrup, from which 3 : 4-*dimethoxyphenylalanine*, hair-like crystals, m. p. 249—250° (decomp.), can be obtained by digestion with barium hydroxide solution.

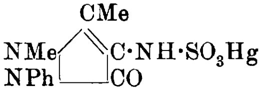
When 4-*p*-hydroxy-*m*-methoxybenzylidenehydantoin is treated with alcoholic potassium hydroxide and methyl iodide, methylation occurs with production of 1-*methyl*-4-mp-*dimethoxybenzylidenehydantoin*, prismatic crystals, m. p. 218°, together with some 1 : 3-*dimethyl*-4-mp-*dimethoxybenzylidenehydantoin*, distorted prisms, m. p. 122—124°, which gives a bright red solution in sulphuric acid. D. F. T.

β-Naphthalaninehydantoic Acid. WILHELM TÜRK (*Biochem. Zeitsch.*, 1913, **55**, 477—480).—Kikkoji (Abstr., 1911, ii, 909) has obtained from the urine, after administration of β-naphthalanine to a dog, a substance to which the formula $C_{15}H_{16}O_3N_2$ was assigned. As it is known that amino-acids on evaporation in urine react with the urea to yield uraminic acids, it is conceivable that the above-mentioned substance is a derivative of this character formed from unchanged β-naphthalanine. By the action of urea on β-naphthalanine in the

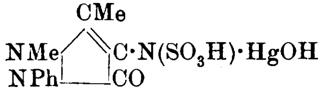
presence of barium hydroxide, a β-naphthalaninehydantoic acid, $C_{14}H_{14}O_3N$, could be obtained with m. p. 194—195°. Kikkoji's substance melted at 190°, so that the identity of the two products cannot yet be regarded as proved, especially as Kikkoji's analyses are not in strict accordance with those of the synthetic substance.

S. B. S.

Preparation of a Mercury Derivative of the Pyrazolone Series. LEON GIVAUDAN and EMIL SCHEITLIN (D.R.-P. 261081 and 261082).—When 300 parts of 4-sulphamo-1-phenyl-2 : 3-dimethyl-5-pyrazolone (A., 1908, i, 688) are gently warmed with freshly prepared mercuric oxide (from 270 parts of mercuric chloride) in 10,000 parts of water, it furnishes a colourless, crystalline *compound*, I or II (the latter being considered most probable); it contains



(I.)



(II.)

41% of mercury, and, when treated with dilute alkalis, part of the mercury separates in the mercurous condition, leaving a compound in solution containing 24% of mercury.

II. States that by altering the proportions of reacting material in the foregoing preparation, a *compound*, a greenish-white powder containing 67—68% Hg, is obtained, by treatment with sodium hydroxide part of the mercury is eliminated, and the solution furnishes the previously described compound containing 24% of mercury.

F. M. G. M.

Antipyrine and Ammonia Compounds of Some Nitrates of the Rare Earths. ADALBERT KOLB (*Zeitsch. anorg. Chem.*, 1913, **83**, 143—148. Compare A., 1909, i, 16).—*Zirconium nitrate antipyrine*, $Zr(NO_3)_4,6C_{11}H_{12}ON_2$, prepared in nitric acid solution, forms colourless tablets, m. p. 217—218° (decomp.), readily soluble in water. *Thorium nitrate antipyrine*, $2Th(NO_3)_4,5C_{11}H_{12}ON_2$, readily forms supersaturated solutions and has m. p. 168—169°. The *lanthanum, cerous*, and *samarium* compounds contain 3 mols. of antipyrine, and have m. p.'s 161—162°, 165°, and 177—178° respectively. *Erbium nitrate antipyrine*, $Er(NO_3)_3,4C_{11}H_{12}ON_2$, forms pink tablets, and has m. p. 175—176°, whilst the *yttrium* compound is colourless and has m. p. 176—177°.

Thorium nitrate combines with ammonia, forming compounds, $Th(NO_3)_4,2H_2O,3NH_3$ and $2Th(NO_3)_4,3H_2O,7NH_3$. An anhydrous salt, formed with the development of much heat, proves to be basic, $ThNO_3(OH)_3$. Zirconium also forms a crystalline basic compound, $ZrO(NO_3)_2,2H_2O,2NH_3$.

C. H. D.

Benzylated Pyrazole Derivatives and a Peculiar Case of Autoalkylation. PAUL JACOBSON and H. JOST (*Annalen*, 1913, **400**, 195—219).—By boiling with about 16% alcoholic potassium hydroxide for one hour, 1-phenyl-2-benzyl-3-methyl-5-pyrazolone decomposes and yields ammonia, 30% of acetoacetanilide, and about 25% of a *substance*,

$C_{24}H_{22}ON_2$, m. p. 152°, colourless leaflets, which proves to be 1-*phenyl-2 : 4-dibenzyl 3-methyl-5-pyrazolone*. The explanation of this curious example of autobenzylation is very probably as follows. The pyrazole nucleus of one molecule of the phenylbenzylmethylpyrazolone is ruptured by the alkali, with the formation of the phenylbenzylhydrazide of acetoacetic acid, $CH_2Ph{\cdot}NH{\cdot}NPh{\cdot}CO{\cdot}CH{:}CMe{\cdot}OH$. Since the union of the benzyl group and the nitrogen atom in benzylated hydrazines is easily loosed, the hydrazide benzylates a second molecule of phenylbenzylmethylpyrazolone forming the substance, m. p. 152°, being itself converted into acetoacetanilide, an atom of nitrogen appearing ultimately as ammonia.

The proofs of the constitution of 1-phenyl-2 : 4-dibenzyl-3-methyl-5-pyrazolone are the following. In accordance with Knorr's experience of 1 : 2-disubstituted pyrazolones, it reacts with alkyl iodides to form ψ-alkyliodides, $CH_2Ph{\cdot}NI{<}{\begin{smallmatrix}NPh{\cdot}C{\cdot}OR\\ \quad\ \ \|\\ CMe{-}C{\cdot}CH_2Ph\end{smallmatrix}}$, which are decomposed by fusion or by aqueous alkalis into the original compound and alkyl iodide. The ψ-*methiodide*, $C_{25}H_{25}ON_2I$, decomp. 234°, pale yellow prisms, prepared at 100°, and the ψ-*ethiodide*, $C_{26}H_{27}ON_2I$, m. p. about 258—260° (decomp.), yellow, crystalline powder, prepared at 120°, are described. The former behaves abnormally with aqueous alcoholic potassium hydroxide in forming, not the original phenyldibenzylmethylpyrazolone, but a *substance*, m. p. 149°, colourless needles (*picrate*, m. p. 176°), the composition of which has not been determined. By heating with 10% sulphuric acid at 130°, 1-phenyl-2 : 4-dibenzyl-3-methyl-5-pyrazolone is decomposed into ammonia, aniline, benzoic aeid, and benzylacetone. The authors show that *s*-phenylbenzylhydrazine by similar treatment at 135—140° yields ammonia, aniline, benzaldehyde, and benzoic acid.

In preparing the compound by the benzylation of 1-phenyl-3-methyl-5-pyrazolone, Stolz did not definitely prove the constitution of 1-phenyl-2-benzyl-3-methyl-5-pyrazolone. The authors have now done so, in consequence of the curious behaviour of the substance recorded above. It is converted into benzyl chloride and 5-chloro-1-phenyl-3-methylpyrazole by phosphoryl chloride at 140—150°. By heating in toluene with sodium in an atmosphere of carbon dioxide and subsequent treatment with ice and heating with dilute sulphuric acid, it yields aniline and benzylamine. C. S.

Derivatives of Pyridazine and of Pyrrole. G. KARL ALMSTRÖM (*Annalen*, 1913, **400**, 131—146).—With the exceptions of 4 : 5-diphenylpyridazine and 1 : 3 : 4-triphenylpyrrole, all the unknown diphenylpyridazines and triphenylpyrroles have been prepared.

3 : 5-*Diphenylpyridazin-6-one*, $N{<}{\begin{smallmatrix}CPh{\cdot}CH_2\\ NH{-}CO\end{smallmatrix}}{>}CHPh$, m. p. 154—165°, long needles, prepared by warming β-benzoyl-α-phenylpropionic acid and hydrazine hydrate in water, reacts with bromine in boiling glacial acetic acid to form 6-*hydroxy*-3 : 5-*diphenylpyridazine* $C_{16}H_{12}ON_2$, m. p. 183—184°, small needles. The latter is soluble in sodium hydroxide, and is converted by boiling phosphoryl chloride into 6-*chloro*-

3 : 5-*diphenylpyridazine*, m. p. 86—88°, which is reduced to 3 : 5-diphenylpyridazine, m. p. 139—140° (*platinichloride*, $2C_{16}H_{12}N_2,H_2PtCl_6$, yellow, crystalline powder ; *picrate*, m. p. 137—138°), by hydriodic acid, D 1·22, at 160°.

In a similar manner, β-benzoyl-β-phenylpropionic acid and hydrazine hydrate yield 3 : 4-*diphenylpyridazin*-6-*one*, $C_{16}H_{14}ON_2$, m. p. 217—218°, from which, by methods similar to the preceding, have been successively prepared 6-*hydroxy*-3 : 4-*diphenylpyridazine*, m. p. 177—178°, 6-*chloro*-3 : 4-*diphenylpyridazine*, m. p. 110—111°, and 3 : 4-*diphenylpyridazine*, m. p. 106—107° (*platinichloride*, $2C_{16}H_{12}N_2,H_2PtCl_6$, dark yellow, microscopic plates ; *picrate*, m. p 155—156°, dark yellow, crystalline powder).

β-Benzoyl-α-phenylpropionic acid and boiling aniline yield 1 : 2 : 4-*triphenylpyrrol*-5-*one*, $NPh<\begin{matrix}CPh:CH\\ \quad\ \ |\\ CO-CHPh\end{matrix}$, m. p. 197—198°, faintly yellow, quadratic prisms. The latter becomes deep green when fused, and almost colourless again after solidification. By treating its solution in acetone and aqueous sodium hydroxide with acetyl chloride at 0°, 5-*acetoxy*-1 : 2 : 4-*triphenylpyrrole*, m. p. 172—173°, almost colourless plates (green when fused), is obtained, whilst phosphorus trichloride at 110—120° converts it into 5-*chloro*-1 : 2 : 4-*triphenylpyrrole*, m. p. 145—146, straw-yellow needles. The latter reacts with phosphoric and phosphoryl chlorides at 140° to form 3 : 5-*dichloro*-1 : 2 : 4-*triphenylpyrrole*, m. p. 152—153°, and is converted by hydriodic acid, D 1·22, and amorphous phosphorus at 150—160° into 1 : 2 : 4-*triphenylpyrrole*, m. p. 151—152°. 5-Chloro-1 : 2 : 4-triphenylpyrrole is converted by hot acetic anhydride and a few drops of concentrated sulphuric acid into 5-*chloro*-3-*acetyl*-1 : 2 : 4-*triphenylpyrrole*, $C_{24}H_{18}ONCl$, m. p. 188—189°, colourless plates, the position of the acetyl group being determined by the fact that the substance is converted into 5-*chloro*-3-*cinnamoyl* - 1 : 2 : 4 - *triphenylpyrrole*, $C_{31}H_{22}ONCl$, m. p. 150—151°, by warm alcohol, benzaldehyde, and sodium hydroxide.

β-Benzoyl-β-phenylpropionic acid and boiling aniline readily yield Klingemann's 1 : 2 : 3-triphenylpyrrol-5-one, m. p. 189°, from which 5-*chloro*-1 : 2 : 3-*triphenylpyrrole*, m. p. 165—166°, and 1 : 2 : 3-*triphenylpyrrole*, m. p. 176—177°, have been successively prepared. C. S.

Phenazine. FRIEDRICH KEHRMANN and EM. HAVAS (*Ber.*, 1913, **46**, 2820).—Methylphenazonium chloride, bromide, and nitrate can readily be isolated from concentrated aqueous solutions of the methosulphate (compare this vol., i, 298). C. S.

Salts of Azine Dyes. II. FRIEDRICH KEHRMANN, EM. HAVAS, and EUGÈNE GRANDMOUGIN (*Ber.*, 1913, **46**, 2802—2808. Compare this vol., i, 908).—The present results are communicated in consequence of the work of Ehrlich and Benda (this vol., i, 904) and of Pummerer and Gassner (*ibid.*, i, 991).

The colour change observed when many azonium bases are converted into salts is not necessarily indicative of constitutive change ; in many cases it is due simply to a change in the auxochromic nature of the

amino-group during salt-formation. A number of dyes, such as *apo*safranine, methyl*apo*safranine, 1:3-diaminophenylphenazonium bromide, 3 : 7- and 3 : 11-diaminophenylphenazonium chlorides, have been separately dissolved in alcohol and the solutions treated with regulated quantities of concentrated sulphuric acid; the amount of acid required for the production of different colours has been measured. The most important deductions made by the authors are as follows. The number of colours, with a given substance, agrees with the number of basic groups present, indicating that the individual basic groups possess different basicities, and that salt-formation proceeds step by step. Extraordinarily slight basicity is exhibited by all the salt-forming groups in a substance with the exception of one, by which the normal colour is conditioned; all other coloured salts exist only in quite strongly acidic solutions, and are immediately hydrolysed by dilution.

The influence of the position of an amino-group on the colour of the salts is also considered. An amino-group in the meta-position to the azine nitrogen is least influenced by hydrolysis. Its basic character is as strong as that of the amino-group in aniline, and a dye containing such a group forms a diacid salt even with only a slight excess of acid. An amino-group in position 11 (that is, in a phenyl nucleus), whether free or in a salt form, has practically no auxochromic influence. Also, such a group plays no part in strengthening the basicity, 3 : 11-diaminophenylphenazonium chloride being in this respect similar to *apo*safranine. C. S.

Action of Nitrous Acid on Ethyl Anilino-oximinoacetate.

LEOPOLD SEMPER and LEO LICHTENSTADT (*Annalen*, 1913, **400**, 302—332).—The substance $C_{10}H_{11}O_4N_3$, m. p. 169°, obtained by Jovitschitsch by the action of nitrous acid on ethyl anilino-oximino-acetate and described by him as ethyl phenyldioxatriazinecarboxylate (A., 1898, i, 93; 1899, i, 239; 1907, i, 98), has the composition $C_{10}H_9O_5N_3$ and m. p. 181·5° when quite pure, and proves to be *ethyl* 7-*nitro*-1 : 2 : 4-*benzoxadiazine*-3-*carboxylate*,

$$NO_2\cdot C_6H_3<\begin{matrix}NH\cdot C\cdot CO_2Et\\ O\text{——}\overset{\|}{N}\end{matrix}$$

The yield of the substance is doubled by using 2 mols. of sodium nitrite instead of one (compare Jovitschitsch, *loc. cit.*). It forms a *potassium* derivative, $C_{10}H_8O_5N_3K$, dark red powder, and *benzoyl* derivative, $C_{17}H_{13}O_6N_3$, m. p. 165°, colourless crystals. Although ethyl oxanilate is obtained as a by-product in the formation of ethyl nitrobenzoxa-diazinecarboxylate, an intermediate product cannot be isolated; the same substance is also obtained, more slowly, by the action of nitric acid on ethyl anilino-oximinoacetate in glacial acetic acid.

By precipitating ethyl nitrobenzoxadiazinecarboxylate from acetone by water and treating the finely divided suspension with 0·2*N*-sodium hydroxide at 0°, an orange-yellow mass of the extremely unstable 7-*nitro*-1 : 2 : 4-*benzoxadiazine*-3-*carboxylic acid*,

$$NO_2\cdot C_6H_3<\begin{matrix}NH\cdot C\cdot CO_2H\\ O\text{——}\overset{\|}{N}\end{matrix},$$

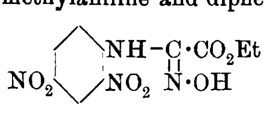
is obtained which can only be examined in the moist state. It decomposes at 118°, yielding nitrobenzoxadiazine, and regenerates the ester by treating its *silver* salt with ethyl iodide. 7-*Nitro*-1 : 2 : 4-*benzoxadiazine*, $C_7H_5O_3N_3$, m. p. 240° (Jovitschitsch's phenyldioxatriazine, $C_7H_7O_2N_3$), is obtained from ethyl nitrobenzoxadiazinecarboxylate under the latter's conditions, except that 0·2*N*-sodium hydroxide is employed; the *hydrochloride*, $C_7H_5O_3N_3,HCl$, m. p. above 300°, is a moderately stable, white substance.

By boiling for forty minutes with 0·2*N*-sodium hydroxide (3 mols.), ethyl nitrobenzoxadiazinecarboxylate or nitrobenzoxadiazine is converted into 4-*nitro*-2-*hydroxyphenylcarbamide*,

$$NO_2\cdot C_6H_3(OH)\cdot NH\cdot CO\cdot NH_2,$$

m. p. 203° (Jovitschitsch's phenyldihydroxydihydrodioxatriazine, $C_7H_9O_4N_3$ [A., 1907, i, 98]), which develops an olive-green coloration with alcoholic ferric chloride, yields 5-nitro-2-aminophenol and 4-nitrocatechol by prolonged boiling with 10% sodium hydroxide, and is converted at 210° into ammonia and nitrobenzoxazolone (nitrocarbonyl-*o*-aminophenyl), m. p. 241° (St. v. Chelmicky, A., 1891, 52). The preceding transformations suffice to establish the constitution of 4-nitro-2-hydroxyphenylcarbamide. The position of the nitro-group in ethyl 7-nitro-1 : 2 : 4-benzoxadiazine-3-carboxylate is proved by the reduction of the ester to 2 : 5-diaminophenol by boiling alcohol and stannous chloride.

The course of the reaction whereby ethyl anilino-oximinoacetate is converted into ethyl 7-nitro-1 : 2 : 4-benzoxadiazine-3-carboxylate by nitrous acid is readily explained in the light of Stoermer's researches on the simultaneous nitriting and oxidising action of nitrous acid on methylaniline and diphenylamine (A., 1899, i, 42). The nitrous acid attacks the aniline group and forms a substance (annexed formula), which, like other such dinitro-compounds, loses nitrous acid with the production of the nitrobenzoxadiazinecarboxylate.



Reactions similar to that exhibited by ethyl anilino-oximinoacetate and nitrous acid are also shown by substances containing the group $NHPh\cdot C(:NOH)\cdot$ attached to $\cdot COPh$ or $\cdot CO\cdot NH_2$. Thus the action of nitrous acid (2 mols.) on anilino-oximinoacetophenone yields 7-*nitro*-3-*benzoyl*-1 : 2 : 4-*benzoxadiazine*, $NO_2\cdot C_6H_3<\begin{matrix}NH\cdot CBz\\ O—N\end{matrix}$, m. p. 178° (decomp.), scarlet needles, which forms a bluish-red solution in alkalis, the solution losing the benzoyl group by long keeping, and yielding 7-nitro-1 : 2 : 4-benzoxadiazine. *Anilino-oximinoacetamide*,

$$NHPh\cdot C(:NOH)\cdot CO\cdot NH_2,$$

decomp. 192°, colourless needles, prepared from concentrated aqueous ammonia and ethereal ethyl anilino-oximinoacetate, reacts with nitrous acid (2 mols.) to form chiefly phenyloxamide; a by-product, however, is 7-*nitro*-1 : 2 : 4-*benzoxadiazine*-3-*carboxylamide*,

$$NO_2\cdot C_6H_3<\begin{matrix}NH\cdot C\cdot CO\cdot NH_2\\ O—N\end{matrix},$$

decomp. 240°, yellow crystals, the constitution of which follows from

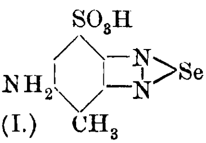
the identity of the substance with the amide produced by the action of ammonia on ethyl 7-nitro-1 : 2 : 4-benzoxadiazine-3-carboxylate.

The action of nitrous acid (2 mols.) on oximinobenzanilide proceeds similarly and yet somewhat differently. Very little benzanilide is produced, the chief product being a *substance*, $C_{13}H_8O_3N_2$, m. p. 177—179°, which is very probably 5-nitro-1-phenylbenzoxazole (Fischer, A., 1906, i, 539).; however, a small amount of a benzoxadiazine derivative is probably also formed, because the reaction product develops a deep violet-red coloration with alkalis. C. S.

Preparation of Alkali Soluble Derivatives of Piaselenols [Benz*iso*selenodiazoles]. FELIX HEINEMANN (D.R.-P. 261412).—Benz*iso*selenodiazole, prepared by the action of selenous acid on *o*-phenylenediamine, is insoluble in water and alkalis, and the following compounds have been prepared with a view to eliminate this drawback.

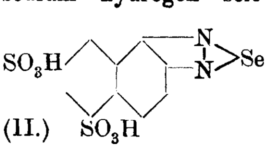
3-*Hydroxybenz*iso*selenodiazole*, $C_6H_4ON_2Se$, yellowish-brown needles, is obtained when an aqueous solution of 3 : 4-diaminophenol hydrochloride is treated with sodium hydrogen selenite (1 mol.); it sinters and reddens at 200°, and has m. p. 209° (decomp.).

*Benz*iso*selenodiazole-3-carboxylic acid*, $C_7H_4O_2N_2Se$, m. p. 222—223°, a crystalline, rose-coloured powder, is prepared in a similar manner from 2 : 3-diaminobenzoic acid.



*Benz*iso*selenodiazole-4-carboxylic acid* is a colourless, crystalline powder with indefinite m. p., darkening at 260°, and decomposing violently at 290°.

When 3-p-*nitro*-o-*sulphobenzeneazotolylene-2 : 5-diamine-4-sulphonic acid* is reduced it yields 2 : 3 : 5-*triaminotoluene-4-sulphonic acid*, and this on treatment with sodium hydrogen selenite gives rise to 4-*amino-3-methylbenz*iso*selenodiazole-6-sulphonic acid* (formula I); whilst naphthylene-1 : 2-diamine-5 : 7-disulphonic acid (A., 1906, i, 713) furnishes *naphtha*iso*selenodiazole-5 : 7-disulphonic acid* (formula II), which is isolated as its crystalline *barium* salt by the addition of barium chloride to the reaction mixture. F. M. G. M.



Rosinduline Isomerides, Nos. 16 and 17. FRIEDRICH KEHRMANN and MARCELIEN CORDONE (*Ber.*, 1913, **46**, 2974—2979. Compare Abstr., 1899, i, 79).—The condensation of 3-acetylamino-1 : 2-naphthaquinone with phenyl-*o*-phenylenediamine has now been improved and much better yields of the two *iso*rosindulines obtained. The methods of preparation and separation of salts of the two acetyl compounds first formed are described.

10-*Acetylaminophenyl*iso*naphthaphenazonium chloride*,

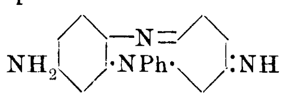
$$C_6H_4<\begin{matrix}N(C_6H_5Cl){:}C\text{---}C_6H_4\\ N\text{=======}C(NHAc)\end{matrix}>CH,$$

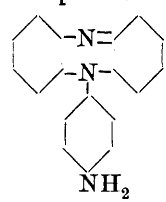
the form in which the substance is isolated, forms crystalline grains,

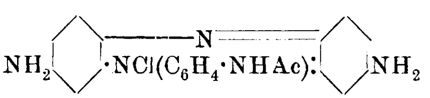
with a metallic lustre, is almost black, but yields a reddish-brown solution in water, and in alcohol a solution which is olive-green in thin layers and purplish-violet in thick layers. The *platinichloride* forms brownish-black crystals, and the *nitrate*, dark brown needles. The salts dissolve in sulphuric acid to form a violet solution, which, after heating and dilution with water, yields 10-*aminophenyl*iso*naphthaphenazine* (iso*rosinduline*, No. 16); the *nitrate* of this forms small, olive-green needles; the *platinichloride* is an olive-green, crystalline precipitate.

5-*Acetylaminophenyl*iso*naphthazonium nitrate*, the form in which this substance is isolated, is an orange-red, crystalline powder; the *platinichloride* is a brick-red, crystalline precipitate, and the *chloride* crystallises from water in long, brick-red needles on salting-out with sodium chloride. All attempts to eliminate the acetyl group led to further decomposition of the substance. T. A. H.

Constitution of Safranine. EM. HAVAS and R. BERNHARD (*Ber.*, 1913, **46**, 2723—2727).—According to Barbier and Sisley (A., 1908, i, 225), phenosafranine is not a single chemical individual, but consists of a mixture of *indo*safranine (I.) and amino*apo*safranine (II.), commercial phenosafranine containing 85% of the latter compound.

(I.) 

(II.) 

(III.) 

A compound of the constitution (II.) has now been prepared by the successive removal of one amino-group and the acetyl group from Ris's *p*-acetylaminosafranine (III.) (A., 1895, i, 148). It possesses the properties of an *apo*safranine, and, therefore, cannot form the main constituent of commercial phenosafranine.

Taken in conjunction with the work of Hewitt, Newman and Winmill (T., 1909, **95**, 577), the present results conclusively prove that phenosafranine is a single chemical individual and has the constitution represented in (I.).

The substances isolated by Barbier and Sisley are either hydrates or homologues, such as occur even in the purest commercial phenosafranine.

Acetylaminosafranine (III) is best prepared by the oxidation of di-*p*-aminodiphenylamine sulphate and acetyl-*p*-phenylenediamine by sodium dichromate in the presence of hydrochloric acid. It may also be obtained by oxidising a mixture of *p*-phenylenediamine, aniline and acetyl-*p*-phenylenediamine. In its appearance, tinctorial properties and absorption spectrum, it very closely resembles phenosafranine.

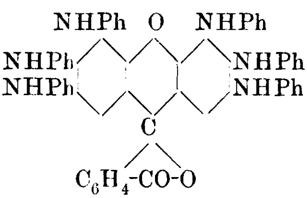
Aminosafranine is obtained in the form of its *sulphate* by boiling the preceding acetyl derivative with 10% sulphuric acid; the *platinichloride*, $C_{36}H_{32}N_{10}PtCl_6$, was analysed.

When treated with hydrochloric acid and sodium nitrite in alcoholic

solution, acetylaminosafranine is converted into *amino*apo*safranine* (II), which forms a *platinichloride*, $C_{36}H_{30}N_8PtCl_6$, and is very similar to *apo*safranine. F. B.

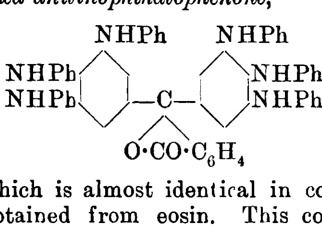
The Degradation of Uric Acid by Hydrogen Peroxide and an Iron Salt. KOHSHI OHTA (*Biochem. Zeitsch.*, 1913, **54**, 439—445).—By the treatment of uric acid with a boiling 30% solution of hydrogen peroxide in the presence of a ferric salt until all the uric acid was dissolved, the following products could be isolated. A crystalline substance, $C_3H_6O_3N_4$, which separated on cooling, with m. p. 235°, which is apparently carbonyldicarbamide; a second crystalline substance separated from the mother liquors, which was not obtained pure and could not be identified. In addition, the following oxidation products were found: carbamide, oxalic acid and ammonia. S. B. S.

Action of Aniline on Halogenated Phthaleins. VASSILI V. SCHARVIN (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 885—890).—The fact that anthraquinone derivatives containing hydroxyls, halogens, sodium or sulpho-groups in the α-positions are converted by the action of ammonia or primary amines into aminoanthraquinones which contain amino- or substituted amino-groups and act as stable violet-blue, blue or greenish-blue colouring matters, has led the author to apply this reaction to halogenated phthaleins.

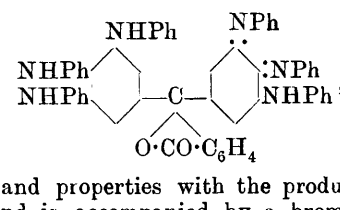


Treatment of eosin with excess of freshly-distilled aniline in a sealed tube at 180—200° yields the *hexaanilinofluoran* (annexed formula), which forms a deep, violet-blue, amorphous powder and yields a bluish-violet alcoholic solution and a pure blue solution in acetic acid. It has no acidic properties, but is faintly basic in character, giving with acids blue salts which exist only in presence of a large excess of acid, and are completely hydolysed on dilution with water. In dilute alcoholic solution it is readily decolorised by hyposulphite, but gradually resumes its original colour in contact with air.

In a similar manner, tetrabromophenolphthalein and aniline yield *hexa-anilinophthalophenone*,



or



which is almost identical in colour and properties with the product obtained from eosin. This compound is accompanied by a bromo-derivative containing 4·16% of bromine, which would indicate a more complex molecule than that given above, since one bromine atom remaining in the molecule would correspond with 9·74% of bromine.

An analogous colouring matter was obtained by the action of aniline on chlorinated eosin containing halogen in the third benzene nucleus.

All the above compounds act as substantive colouring matters, and dye silk and wool violet-blue in an acid bath. The absence of the connecting oxygen atom between the two benzene nuclei of the substituted hexa-anilinophthalophenone renders the latter a somewhat less fast colouring matter than the fluoran derivative. These colouring matters may be converted into sulpho-salts soluble in water by treatment at 120° with fuming sulphuric acid containing 12% of sulphur trioxide. T. H. P.

Preparation of Chlorinated Products in the Anthraquinone Series. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 262076).—Chlorinated products are obtained when diazotised aminoanthraquinones are treated with hypochlorites; the *compound* from anthraquinone-2-diazonium sulphate is a pale yellow powder, decomp. 90°, whilst anthraquinone-2 : 6-bisdiazonium sulphate gives rise to a yellow powder. F. M. G. M.

Saponification of Ethers of Hydroxyazo-compounds. G. CHARRIER and G. PELLEGRINI (*Atti R. Accad. Sci. Torino*, 1913, **48**, 978—981).—These ethers can be readily saponified by acting on them with anhydrous aluminium chloride. When *o*-anisoleazo-β-naphthol is heated for a short time at 120—130° with four or five times its weight of aluminium chloride and the reaction mixture boiled with dilute sodium hydroxide, the *sodium* salt of phenol-2-azo-β-naphthol, $C_{16}H_{11}O_2N_2Na,3H_2O$, is obtained, and from it *phenol*-2-*azo*-β-*naphthol*, m. p. 193°, can be prepared. *o*-Phenetoleazo-β-naphthol behaves similarly.

p-Anisoleazo-β-naphthol yields *phenol*-4-*azo*-β-*naphthol*,

$$C_{16}H_{12}O_2N_2,$$

which crystallises in cantharides-green needles, m. p. 194°, and the same substance can be prepared similarly from *p*-phenetoleazo-β-naphthol. R. V. S.

***o*-Aminoazobenzene. II.** FELIX H. WITT (*Ber.*, 1913, **46**, 2557—2559. Compare A., 1912, i, 921).—As mentioned in the earlier paper, the researches of Gattermann and Wichmann (A., 1888, 829) indicate that the rearrangement of diazoaminobenzene must give rise to some *o*-aminoazobenzene besides the para-isomeride, because phenylazoiminobenzene, a dehydration product of the former, is present in the reaction product.

By maintaining the temperature below 40° during the rearrangement, the subsequent dehydration is checked, and up to 4% of the ortho-isomeride is found in the product and can be separated by recrystallisation of the mixture from benzene, in which the ortho-compound is much more soluble.

In common with other *o*-aminoazo-compounds (Goldschmidt and Rosell, A., 1890, 616; Goldschmidt and Poltzer, A., 1891, 839; Noelting and Wegelin, A., 1897, i, 155), *o*-aminoazobenzene condenses with aldehydes producing triazine compounds; thus when warmed with

formaldehyde in solution in acetic acid to which a little concentrated hydrochloric acid has been added, it gives 2-*phenyl*-2 : 3-*dihydro*-1 : 2 : 4-*triazine*, $N\langle\begin{smallmatrix}-C_6H_4-\\ NPh\cdot CH_2\end{smallmatrix}\rangle N$, yellowish-white needles, m. p. 210° (decomp.); a similar reaction with benzaldehyde in place of formaldehyde gives rise to 2 : 3-*diphenyl*-2 : 3-*dihydro*-1 : 2 : 4-*triazine*, $N\langle\begin{smallmatrix}-C_6H_4-\\ NPh\cdot CHPh\end{smallmatrix}\rangle N$, very pale red crystals, decomp. at 215°.

D. F. T.

Hydrolysis of Proteins with an Alcoholic Solution of Hydrogen Chloride. I. CHARLES WEIZMANN and GANESH SAKHARAM AGASHE (*Biochem. J.*, 1913, **7**, 437—440).—The method is an attempt to shorten the usual process, by using a saturated alcoholic solution of hydrogen chloride from the beginning to serve both as a hydrolysing and an esterifying agent. The reagent is not so powerful as an aqueous solution for hydrolysis, as it contains less hydrogen chloride, and cannot be heated to so high a temperature. As expected, therefore, hydrolysis is not so complete. The proteins used, caseinogen and silk fibroin are only partly attacked, and the yield of separate amino-acids is poor.

W. D. H.

Indole Formation in the Hydrolysis of Proteins by Alkalis. E. HERZFELD (*Biochem. Zeitsch.*, 1913, **56**, 82—94).—The indole was quantitatively estimated with the use of the colour reaction with the *p*-dimethylaminobenzaldehyde reagent, the spectrophotometric method of Herzfeld and Bauer being employed. It was found that small amounts of indole are obtainable from proteins on gentle warming with water. If proteins are treated with 0·5% sodium carbonate, indole is also produced; addition of hydrogen peroxide diminishes the amount, but addition of copper sulphate increases it. Similar results were obtained with 0·2% sodium hydroxide solution, but barium and calcium hydroxides gave smaller yields. It was found that larger yields were obtainable by increasing the concentration of the alkali hydroxide, the best results being produced with 9% sodium hydroxide; increase of the alkali concentration beyond this limit diminished the yield. One gram of protein was treated with 1000 c.c. of the alkaline solution. Under optimal conditions, tryptophan itself gives about 60% of the theoretical yield of indole. A pancreatic digestion product of caseinogen yielded 6·5% of the theoretical amount of indole, calculated on the assumption that this protein contains 0·8% tryptophan. Experiments were also arrived at with the object of ascertaining whether pyrrole and scatole are produced at the same time. The colour reactions employed for this purpose are described in some detail. No evidence of the production of these substances could be obtained.

S. B. S.

Separation of Proteins. III. Globulins. HENRY C. HASLAM (*Biochem. J.*, 1913, **7**, 492—516).—The water-insoluble globulin of serum contains, or is closely associated with. rather more than 0·1

phosphorus %. About half of this belongs to a lecithin-like substance which amounts to 8—10% of the globulin freed from ψ-globulin. ψ-Globulin contains no phosphorus. By fractional salt precipitation, the details of which are given, the true globulin, ψ-globulin, and albumin can be satisfactorily separated. W. D. H.

Racemisation of Proteins and their Derivatives Resulting from Tautomeric Change. II. The Racemisation of Casein. Henry D. Dakin and Harold W. Dudley (*J. Biol. Chem.*, 1913, **15**, 263—269).—It has been shown by Dakin (this vol., i, 208) that the treatment of gelatin by dilute alkalis at low temperatures produces racemisation, which is explained on the assumption of a ketol-enol tautomerism of the CH·CO-group. From the character of the amino-acids obtained by hydrolysis, it is claimed that some conception may be formed as to their position in the protein molecule, the occurrence of optically active amino-acids being taken as evidence of their being terminal groups. The preparation of a "racemised" casein is described, which is in fact a hydrolysis product of caseinogen (scission of phosphoric acid having taken place), which on hydrolysis yields inactive alanine, *d*- and inactive valine, *l*- and inactive leucine, *l*-proline and inactive tyrosine, phenylalanine, aspartic and glutamic acids, arginine, lysine, and histidine. As alkalis are used in the synthesis of polypeptides, it is presumed that with present methods it is not possible to synthesise a naturally-occurring protein. S. B. S.

The Proline Fraction Obtained by the Hydrolysis of Caseinogen. The Isolation of Aminobutyric Acid. Frederick William Foreman (*Biochem. Zeitsch.*, 1913, **56**, 1—10).—From the proline fraction of the hydrolysis products, chloroform extracts a non-crystallisable, coloured substance. The residue after extraction with cold alcohol leaves a product which is aminobutyric acid. Further quantities of this substance can also be isolated from the extract in hot alcohol. The cold alcoholic extract when concentrated and treated with cold alcohol yields a precipitate, which is not entirely soluble in amyl alcohol at 60°. From this insoluble fraction, a glassy substance was obtained, which gives a characteristic copper salt, and contains only half its nitrogen in the form of an amino-group, and apparently a piperidine ring. In the same fraction there is also probably a basic substance. There appear to be also in the proline fraction other substances in which the nitrogen is not in the form of amino-groups. A method is also described for preparing fresh *l*-proline, which consists in treating an alcoholic solution of the proline fraction with freshly precipitated, dried and powdered copper hydroxide. The copper salt of the proline passes into solution. S. B. S.

Colloidal Properties of Hæmoglobin. Filippo Bottazzi (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 141—144).—By dialysis of the colouring matter of blood for four or five months, a pure product is obtained, which is gradually precipitated in the dialyser in very finely-divided form. It consists chiefly of methæmoglobin (95%).

It is almost insoluble in water and in neutral salts, but dissolves on addition of a trace of alkali, yielding a colloidal solution in which the colloid is electronegative. The product also dissolves in presence of a trace of acid, and the colloid in solution is then electropositive.

R. V. S.

The Combinations of Hæmoglobin with Oxygen and Carbon Monoxide. I. ARCHIBALD V. HILL (*Biochem. J.*, 1913, **7**, 471—480).—The oxygen and carbon monoxide dissociation curves of hæmoglobin differ according as salts and carbon dioxide are present or not. This has been explained on the theory that the simple molecules of hæmoglobin are aggregated into clusters. This explains all the facts provided two assumptions are made: (1) that the half-saturated molecules Hb_2O_2 and Hb_2CO are unstable, and change into either Hb_2, or $Hb_2(O_2)_2Hb_2(CO)_2$ or $Hb_2\cdot CO\cdot O_2$; (2) that the half-saturated molecules combine much more readily with carbon monoxide than with oxygen. The first assumption can be explained as due to the fact that Hb_2 is Hb⁚Hb, whilst Hb_2O_2 is ⁚Hb·Hb⁚O_2 with two unsaturated bonds which tend to combine at once with O_2 to form O_2⁚Hb·Hb⁚O_2. If these assumptions are justified, the deduction may be made that since carbon monoxide combines much more readily with Hb_2O_2 than with Hb_2, hæmoglobin will take up more carbon monoxide at a given tension if a little oxygen is present than if it is completely absent. W. D. H.

The Combinations of Hæmoglobin with Oxygen and Carbon Monoxide. II. JOSEPH BARCROFT (*Biochem. J.*, 1913, **7**, 481—491).—The available data for the dissociation curves of blood agree very closely with the theoretical curves deduced from the following physical conceptions: (1) That the reaction is reversible:

$$Hb_n + nO_2 \rightleftharpoons Hb_nO_{2n};$$

(2) that n is the average number of molecules aggregated together, its value depending on the nature and concentration of the electrolytes in solution; (3) that acids change the equilibrium constant of the reaction without altering the degree of aggregation; (4) that the action does not involve the breakdown and reformation of the aggregates; and (5) that unsaturated oxides are unstable and break up into hæmoglobin and saturated oxides. An entirely similar conception of carboxyhæmoglobin is supported by the available data. So far as the curves deduced from Hill's formula, $\gamma/100 = Kx^n/1 + Kx^n$, can be distinguished from those held by Haldane and Douglas's more complex formula, the experimental evidence favours the former.

W. D. H.

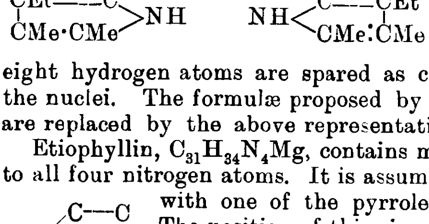
Action of Alkyloxides on Hæmin and its Derivatives. II. Conversion of Hæmin into Mesohæmin. HANS FISCHER and HEINRICH RÖSE (*Zeitsch. physiol. Chem.*, 1913, **88**, 9—24. Compare this vol., i, 1006).—By the action either of potassium hydroxide in methyl alcohol or of potassium ethoxide on hæmin, the crystalline iron salt of mesoporphyrin, for which the name mesohæmin is suggested, is obtained. This transformation proves the presence of four pyrrole

nuclei in hæmin. Hæmatoporphyrin likewise yields mesoporphyrin on treatment with alkyloxides, but the quantity is small.

On reducing hæmatoporphyrin solutions with sodium amalgam until they became colourless, crystalline hæmatoporphyrinogen could not be isolated, but the solution of the leuco-base was used for physiological experiments. For two days after injection into rabbits it had no action, on the third day it had a sensibilising action indicating conversion into an active porphyrin. The physiological bearing of the inactivity of the leuco-base is discussed. E. F. A.

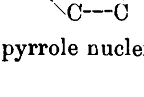
Blood Pigments. I. Degradation of Hæmins to the Porphyrins. Richard Willstätter and Max Fischer (*Zeitsch. physiol. Chem.*, 1913, **87**, 423—498).—I. *Constitution of Haemin.*—There is a certain resemblance between the porphyrins derived from hæmin and from chlorophyll; hæmatoporphyrin and mesoporphyrin, for example, having many points of similarity with phyllo-, pyrro-, rodo-, erythro- and rubi-porphyrins. On far reaching degradation of both classes of porphyrins by oxidation or reduction, similar simple pyrrole derivatives are obtained.

When hæmin and hæmatoporphyrin are heated with potassium hydroxide in methyl alcohol in presence of much pyridine, they are converted cleanly into crystalline porphyrins. Hæmatoporphyrin yields a product *haemoporphyrin* with four oxygen atoms; hæmin gives the complex iron compound of mesoporphyrin. Brief heating of the magnesium derivative of hæmoporphyrin with soda-lime eliminates the carboxyl groups and yields a substance identical with aetioporphyrin, $C_{31}H_{36}N_4$, from chlorophyll in composition, properties, spectrum and basic character. Accordingly, hæmoporphyrin has the composition $C_{33}H_{36}O_4N_4$, which assigns the formula $C_{33}H_{32}O_4N_4FeCl$ to hæmin instead of that usually adopted with 34 atoms of carbon. The new formula is in agreement with the analyses of hæmin derivatives and also with the older analyses of Küster (A., 1904, i, 357).

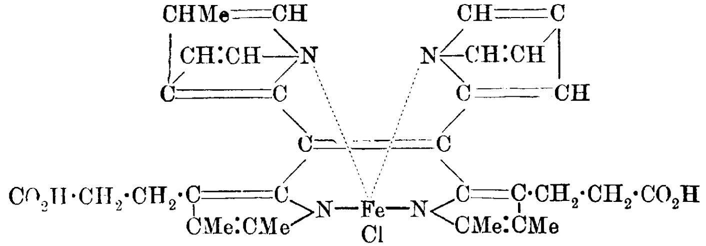


The basic skeleton of aetioporphyrin is composed of four pyrrole nuclei so united that eight hydrogen atoms are spared as compared with simple junction of the nuclei. The formulæ proposed by Küster, Piloty and H. Fischer are replaced by the above representation of aetioporphyrin.

Etiophyllin, $C_{31}H_{34}N_4Mg$, contains magnesium, presumably attached to all four nitrogen atoms. It is assumed that a vinyl residue is united with one of the pyrrole nuclei to a *cyclo*butene ring. The position of this ring and of the substituting methyl groups is uncertain.



It is considered that hæmin contains a bridged ring, such as is known in several alkaloids, in two of the pyrrole nuclei, and it is represented as follows:



When hæmin is converted into hæmatoporphyrin, the two bridged rings are broken, >C:C< becoming >C·C<, and one vinyl residue only becomes coupled with a carbon atom of the pyrrole nucleus. In mesoporphyrin the vinyl group CH:CH is saturated, although analysis does not allow the number of hydrogen atoms in this compound to be settled definitely. This conception is in harmony with the observed unsymmetric way in which the hæmin molecule alters on degradation.

II. *Intermediate products in the formation of haematoporphyrin.*—Aqueous hydrogen bromide saturated at 0° converts hæmin into the *dihydrobromide*, $C_{33}H_{34}O_4N_4FeBr_3$, which crystallises similarly to hæmin in large, obliquely-cut prisms of blackish-blue lustre, and forming a dark blue powder. The solution in concentrated sulphuric acid is a bluish-red.

Hydrogen bromide and acetic acid acting on hæmin yield a *trihydrobromide*, $C_{33}H_{35}O_4N_4FeBr_4$. This forms a brownish-red powder.

When ether is added directly the hæmin has dissolved in the hydrogen bromide-acetic acid mixture; the *salt*, $C_{33}H_{36}O_4N_4Br_2,2HBr$, is obtained in bright red flakes: it is hygroscopic.

When sodium acetate is added to the solution in acetic acid and ether the colour changes from green to brownish-red, and finally the *monoacetate*, $C_{33}H_{36}O_4N_4Br·OAc$, is obtained as a brownish-red powder.

By the action of liquid anhydrous hydrogen bromide on hæmin the iron is eliminated, and a *bromide*, $C_{33}H_{39}O_4N_4Br_5$, obtained in lustrous, violet-red or red, crystalline leaflets.

Liquid hydrogen chloride allowed to act on hæmin for a few minutes only gives rise to a *compound*, $C_{33}H_{36}O_4N_4FeCl_5$, which forms a hygroscopic, lustrous, violet residue. Methyl alcohol converts it into a *dimethyl* ester, crystallising in lustrous, brown, rhombic platelets; it is less basic than any known methyl derivative of hæmatoporphyrin.

By the action of methyl alcohol on the pentabromide a *dimethyl ether dimethyl ester* was obtained, which crystallised in large, lustrous, double pyramids, m. p. 163°.

Hæmin dissolves in liquid hydrogen chloride in sealed tubes with a bluish-red coloration. The product could not be properly purified. Methyl alcohol converted it into a *tetramethyl* compound differing from that above. It crystallises in long, thin, brown, matted needles, m. p. 165°.

III. *Porphyrins with more than four oxygen atoms.*—A convenient method of obtaining hæmin from centrifugalised blood is described.

Hæmatoporphyrin, $C_{33}H_{38}O_6N_4$, previously only known in an amorphous condition, crystallises in lustrous, violet ounded plates, which are reddish-brown by transmitted light. The hydrochloride crystallises in needles which are olive-green under the microscope, but form a red powder. A *dimethyl* ester forms a lustrous, dark red, crystalline crust, m. p. 149°. A second *ester* formed on heating with weaker acid is an intense red powder, m. p. 121°.

The crystalline tetramethyl derivative (Küster and Deihle, this vol., i, 1004) has the molecular weight about 600, agreeing with the formula $C_{37}H_{46}O_6H_4$.

The *dimethyl ether*, $C_{31}H_{34}N_4(OMe)_2(CO_2H)_2$, crystallises in very fine, brownish-red, lustrous, prismatic plates, obliquely-cut and often forming twins resembling a swallow's tail. It sinters on heating, m. p. above 270°.

The *monoacetate*, $OAc{\cdot}C_{31}H_{34}N_4(OH)(CO_2H)_2$, is a bluish-violet powder.

By the action of liquid hydrogen chloride on hæmin and hydrolysis of the intermediate product, $C_{33}H_{37}O_4N_4Cl_6$, with acids, *haeminoporphyrin* is formed, having the composition $(C_{33}H_{37}O_{5\frac{1}{2}}N_4)_2$. When heated in a vacuum at 105° no water is eliminated as is the case with hæmatoporphyrin. It forms a heavy, dark violet powder consisting of metallic, rectangular platelets with rounded corners. The *trihydrochloride* forms bright red needles. The *methyl* ester is an intense red powder. Solution in saturated hydrogen bromide and dilution with water converts hæminoporphyrin into hæmatoporphyrin.

Another compound, *haemidoporphyrin*, is obtained from hæmin hydrochloride on treatment with sodium acetate in warm acetone solution. It crystallises in very large prisms with a brownish-violet lustre, and behaves as an hydroxy acid.

All these compounds are differentiated by their basic properties as determined by their distribution between hydrochloric acid and ether (compare Willstätter and Mieg, A., 1907, i, 69).

IV. *Porphyrins with four oxygen atoms.*—Hæmoporphyrin is shown to have the formula $C_{33}H_{36}O_4N_4$. It is more strongly basic than the isomeric porphyrins obtained from chlorophyll. The *dimethyl* ester crystallises in obliquely-cut prisms with a number of twin forms.

On heating hæmin with potassium hydroxide in methyl alcohol and pyridine, the compound, $C_{33}H_{32}O_5N_4FeK_3$, is obtained in long, transparent, red prisms. Mesohæmin is obtained from this in lustrous prisms or thin, yellowish-brown plates. The *dimethyl* ester,

$$C_{33}H_{32}N_4(CO_2Me)_2{:}FeCl,$$

forms brown needles of metallic lustre.

Aetioporphyrin from hæmoporphyrin crystallises in small, reddish-brown prisms with oblique faces, m. p. 265° (decomp.). Despite minor differences, it is shown to be identical with the product derived from chlorophyll. E. F. A.

The Saturated Fatty Acid of Kephalin. JAKOB PARNAS (*Biochem. Zeitsch.*, 1913, **56**, 17—20).—The only fatty acid obtained by the hydrolysis of kephalin with barium hydroxide was stearic acid. There is no evidence of the existence of a "palmitylkephalin"

in addition to the "stearylkephalin" as has been assumed by other authors. S. B. S.

The Nitrogenous Constituent of Kephalin. MONTAGUE H. RENALL (*Biochem. Zeitsch.*, 1913, **55**, 296—300).—An improved process for the preparation of kephalin from ox and sheep brain is described. The disintegrated brain is treated with acetone, then with alcohol, and then with light petroleum. The crude kephalin from the latter extract is precipitated by alcohol, and is purified by precipitating from its solution in ether by alcohol, and from its solution in water by hydrochloric acid. Like the human brain, the brains of ox and sheep contain the nitrogen in the form of a primary base, and in ox brain the presence of aminoethyl alcohol could be detected. S. B. S.

Phosphatides, particularly those in Egg-Yolk. JULIUS EPPLER (*Zeitsch. physiol. Chem.*, 1913, **87**, 233—254).—The products of hydrolysis of that portion of the phosphatides of egg-lecithin which is not precipitated by cadmium chloride consist of aminoethyl alcohol (compare Trier, A., 1912, i, 233) in addition to choline.

The phosphatide soluble in alcohol after complete extraction of egg-yolk with ether is a monaminomonophosphatide.

Comparison of the organic portion of cadmium chloride compounds with the original phosphatides shows a diminution in the amount of carbon, hydrogen and oxygen. Some elimination of fatty acid molecules has perhaps taken place. E. F. A.

Plastein Formation. II. P. GLAGOLEV (*Biochem. Zeitsch.*, 1913, **56**, 195—208).—The grade of formation of more complex products, as measured by the Sörensen formaldehyde titration method, from dialysed hydrolysis products of proteins by dialysed ferments is not smaller than in the case of peptones containing the salt content of ordinary undialysed fermentation mixtures. The addition of salts, however, especially of sodium chloride, facilitates the formation of precipitates during plastein formation. The addition of sodium chloride up to 1·84%, and of calcium chloride up to 0·6%, exert no influence on the number of free amino-groups which disappear (as measured by Sörensen's method) during plastein formation; in fact, there is no definite relationship between the amount of precipitate formed during plastein formation and the amount of apparent synthesis, as measured by the diminution of free amino-groups. Plastein formation can also take place in absence of added hydrochloric acid in the presence of dihydrogen potassium phosphate. S. B. S.

Action of Nuclease. P. DE LA BLANCHARDIÈRE (*Zeitsch. physiol. Chem.*, 1913, **87**, 291—309).—The gradual liquefaction of sodium α-thymus-nucleate is conveniently followed by viscometric methods. In this way nuclease may be identified, and its activity approximately determined. Nuclease has been proved to be present in the liver, thymus, pancreas, and in the seeds of the soja bean (*Glycina hispida*). The amount is largest in the pancreas. Nuclease is soluble in glycerol. It has a smaller affinity for colloids than trypsin, and may be protected

from tryptic digestion by treatment with colloids or animal charcoal. Yeast-nucleic acid, although differing in composition from thymus-nucleic acid, is hydrolysed by the nuclease of the thymus and the liver. Pancreas extract and the pancreatic secretion behave differently in decomposing nucleic acid. The liquefying and hydrolysing activities of nuclease are not parallel, from which it is inferred that two separate enzymes exist, or that the same enzyme contains two different active groups. E. F. A.

Studies on Amylases. V. Experiments on the Purification of the Amylase of Malt. HENRY C. SHERMAN and M. D. SCHLESINGER (*J. Amer. Chem. Soc.*, 1913, **35**, 1617—1623. Compare A., 1912, i, 815).—By extracting ground malt with two and a-half times its weight of water, dilute alcohol, or very dilute acid phosphate solution at as low a temperature as possible, with subsequent dialysis followed by fractional precipitation by alcohol or acetone, products have been obtained of diastasic power of 1800—2200 (Lintner's scale). The preparations resemble pancreatic amylase in appearance, but are less readily soluble in water; their solutions coagulate at 80°, giving large flocks. D. F. T.

The Action of Maltase on Starch. ZENON WIERCHOWSKI (*Biochem. Zeitsch.*, 1913, **56**, 209—219).—The saccharification of starch by the maltase of maize yields, in every stage, dextrose and soluble starch as the sole products of hydrolysis. The small amounts of dextrins, which yield a violet or red colour with iodine, owe their existence only to the presence of diastase. Maize diastase causes scission of all three kinds of carbonyl bonds in the starch with equal intensity, so that no dextrins are formed as intermediate products. Maize diastase appears, therefore, to be an ideal enzyme for the complete saccharification of starch. S. B. S.

Enzymes. Asymmetric Syntheses through the Action of Hydroxynitrilases. I. VERNON K. KRIEBLE (*J. Amer. Chem. Soc.*, 1913, **35**, 1643—1647).—The result obtained earlier by the author (A., 1912, i, 482) that a certain sample of emulsin when acting on amygdalin gave a residue of *l*-mandelonitrile, whilst its action on a mixture of benzaldehyde and hydrocyanic acid effected the formation of *d*-mandelonitrile can be attributed to the occurrence of varying quantities of two hydroxynitrilases in emulsin, one correlated with the *d*- and the other with the *l*-nitrile.

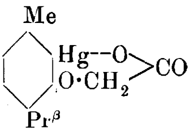
These two enzymes might be expected separately in plants which contain prunasin or amygdalin, and sambunigrin which are glucosides derived from the *d*- and *l*-nitrile respectively. An enzyme activating the combination of benzaldehyde and hydrocyanic acid to *d*-mandelonitrile was actually found in the leaves and bark of *Prunus serotina*, and in the leaves of the peach tree; the product obtained under its influence was not the pure *d*-isomeride, but the small quantity of racemic product present may have been due to the spontaneous combination of the constituents. The amount of racemic product given by emulsin cannot be explained in this way, and is probably to be ascribed to the concurrent action of two enzymes.

The leaf extract of the common elder, which contains sambunigrin, did not give rise to the formation of any optically active compound from benzaldehyde and hydrocyanic acid; whether this is to be explained by the presence of two enzymes concurrently producing *d*- and *l*-isomerides has still to be decided. D. F. T.

The Influence of Acids and Alkalis on the Diastatic Ferment during the Stages of Regeneration. M. J. GRAMENITZKI (*Biochem. Zeitsch.*, 1913, **56**, 78—81).—It has been shown by the author that the properties of the diastatic ferment, which have been lost by heating, can, under certain circumstances, be regenerated on keeping. It is now shown that the regenerative process is inhibited by acid, but accelerated by alkalis in certain low concentrations. This is in direct contrast to the action of acids and alkalis on the extracted ferment, of which the former class of substances function as activators and the latter as inhibitors. S. B. S.

Preparation of Soluble, Stable Derivatives of 3:3′-Diamino-4:4′-dihydroxyarsenobenzene. ANTON DERING (D.R.-P. 261542).—It is found that 3:3′-diamino-4:4′-dihydroxyarsenobenzene hydrochloride combines with albumin acids to furnish compounds which are soluble in water or alkalis, and are of therapeutic value. The preparation of the following *compounds* is described with (1) sodium nucleinate; (2) sodium caseinate; (3) sodium protalbinate; (4) sodium lysalbinate, and (5) from a mixture of sodium protalbinate and lysalbinate; the dry substances are yellow, amorphous masses, the alkali salts greenish-grey lamellæ. F. M. G. M.

Preparation of Nuclear-substituted Mercury Derivatives of Aryloxy-fatty Acids and their Salts. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 261229).—*Mercurithymolacetic anhydride* (annexed formula), a sand-like powder, is obtained when mercuric acetate and thymolacetic acid are heated together in aqueous-alcoholic solution at 70°.



a-Guaiacolpropionic acid, m. p. 55°, is prepared by the action of sodium guaiacol on *a*-bromopropionic acid; on heating with mercuric acetate it gives rise to *mercuri-a-guaiacolpropionic acid*. These compounds are of therapeutic value, and others having the general formula

$$CO_2H\cdot R_1O\cdot R\cdot Hg\cdot OH,$$

where R is phenyl, naphthyl or their substituted derivatives, and R_1 alkyl or substituted alkyl groups, are also discussed.

F. M. G. M.

Preparation of Soluble Silver Salts of Mercury Derivatives of Hydrocarbons. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 261875).—When the insoluble silver salts of the substituted mercury derivatives of hydrocarbons are treated with the alkali salts of amphoteric or faintly acidic substances they furnish soluble additive

compounds, and the following have been prepared: from hydroxymercurithymoxyl acetate with sodium diethylbarbiturate and from silver hydroxymercuribenzoate with sodium succinimide.

F. M. G. M.

Physiological Chemistry.

Physiological Observations following Descent from Pike's Peak to Colorado Springs. EDWARD C. SCHNEIDER (*Amer J. Physiol.*, 1913, **32**, 295—308).—The return of the blood to a normal state after descent from a great altitude is very slow. Details regarding the percentage of hæmoglobin, red corpuscles, blood volume, pulse rate, alveolar carbon dioxide pressure, etc., are given. The respiratory capacity is not greater in men who live high up than those of similar physique at sea level. W. D. H.

The Respiration of Pulverised Insects. FRED. BATTELLI and (Mlle.) LINA STERN (*Biochem. Zeitsch.*, 1913, **56**, 35—49).—Pulverised insects exhibit a high respiratory exchange, which in certain cases is as large at 40° as that of the living animals, but in others (flies, silk-worm moths) markedly smaller. The respiratory exchange increases with rising temperature up to 30°, and remains from this point constant until about 55°. A slight alkalinity increases in some cases the respiratory exchange, but higher alkalinities exert an inhibitory action, notably on the carbon dioxide production. In acid media both the oxygen consumption and carbon dioxide production are diminished. The gas-exchange takes place both in hypo- and iso-tonic solutions, and is not affected by addition of disodium hydrogen phosphate. It is not much larger in an atmosphere of oxygen than in one of air, and is not influenced by the addition of mammalian blood or of pnein. The addition of trypsin only depresses the respiratory exchange to a small extent. The alcohol and acetone preparations of pulverised insects also exhibit a distinctly high respiratory exchange. Attention is called by the authors to the differences between the respiratory exchanges of pulverised insects and of mammalian tissue; the former are to be ascribed to the presence of oxydases of unknown character.

S. B. S.

The Intensity of the Respiratory Exchanges of Insects. FRED. BATTELLI and LINA STERN (*Biochem. Zeitsch.*, 1913, **56**, 50—58). —The oxygen consumption, carbon dioxide production, and respiratory quotients of cockroaches, silk-worms, and of flies in various stages of development are tabulated. There is an increased respiratory exchange with increasing temperatures. This is also greater in the fully developed insects than in the larvæ, and the latter are more active than the chrysalis. S. B. S.

The Cholesterol and Cholesterol Ester Content of the Blood of Various Animals. FELIX KAUDERS (*Biochem. Zeitsch.*, 1913, **55**, 96—100).—A series of analytical results obtained by the Windaus digitonin method is tabulated. The cholesterol and cholesterol esters were estimated both in the serum and corpuscles.
S. B. S.

Lactic Acid in Blood. WALTER GRIESBACH and SIEGFRIED OPPENHEIMER (*Biochem. Zeitsch.*, 1913, **55**, 323—334).—The formation of lactic acid from various substances by the action of blood corpuscles was investigated. Dextrose, lævulose, mannose, and galactose were found to be capable of forming this acid, whereas arabinose and glucoheptose were not. Inositol was in the majority of cases found to be inactive, but in two cases a slight increase of lactic acid was found. Alanine was indifferent, and glycerol was also generally indifferent, although in one case it gave rise to a considerable amount of acid. It appears as if the same tissue from different individuals of the same species shows an inconstant behaviour as regards the formation of lactic acid from the same substance. S. B. S.

Method for Extraction of Amino-acids from Different Constituents of the Blood. A. COSTANTINO (*Biochem. Zeitsch.*, 1913, **55**, 419—424).—One hundred c.c. of the blood or serum are mixed with 500 c.c. of 2% mercuric chloride solution containing 0·8% hydrochloric acid. The proteins are thereby precipitated. An aliquot part of the filtrate, obtained after centrifugalisation, is evaporated in vacuum after addition of magnesium oxide (in order to separate ammonia) to a small bulk, in which the formalin titration process is carried out. This is done after addition of solid barium chloride and hydroxide, filtering off the precipitate, and neutralising the filtrate to azolitmin. Where very small amounts of amino-acids are present, a certain known amount is added before these manipulations, so that larger amounts of alkali are required for titration. S. B. S.

The Normal Sugar Content of the Blood of Rabbits and Dogs. ADOLF LOEWY and SIEGFRIED ROSENBERG (*Biochem. Zeitsch.*, 1913, **56**, 114—116).—The statement has often been made that the sugar in the blood of rabbits occurs abnormally as a result of the treatment of the animals (binding, exposing the arteries, etc.). The authors now show that a similar phenomenon can be observed in dogs. It was noticed, furthermore, that the blood removed under conditions of local anæsthesia (novocaine) contained less sugar than that removed from the same animals without anæsthesia, and that pain probably has some influence on the abnormally high sugar content in the blood of animals. S. B. S.

Blood Glycolysis: its Extent and Significance in Carbohydrate Metabolism. The Supposed Existence of "Sucre virtuel" in Freshly Drawn Blood. JOHN J. R. MACLEOD [with A. M. WEDD] (*J. Biol. Chem.*, 1913, **15**, 497—514).—Unclotted

(hirudin) and defibrinated blood have the same glycolytic power, but potassium oxalate has a depressing action. The rate of glycolysis varies greatly, but in the mean about half the sugar disappears, in two and a-half hours at 40°. This is a function of the corpuscles. If much dextrose is added to the blood, the process may be depressed. The rate is the same in diabetic blood. The destruction of sugar in the blood in the intact animal is an almost negligible fraction of the total glycolysis. W. D. H.

Permeability of Blood Corpuscles for Amino-acids. A. COSTANTINO (*Biochem. Zeitsch.*, 1913, **55**, 411—418).—By suspending blood corpuscles in serum in which an excess of amino-acid had been dissolved, and estimating the nitrogenous substances titratable in the presence of formalin, it was found that these diminished in the serum and increased in the corpuscles. From this it follows that the latter are permeable to amino-acids, but, as experiment showed, only up to a certain limit. This corresponded nearly with the amount of amino-acids in the corpuscles of a dog at the time of digestion of food, that is, 45 mg. nitrogen per litre of corpuscles. The amount reached did not differ greatly whether asparagine, the acid hydrolysis products of caseinogen, or glycine was added to the serum. S. B. S.

The Amino-acid Nitrogen, which can be Estimated by the Formalin Method, in the Blood Corpuscles and Serum of Fasting and Fed Animals. A. COSTANTINO (*Biochem. Zeitsch.*, 1913, **55**, 402—417).—The author, by various methods described in some detail, is able to confirm the presence of amino-acids in the blood. The amount in fasting animals is less than that in fed animals, although there is no difference in the amounts in the serum in animals at different stages of nutrition. From this it follows that the excess of amino-acids in the blood of fed animals over that in blood of fasting animals is present in the corpuscles, which must consequently be permeable to these acids. The content of both serum and corpuscles in amino-acids is the same in all parts of the circulation, and this fact negatives the supposition of the deaminisation of the digestion products in the intestinal wall. Lymph contains only a small amount of nitrogen titratable in the presence of formalin. S. B. S.

The Influence of Lipoids on the Coagulation of Blood. FRIEDRICH RUMPF (*Biochem. Zeitsch.*, 1913, **55**, 101—115).—Lipoid emulsions (prepared from ox-brain) hasten the coagulation of oxalate plasma, but only to a slight extent, which is quantitatively far below the action of tissue extracts. There is no species specificity in this action. Plasma which has been deprived of its lipoids by light petroleum will only coagulate after addition of lipoids. This fact does not prove, however, that thrombokinase is a lipoid. The statement of Bordet and Delange, that lipoids, like tissue juices, cause the development of large quantities of thrombin in serum, appears to be incorrect, as the acceleration of clotting

caused by the former is insignificant compared with that caused by the latter (30 : 600). Peptone and hirudin bloods can be made to clot by tissue extracts, but not by lipoids. The lipoids, therefore, do not appear to be the actual active agents, although they do play some part in the clotting process. It seems therefore advisable to retain the term thrombokinase for the active substance of tissue juices. S. B. S.

The Nature of Thrombin and Anti-thrombin. BERTRAM J. COLLINGWOOD and M. T. MACMAHON (*J. Physiol.*, 1913, **47**, 44—53).—Thrombin is destroyed by heat (50—60°), by acid, alkali, and trypsin. After destruction of Gamgee's thrombin, thrombokinase is still present; this preparation also contains fibrinogen. Antithrombin is destroyed by heat (60—65°) and by acid. It will act only in an alkaline medium; neutralisation inhibits, but does not destroy it. The rate of action of antithrombin varies directly with temperature in contrast with thrombin. It is suggested that thrombin is a protein, that antithrombin is a proteolytic enzyme, and that fibrin is a combination of thrombin and fibrinogen. W. D. H.

The Properties of Rabbit's Serum after Treatment of the Animals with Emulsin. KOHSHI OHTA (*Biochem. Zeitsch.*, 1913, **54**, 430—438).—When rabbits have been immunised by several injections of emulsin, their serum exerts a greater inhibitory action on the action of the ferment than the serum of normal animals. This difference of action is, however, only marked when the serum is present in sufficient quantities. If *d*-galactose and dextrose are incubated together in the presence of immune serum, there is evidence of the formation of a disaccharide, of which small quantities of a phenylosazone could be isolated. S. B. S.

Hæmolytic Action of Cyclamin-Cholesterol Mixtures. ERNST H. RIESENFELD and H. LUMMERZHEIM (*Zeitsch. physiol. Chem.*, 1913, **87**, 270—290).—On mixing equivalent quantities of cyclamin and cholesterol, a mixture is obtained in which the hæmolytic action of cyclamin is only partly suspended. Further addition of cholesterol has the effect of lessening the poisonous action. It is therefore inferred that the cyclamin-cholesterol complex is dissociated in solution. If the hæmolytic action of any cyclamin-cholesterol mixture is regarded as a measure of the amount of free cyclamin, it is possible to determine the dissociation constant K of the cyclamin-cholesteride, provided that the total amount of cyclamin and cholesterol in the mixture is known. Constant values for K are obtained by this method so long as the same blood solution is used, but different values of K are obtained with different blood solutions, owing probably to the presence of the serum. The serum has the property of lowering the hæmolytic activity of cyclamin, but acts quantitatively in a very variable manner. E. F. A.

The Hæmolytic Lipoids of the Organs and the Influence on them of Administration of Dextrose. ARNO KIRSCHE (*Biochem. Zeitsch.*, 1913, **55**, 169—188).—Various investigators have shown that the liver contains hæmolytic lipoids, which appear to have a special pathological significance in certain diseases, such as pernicious anæmia. The conception is now advanced that in fatty degeneration of the liver the lipoids are of two-fold origin, namely, those due to degeneration of the cell material itself, and those due to infiltration. To the former class only is to be ascribed the hæmolytic activity. This hypothesis has been tested in the following way: In a number of rabbits fatty degeneration was produced by the following methods: starvation, phloridzin, acute and chronic poisoning with tolylenediamine, maintenance of the animal at high temperatures, post-mortal autolysis. The lipoids were obtained from the liver by heating this organ with alcohol, then extracting with ether, and precipitating the lecithins from the ethereal extract by acetone; after distillation of the ether–acetone mixture the residue was weighed and used for experiment in methyl-alcoholic solution. The hæmolytic value of this solution was then determined. It was found that in all cases, both the quantity of extract and its hæmolytic value were increased in cases of fatty degeneration, especially in that produced by autolysis. Now it is supposed that administration of dextrose inhibits infiltration. A series of experiments similar to the above was carried out with this addition. If the action of sugar is correctly interpreted, then the lipoids derived from the sugar-fed animals should contain relatively larger amounts of fats derived from the cell degeneration, and consequently a higher hæmolytic value. This was actually found to be the case. Attention is also called to differences in the fatty-degenerated livers produced by different methods. S. B. S.

Digestion and Absorption under Normal and Pathological Conditions. EFIM S. LONDON (*Zeitsch. physiol. Chem.*, 1913, **87**, 313—370).—This is a series of short papers on various aspects of the subject carried out on fistula dogs by London's methods.

I. *General Remarks.* E. S. LONDON.—Introductory.

II. *Does Absorption Occur in the Stomach?* J. S. TSCHEKUNÒV.—Many previous authors have stated that absorption occurs in the stomach. In the present experiments finely-divided meat alone or mixed with gliadin was given by the mouth, or solution of dextrose or sodium chloride by the gastric fistula. The material which left the stomach contained the same amount of sugar as given, and protein substances entirely leave the stomach with an accession of nitrogen. In no case was there a deficit in the food material introduced. The proteins were not much broken up in the stomach (amide nitrogen = 11—18%).

III. *Absorption Products of Protein.* N. A. DOBROVOLSKAJA.—Two hundred c.c. of a 5% solution of alanine was placed in the intestine. In five minutes excess of amide nitrogen was found in the blood of the jugular vein. During digestion, the amide

nitrogen rises in the portal blood; the rise in the general blood stream is smaller. In no case did the blood give a biuret reaction.

IV. *The Amount of Amide Nitrogen in the Peripheral Blood during Digestion.* A. D. VOLKOV.—In all stages of digestion the jugular blood contains a small excess of amide nitrogen (almost 4 mg. per 100 c.c. of serum).

V. *The Influence of Surgical Changes in the Stomach on Digestion.* S. F. KAPLAN.—The pyloric section of the stomach plays an important rôle in the proper evacuation of the organ. Hydrochloric acid stimulates the fundus, and inhibits the pylorus. Sodium hydrogen carbonate also stimulates the fundus. Partial extirpation of the fundus hastens the emptying of the stomach. Observations on the rate of emptying an "hour glass" stomach are also given.

VI. *Digestion in Intestinal Resections.* P. P. BRJUCHANOV.—Resection of the jejunum makes no difference on the course of excretion of the constituents of the chyme through a fistula, but the rate of output is raised. The complete compensation for the defect does not, however, occur in the upper section of the digestion canal; the ileum takes no special share in the work of compensation; the main share falls on the large intestine. Opium and tannalbin do not lessen, but increase, the discharge through the fistula. Similar details are given in reference to removal of other parts of the bowel.

VII. *The Course of Digestion of Anomalous Constituents of the Gastric Contents.* R. S. KRYM.—Preliminary digestion of the meat-powder given does not hasten the emptying of the stomach. Excess of hydrochloric acid inhibits it.

VIII. *Digestion of Peptonised Milk.* Z. O. MITSCHNIK.—In vitro, peptonised milk is more rapidly digested by gastric, but not by pancreatic, juice. In dogs it causes an increase in the flow of bile. In weakly children, and certain pathological conditions, its use is advised. Further work is in progress.

IX. *The Physiological Importance of the Omentum.* M. R. GILLELS.—The experiments confirm the conclusion that the omentum is of importance, but compensation by the mesentery takes place. Further work is in progress.

X. *The Digestive Glands in Normal and Defective Digestion.* P. P. BRJUCHANOV.—The injection of an aqueous solution of Witte's peptone into the jejunum increases the excretion of bile; this is not affected by acidification of the solution with hydrochloric acid, but if the solution is made alkaline by sodium hydrogen carbonate, it stops the bile flow. Neutral or alkaline peptone solution has no effect on the pancreas, but hydrochloric acid excites a flow of pancreatic juice.

XI. *Maximal Reduction of the Alimentary Tract.* With S. F. KAPLAN.—Experiments are recorded which show how greatly the canal may be reduced without serious harm in dogs. Large amounts of the small intestine, and the whole colon were removed, and the dogs were in good condition months afterwards. W. D. H.

Absorption of Yeast-Nucleic Acid after Extensive Resection of the Small Intestine in Dogs. JUNICHI MAYESIMA (*Zeitsch. physiol. Chem.*, 1913, **87**, 418—422).—Removal of the greater part of the small intestine in dogs has no practical effect on the absorption of yeast-nucleic acid. Whether this is due to the remnants of the intestine, or to the activity of micro-organisms, is uncertain. W. D. H.

The Influence of Chronic Insufficient Nutrition on Metabolism. NATHAN ZUNTZ, S. MORGULIS, and M. DIAKOV (*Biochem. Zeitsch.*, 1913, **55**, 341—354).—A dog was kept over a prolonged period (more than a year) on a diet insufficient for the energy needs of the organism, during which time the weight sank from 10 to 4·19 kilos. The animal then died of inanition. The caloric value of the food administered (rice and meat) was controlled during the whole time, and repeated measurements of the respiratory exchanges were made; the nitrogen excreted was also repeatedly estimated. It was found that the energy consumption per square metre of surface sank during this period from 931 cal. per 10 kilos. of weight to a minimum of 631 for half that body weight, and rose again towards the end of the life of the animal to 921 calories for a weight of 4·1 kilos. There was no indication of a gradual accommodation of the energy consumption to the diminished food supply. S. B. S.

Metabolism during Pregnancy and Lactation. LUDWIG DIENES (*Biochem. Zeitsch.*, 1913, **55**, 124—133).—The gaseous metabolism of a tracheotomised dog during pregnancy and lactation was carried out by a method, described in some detail, based on the Regnault-Reiset principle. The results indicate that there is a large increase in the metabolism during the later stages of pregnancy. During lactation, on the other hand, the increase in the metabolism is relatively small. S. B. S.

The Carbohydrate Metabolism of the Isolated Heart–Lung Preparation. S. W PATTERSON and ERNEST H. STARLING (*J. Physiol.*, 1913, **47**, 137—148).—Starling and Knowlton stated that the diabatic heart is unable to utilise sugar as well as the normal heart. Further more accurate work has shown that this is not the case. The main purport of the present paper is to withdraw the former conclusions, and explain Maclean and Smedley's results, which seemed to confirm it; the glycogen of the heart muscle is a varying and disturbing factor, which may account for certain discrepancies. The view that the primary factor in diabetes is an absence of the power of the tissues to consume sugar is abandoned. W. D. H.

The Rate of Resorption of Proteins and their Degradation Products from the Small Intestine. HERMANN MESSERLI (*Biochem. Zeitsch.*, 1913, **54**, 446—473).—The experiments were

carried out on a dog with a Thiry-Vella fistula. The various products under investigation were introduced into the fistula, and removed after a definite interval by a method described by the author. The amount of resorption of proteins and degradation products was determined by estimations of nitrogen. All experiments were carried out on the same animal. The amounts of genuine proteins taken up in ten minutes may be represented by the following numbers: Serum, 20; gliadin, 16; caseinogen, 12; hæmoglobin, 8. The less degraded proteins, such as peptones, are resorbed more rapidly than the products of complete acid hydrolysis. This fact indicates that the proteins are not degraded completely in the small intestines. During a diet poor in proteins, the resorbability of various proteins progressively diminished, but increased again when the animal reverted to a protein-rich diet. This phenomenon was observed, however, only in the first experiments. In later experiments the resorption was less during the subsequent period of rich protein diet. This is probably due to the fact that after the various treatments to which the animal had been subjected, the cells of the intestine had lost their physiological functions as regards the resorption of nitrogenous products. Their capacity for taking up sugar remained, however, unimpaired.

S. B. S.

The Pentoses as a Source of Energy in the Animal Organism. P. SCHIROKICH (*Biochem. Zeitsch.*, 1913, **55**, 370—392).—The experiments were carried out with *l*-arabinose prepared from cherry-gum. It was found that the addition of this carbohydrate to a given basal diet caused very little rise in the respiratory quotient, and about half of the amount ingested was excreted unchanged in the urine. When dextrose was given in corresponding quantities, a certain increase in the respiratory quotient could be ascertained. The increased oxygen consumption, which takes place normally after a meal, is slightly diminished by the addition of dextrose to the diet, and largely diminished by arabinose.

S. B. S.

The Biological Significance of Phosphorus for the Growing Organism. I. The Influence of Phosphorus on the Growth of Animals and on the Phosphorus and Nitrogen Metabolism. M. MASSLOV (*Biochem. Zeitsch.*, 1913, **55**, 45—62).—The rate of growth of puppies from three different litters on diets rich and poor in phosphorus was investigated. As basal diets a gruel containing rice, albumin and sugar, cow's milk alone, cow's milk in which the caseinogen was replaced by egg-albumin, which was therefore poor in phosphorus content, and mixed diets of meat, milk, and porridge were employed. The animals were found to thrive only on the mixed diet. The animal fed on milk lived longer than the other animals, but even in this case it finally died of inanition. Phosphorus was added in other experiments after a period on the phosphorus-poor basal diets, in the form either of lecithin, glycerophosphate, or inorganic phosphate. The addition of

lecithin caused a temporary improvement of condition, but in this, as in all the other cases in which phosphorus was added, the animals finally succumbed. The rate of growth when the animals were transferred from a normal to a special diet was not affected immediately, but loss of weight occurred only when they had been a certain time on the abnormal diet. The experiments here recorded do not show conclusively whether the normal growth is due to phosphorus in any special form of combination, or to some other factor. S. B. S.

The Biological Significance of Phosphorus for the Growing Organism. II. The Content of Phosphorus and Intracellular Ferments in the Various Organs. M. MASSLOV (*Biochem. Zeitsch.*, 1913, **56**, 174—194).—The author gives the content in inorganic, organic, and phosphatide phosphorus of the organs of the animals fed by the methods described in the former paper (preceding abstract). The chief loss of the organs during a period of phosphorus starvation is in the inorganic phosphorus. The least loss is in the "organic" phosphorus (nucleoproteins, etc.). The lipoid phosphorus is less stable. Heart and brain do not under any conditions suffer loss in phosphorus, whereas the liver, intestines, muscles, bone-marrow, and kidneys lose considerable quantities during phosphorus starvation. When this loss attains certain limits, the animals die. The only phosphorus compound which produced, when added to the phosphorus-poor diet, an increase in the phosphorus-content of the organs, was lecithin. As regards the intracellular ferments, it was found that on a mixed milk and meat diet, there was a general increase in the fermentative energy of the organs, especially of the lipolytic, amylolytic, and diastatic energy. The development of the catalytic and nucleolytic energies was less marked. Under the influence of phosphorus starvation, not only is there no increase of fermentative energy of the organs, but in certain cases there is a distinct diminution. S. B. S.

The Soft Roes of Fish as Foodstuff for Man. JOSEF KÖNIG and J. GROSSFELD (*Biochem. Zeitsch.*, 1913, **54**, 333—350).—The soft roes from herring and carp were submitted to chemical examination by methods described in some detail, and found to contain meat bases (xanthine and creatinine) and free amino-acids in addition to the protamines, which exist combined with nucleic acid. The fatty substances consist to a large extent of lecithin (20·2—20·7%) and cholesterol (11·2—17·9%). S. B. S.

The Hard Roes of Fish as Foodstuff for Man. JOSEF KÖNIG and J. GROSSFELD (*Biochem. Zeitsch.*, 1913, **54**, 351—394).—The eggs of fish contain a relatively small amount of water as compared with hen's egg; they contain also meat bases, amino-acids, together with ichthulin, as chief protein (which is insoluble in water), albumin, and quantities of fat, which vary in the different species. All the roes investigated contain xanthine substances and creatinine. Xanthine and hypoxanthine were isolated, and the presence of the

following amino-acids was proved, viz., taurine, *l*-tyrosine, and glycine. The presence of thymine was also determined. The proteins contain relatively large quantities of sulphur and phosphorus. No protamines could be isolated from the ichthulins. These substances, on hydrolysis with sulphuric acid, yield purine bases, as Hammarsten and Levene and Mandel have already shown. The ichthulins and albumins yield, furthermore, on hydrolysis, tyrosine, leucine, arginine, histidine, and small quantities of lysine. The ichthulin of carp yields also glutamic acid. The fats contain large quantities of lecithin (up to nearly 60%), and not inconsiderable amounts of cholesterol (3·9—14%). The roes which are poorest in fats contain the largest amounts of lecithin. Caviare and other roes contain free acids, which increase in amount on putrefaction. Of the mineral matter, the acid ions are in excess of the basic ions, as the sulphur and phosphorus are in organic combination.

S. B. S.

Chemical Differentiation of the Central Nervous System. III. Chemical Differentiation of the Brain of the Albino Rat during Growth. WALDEMAR KOCH and (Miss) MATHILDE L. KOCH (*J. Biol. Chem.*, 1913, **15**, 423—448).—The principal chemical changes which occur in the rat's brain during growth are: a decrease in water which begins before medullation sets in; a relative fall in protein due to appearance of lipoids. The lipoids which appear with medullation are cerebrosides and sulphatides. The phosphatides increase before medullation, and occur both in cells and sheaths. Organic sulphur compounds diminish relatively with age, whilst the colloidal sulphur rises. The increase of colloidal matter, which is relatively inactive supporting matter, is one factor in the slowing of metabolism which characterises senescence. W. D. H.

The Action of Ions and Lipoids on the Frog's Heart. A. J. CLARK (*J. Physiol.*, 1913, **47**, 66—107).—An excised frog's heart after perfusion for a few hours passes into a hypodynamic state, and is more readily affected by ionic changes in the fluid perfused. It is improved by increase in the calcium relative to sodium and potassium, and not much improved by increase in hydroxyl ions. The hypodynamic state is caused by a loss of power to combine with calcium. The hydrogen ion concentration must be within narrow limits ($10^{-6\cdot7}$ and $10^{-8\cdot5}$), and a buffer must be present to stabilise the concentrations. A slight increase of carbon dioxide, amino-acids, glycogen, and sugars to a less extent benefit the hypodynamic heart. But the best of all are soaps of the high aromatic fatty acids higher than decoic acid; these soaps form insoluble calcium compounds, but other substances which form similar compounds injure the heart. Serum (but not the serum proteins) is beneficial; the same is true for serum lipoids, lecithin, and saponified serum lipoids. The loss of lipoids is the chief cause of the hypodynamic state; and the function of calcium is to cause an alteration in the colloidal state of the lipoids at the cell-surface. W. D. H.

The Mucin of the Stomach. J. López-Suárez (*Biochem. Zeitsch.*, 1913, **56**, 167—175).—By extraction of mucin from pig's stomach with 2% potassium hydroxide solution, and addition of acetic acid to the extract, a product was obtained which contained purine bases and also lipoids. By repeated solution in alkali and reprecipitation, a substance free from purine bases could be obtained. This contained (after extraction with alcohol and ether), 53·8% carbon, 7·29% hydrogen, 16·30% nitrogen, 1·47% sulphur, and 4·45% phosphorus. Chondroitinsulphuric acid, prepared from the mucin by Kondo's method, contained 43·3% carbon, 5·47% hydrogen, 5·37% nitrogen, and 4·29% sulphur. The former product contains less oxygen and sulphur than a true mucin, and in other respects differs from it widely in chemical composition. The stomach mucin appears to be a mixture of proteins, in which the chondoprotein is largely replaced by a nucleoprotein. S. B. S.

Carbon Dioxide Formation in the Liver. Eduard Freise (*Biochem. Zeitsch.*, 1913, **54**, 474—502).—An apparatus is described for perfusing liver with blood, and for estimating the carbon dioxide formed in the process, for which purpose the blood is treated with a stream of oxygen, and the mixture of gases is then led through a special absorption apparatus containing barium hydroxide solution. By the artificial perfusion of livers of rabbits or dogs with the blood of calf or ox, 54·74—192·48 mg. of carbon dioxide were formed per minute by 1 kilo. of the organ. This amount could be increased up to 50% by the addition of various oxidisable substances, such as dextrose, pyruvic acid, glyceric acid, and lactic acid. The addition to the blood, on the other hand, of galactose, glyoxylic acid, glycollic acid, and acetic acid, exerted no such influence. S. B. S.

The Effect of Water Ingestion on the Fatty Changes of the Liver in Fasting Rabbits. M. R. Smirnow (*Amer. J. Physiol.*, 1913, **32**, 309—314).—Fasting causes in rabbits fatty infiltration of the liver; if water is given, however, this as a rule does not occur. W. D. H.

Formation of Sugar in the Frog's Liver. Ivar Bang (*Biochem. Zeitsch.*, 1913, **56**, 153—157).—A reply to the criticisms of Lesser (this vol., i, 931). S. B. S.

Glyoxalase. III. The Distribution of the Enzyme and its Relation to the Pancreas. Henry D. Dakin and Harold W. Dudley (*J. Biol. Chem.*, 1913, **15**, 463—474).—This enzyme converts α-ketonic aldehydes, such as methyl- and phenyl-glyoxals, into optically active lactic and mandelic acids. It is probably important in carbohydrate metabolism. It is found in all tissues except the pancreas, which tissue contains an anti-glyoxalase, that is very powerful, and thermolabile. The inhibiting action is not limited to glyoxalase derived from the same species. It is present in pancreatic juice, in commercial pancreatic preparations, and in

the dry state lasts indefinitely (eight years in one case). It is destroyed at 85°, and by digestion with weak hydrochloric acid. Weak alkali is less injurious. The inactivation it produces is a function of the time of action. Whether it is an enzyme or not is unsettled. It is not trypsin, lipase, or diastase. The pyloric caeca of the fish (considered to be homologous with the pancreas) contain no anti-glyoxalase. The blood and tissues of diabetic men and dogs contain less glyoxalase than the normal, but this conclusion demands further work. W. D. H.

Influence of Pancreatic and Duodenal Extracts on the Glycosuria and Respiratory Metabolism of Depancreatised Dogs. JOHN R. MURLIN and B. KRAMER (*J. Biol. Chem.*, 1913, **15**, 365—383).—The effect of injecting pancreatic extract by itself and when mixed with duodenal mucosa extract on the dextrose: nitrogen ratio in the urine of a depancreatised dog, was investigated. This ratio was increased in the day following the injection, but a slight fall followed in the hourly elimination shortly after the injection, which was followed by a compensatory increase. In one case, when the mixed extracts were injected, there was for a short interval a complete disappearance of sugar. A similar effect could be produced by making Ringer's solution as alkaline as the extracts, and a marked diminution of sugar output could also be caused temporarily by injection of 2% sodium carbonate solution. The effects of the extracts are to be explained possibly by the alteration of the acidity. It is also possible that pancreatic extracts alter the permeability of the kidneys. The extracts, within the time of maximal glycosuria, produced no effect on the respiratory quotient, and there is therefore no evidence that they increased the combustibility of sugar in the organism. S. B. S.

The Production and Utilisation of Glycogen in Normal and Diabetic Animals. E. W. H. CRUICKSHANK (*J. Physiol.*, 1913, **47**, 1—14).—After extirpation of the pancreas, the liver rapidly and almost completely loses its glycogen, and becomes loaded with fat. Minkowski's statement that feeding diabetic animals on lævulose produces glycogen-storage was not confirmed. The percentage of glycogen in heart muscle varies, but averages 0·5; it is increased by copious carbohydrate food, and lessened by a diet devoid of protein and carbohydrate. During great activity, the heart may use all its stored glycogen in a few hours. In pancreatic diabetes, the cardiac glycogen rises, and may be entirely consumed if great activity of the heart occurs, as, for instance, after adrenaline. After death, both normal and diabetic hearts contain a glycogenolytic enzyme, so that the glycogen rapidly disappears if the heart is kept warm after the incubation has ceased. W. D. H.

Influence of Extirpation of the Pancreas on the Endocellular Activity of the Liver Diastase. I. ERNST J. LESSER (*Biochem. Zeitsch.*, 1913, **55**, 355—356).—The extirpation of the pancreas from frogs causes changes in the organism in many

respects analogous to those produced by diabetes in the human subject. It was shown that whereas the post-mortem diminution of the liver glycogen in frogs with intact pancreas was 4·2% in three and a-half hours at 22°, that of the depancreatised animals was 15·5%. The difference is explained, as the result of the author's previous experiments (this vol., i, 1129), by the assumption that the inhibition of the diffusion of the diastase to the glycogen which exists in the intact frogs has been removed. The experiments were carried out by the method already described, care being taken to keep the livers as free from damage as possible after removal from the body. S. B. S.

The Physiology of the Glands. XIV. The Function of the Spleen as an Organ of Protein Metabolism, and the Compensatory Processes after Splenectomy. LEON ASHER and HANS SOLLBERGER (*Biochem. Zeitsch.*, 1913, **55**, 13—44).—Immediately after the extirpation of the spleen of a normal rabbit on an iron-rich diet, there is an increase in the hæmoglobin content, and the number of red corpuscles in the blood, which may be explained by diminution of hæmolysis in the absence of the spleen and possibly an increased functioning capacity of the bone-marrow. The withdrawal of a small quantity of blood from the splenectomised animal causes a smaller diminution of hæmoglobin and of blood corpuscles than in a normal animal, and in the former case the blood much more rapidly attains its normal, or even hypernormal, condition. This fact indicates increased functional capacity of the bone-marrow when the spleen is absent. A similar difference between the splenectomised and normal animals was observed when larger amounts of blood were withdrawn. A difference was also observed when the organism was deprived of oxygen by the administration of hydrocyanic acid administered subcutaneously in the form of *aqua amygdalarum amarum*. In the splenectomised animal the treatment resulted again in a smaller diminution of hæmoglobin and red corpuscles, and the reversion to the normal condition of the blood was also more rapid. The extirpation of the thyroids had no specific effect on the hæmoglobin formation in splenectomised animals, or on the effect of hydrocyanic acid on either the splenectomised or normal animals. The general conclusion from the experiments seems to be that on iron-rich diet the functions of the bone-marrow are increased in the absence of the spleen.
S. B. S.

The Intra-renal Resorption of Chlorides in Different Conditions of the Kidney. RAPHAEL LÉPINE and RAYMOND BOULUD (*Compt. rend.*, 1913, **157**, 487—490. Compare *ibid.*, 1913, **156**, 1958).—The resorption of chlorides by the kidneys, on exercising a contra-pressure by means of a canula inserted in the urether and connected to a vessel of water, is reduced to an almost negligible quantity if the water is replaced by a solution of quinine sulphate (1 in 250), or by solutions of numerous toxic substances, or by the use of water after previous section of the splanchnic nerve.
W. G.

The Iodine Content of Fish Thyroids. ALEXANDER T. CAMERON (*Biochem. J.*, 1913, **7**, 466—470).—Although iodine has been found in many marine animals, no estimations have hitherto been made for the thyroids of fishes; the percentage in the thyroids of the ray and dogfish averages 1·16%. The highest figure previously obtained in mammals is 0·7 in the dog. W. D. H.

The Carbon Dioxide Formation in Surviving Perfused Muscles. HERBERT ELIAS (*Biochem. Zeitsch.*, 1913, **55**, 153—168).—The hinder extremities of dogs were employed, and they were perfused with ox-blood by the apparatus described by Freise (this vol., i, 1267), whose method of estimating the amount of carbon dioxide formed, was employed. At rest, the muscles produce about 7 mg. of carbon dioxide per kilo. per minute, which quantity can be largely increased by tetanisation (up to fifteen times the amount). S. B. S.

Glycolysis by Muscular Tissue. ALFRED GIGON and MAX MASSINI (*Biochem. Zeitsch.*, 1913, **55**, 189—194).—This work was undertaken with the object of reinvestigating the statement of Cohnheim, that sugar is destroyed by incubation with muscular tissue, only in presence of pancreatic substances, as this result has not been confirmed by subsequent observers. A method is described for removal from rabbits of muscular tissue under aseptic conditions. This was disintegrated by freezing with solid carbon dioxide in sterile leather bags and breaking up in the frozen state. It was found that muscular tissue alone, in the absence of pancreas or liver powder, was capable of destroying 85% of the added sugar within twenty-four hours. Salts appear to be necessary for the process, and the best results were obtained when the sugar was incubated with the tissue in Ringer's fluid in the presence of small quantities of sodium hydrogen carbonate. The addition of pancreas, liver, or suprarenal tissue did not appear to increase the amount of sugar destruction. S. B. S.

Pigments. A New Method for the Preparation and a Comparison of the Various Hair Pigments. HUGO FASAL (*Biochem. Zeitsch.*, 1913, **55**, 393—401).—The method of preparation consisted in treating the hair or other keratinous material with twenty-five times the weight of cold saturated potassium hydroxide solution. The protein is thereby dissolved, and the pigment separates; it is purified by dissolving in hot 5% potassium hydroxide solution, in which it dissolves; the solution is filtered off from any undissolved inorganic matter when cold, and the pigment is then precipitated by addition of acid. The examination of hair of different colours indicated that the difference in colour is due to the differences in the amount of pigment, and dark hair which has been deprived of its colour by hydrogen peroxide is nearly free from pigment. White hair contains but very small quantities. The ratio of the amount of pigment in the most strongly coloured hair to that in the least coloured was found to be 30 : 1. S. B. S.

Investigations on Cell Proteins by means of Addition of Formalin. HUGO WIENER (*Biochem. Zeitsch.*, 1913, **56**, 122—152).—The cells of organs of different animals contain soluble proteins, which can be divided into two classes. The chief difference between these is that one class is precipitated by formalin, whereas the other is not. The proteins, which are precipitable by formalin, are considered by the author to belong to the tissue proteins. On washing out the organs in situ, the soluble proteins do not go entirely into the saline solution, owing, apparently, to the semipermeability of the cell-walls. They are only extractible when the cells are destroyed, either by grinding to a paste, or better still, by drying to a powder by Wiechowski's method. If, however, formalin (2%) is added to the saline perfusion liquid, the cell walls are injured, and the semipermeability is destroyed. The soluble proteins can then be readily washed out. In this case, only the soluble proteins which are not precipitated by formalin are obtained. By long perfusion with saline, the walls are also slightly injured, and a small amount of soluble proteins will pass out, so that it is difficult to obtain a perfusion liquid protein-free. Formalin can be used to separate three kinds of protein in the cell, namely, the insoluble proteins, the soluble proteins precipitable by formalin, and the soluble proteins not precipitable by formalin. From a comparison of the amounts obtained from the livers of fed and fasting dogs (the latter, for example, contains small quantities of soluble protein not precipitable by formalin), the conclusion is drawn that the three classes represent stages in the conversion of the protein of the food into the protein of the organ; there is, that is to say, no hard and fast line between the fixed and circulating proteins.

S. B. S.

The Distribution of a Keto-reductase in Tissues. L. VON LAGERMARK (*Biochem. Zeitsch.*, 1913, **55**, 458—462).—Friedmann and Maase have shown that the liver contains a ferment capable of reducing acetoacetic acid to *l*-β-hydroxybutyric acid. It is now shown that this ferment exists also in the muscles and in the kidneys, but not in blood, lungs, the pancreas, or the spleen. The organs investigated were removed from fasting dogs. S. B. S.

Changes in the Reaction of Growing Organisms to Narcotics. HORACE M. VERNON (*J. Physiol.*, 1913, **47**, 15—29).—As tadpoles grow, the narcotising concentration of methyl and ethyl alcohol falls, but that of propyl alcohol remains constant, and of higher alcohols increases; the quotients between the narcotising concentration of successive alcohols vary. The effect of ethyl acetate, propionate, butyrate, and valerate does not alter with age; that of three ketones diminished during growth. The fatal concentrations of monohydric alcohols vary greatly with age. These changes are attributed in most part to changes in the composition of cell-lipoids. W. D. H.

The Function of the Ferments in the Animal Body after Introduction of Killed Tubercle Bacilli. NINA KOTSCHNEV (*Biochem. Zeitsch.*, 1913, **55**, 481—494).—The introduction of killed tubercle bacilli into rabbits and guinea-pigs caused a diminution of the lipoclastic properties of the serum and organs, and an increase in their antitrypsin and nuclease content. The catalase of the serum and organs was diminished in energy in the case of guinea-pigs only. There was a slight diminution of the amylase and diastase content of serum and organs. S. B. S.

The Presence of Adenase in the Human Body. ESMOND R. LONG (*J. Biol. Chem.*, 1913, **15**, 449—462).—Adenase could not be found in human adult liver, the placenta or fœtal liver, brain, bone, thymus, stomach, intestine, pancreas, lungs, and spleen. It is, however, present somewhere in the fœtus, for if the entire fœtal material is mixed with adenine, hypoxanthine is formed. Hypoxanthine is always formed in the autolysis of human tissues, and in the absence of adenase is probably due to the action of adenosine deamidase and inosine hydrolase. W. D. H.

The Tyrosineoxydase, Polyphenoloxydase, and Oxydones of Insects. FRED. BATTELLI and LINA STERN (*Biochem. Zeitsch.*, 1913, **56**, 59—77).—All the above ferments are contained in the insects investigated. The fully developed insect contains less polyphenol oxydase than the larva and chrysalis of the same species. *p*-Phenylenediamine is oxidised less energetically than quinol and pyrogallol by pulverised insects, which is in marked contrast to the action of vertebrate tissue. There is no parallelism between the polyphenoloxydase content of insects and the respiratory exchange of the living insect. As a rule, those insects which have the largest content in polyphenoloxydase have also the largest amount of tyrosineoxydase. Both ferments can be obtained in powder form by treatment of an insect paste with acetone or alcohol. Tyrosine is oxidised with evolution of carbon dioxide. Insects contain no uricoxydase. There is no alcohol oxydase in silk-worms. Insects contain a succino-oxydone, but the oxidation of succinic acid is much weaker than that of the polyphenols and tyrosine. This oxidation is also weaker in the case of insects than in the case of muscular or liver tissue of mammals. There is a rough parallelism between the oxidation of succinic acid by pulverised insects and the oxidation energy of the living animals. Citric acid is not oxidised by insect paste, and the intensity of the oxidation by pulverised insects is uninfluenced by the addition of sodium acetate, sodium lactate, or dextrose. S. B. S.

Physical Properties and Chemical Composition of Frog's Urine. SHOZO TODA and KATSUTA TAGUCHI (*Zeitsch. physiol. Chem.*, 1913, **87**, 371—378).—The reaction of frog's urine is usually feebly acid to litmus paper; D 1·0009 to 1·0018; $\Delta = 0{\cdot}106$. The electrical conductivity in reciprocal ohms is $0{\cdot}78 \cdot 10^{-3}$. In summer frogs, the urine contains 0·193 of organic and 0·053 of inorganic con-

stituents %; of the latter 0·0467 are salts soluble in water. There is a relative large amount of phosphoric acid and sodium. The proportion of sodium to potassium is 1·7 : 1. W. D. H.

The Chemistry of Cancerous Tumours. B. WOLTER (*Biochem. Zeitsch.*, 1913, **55**, 260—265).—Analyses of the total phosphorus and its distribution as inorganic, phosphatide and protein phosphorus from a liver sarcoma, from the surrounding liver tissue, and from the tissue of normal liver, are given. The most marked difference in the analyses of the tumour and other tissues was the somewhat smaller percentage (both relative and absolute) of the phosphatide phosphorus in the former. The amount of cholesterol in the tumour was 0·25% of the fresh tissue. S. B. S.

Disturbances in the Protein Metabolism in Cancer. (The Excretion of Thiocyanates.) PAUL SAXL (*Biochem. Zeitsch.*, 1913, **55**, 224—244).—It has been found that the urine in cases of cancer generally contains excess of nitrogen, but the amount of urea is less than the normal, whereas the quantities of oxyproteic acid and ammonia are greater. The urine of cancer patients is also characterised by containing a certain amount of sulphur in a form in which it is readily oxidised to sulphuric acid. These results suggest the presence of thiocyanates, due to hydrogen cyanide, split from proteins, and not completely oxidised. Similar urines were obtained from normal individuals after administration of thiocyanates. It is now directly shown that, in the majority of cancer cases, the urine contains abnormally large amounts of thiocyanate, which is the source of the easily oxidised sulphur. Other pathological urines also yield abnormally large amounts, but not to quite the same extent as those from cancer patients. The thiocyanate was estimated by precipitation with silver nitrate in acid solution; the silver salt was then dissolved in sodium hydrogen carbonate, and treated with excess of $N/10$-iodine solution and potassium iodide. After four hours, hydrochloric acid is added, and the excess of iodine estimated by titration. The amount of thiocyanate can be calculated from the equation:

$$CNSK + 3I_2 + 4H_2O = H_2SO_4 + 5HI + KI + HCN.$$

S. B. S.

Protozoan Protoplasm as an Indicator of Pathological Change. II. In Carcinoma. FRANK P. UNDERHILL and LORANDE LOSS WOODRUFF (*J. Biol. Chem.*, 1913, **15**, 401—414).—Extracts of breast cancer depress the division rate of *Paramœcium*, and kill the protozoon. Extracts of normal mammary tissue do not possess this property. Weak concentrations of the abnormal extracts may stimulate the *Paramœcium*. W. D. H.

The Tryptophan Content of Normal and Pathological Cutaneous Tissues, and of Malignant Tumours. HUGO FASAL (*Biochem. Zeitsch.*, 1913, **55**, 88—95).—By means of the author's colorimetric method, the tryptophan content in various normal

and pathological tissues was estimated. The epidermis is relatively rich in this substance, as are certain tumours, such as carcinoma of the liver. Mammary tumours, on the other hand, do not contain a trace. S. B. S.

A Case of Pentosuria. PHŒBUS A. LEVENE and FREDERICK B. LAFORGE (*J. Biol. Chem.*, 1913, **15**, 481—486).—Neuberg states that the usual pentose in cases of pentosuria is *dl*-arabinose. Elliott and Raper described a case in which it was probably ribose. In the present case much of the pentose was lost in the methods adopted for its separation, and the identification of the sugar was not complete, but it was probably *l*-ribose. W. D. H.

The Origin of the Sugar Secreted in Phloridzin Glycosuria. RAPHAEL LÉPINE and RAYMOND BOULUD (*Compt. rend.*, 1913, **157**, 530—532. Compare A., 1904, ii, 753).—The authors quote experiments which, they maintain, contradict the generally accepted hypothesis that the sugar eliminated in phloridzin glycosuria comes from the renal cells. They consider that the point of attack of the phloridzin in the kidney is the vascular endothelium. W. G.

The Production of Fever. MAX CLOETTA and ERNST WASER (*Arch. expt. Path. Pharm.*, 1913, **73**, 436—456).—By subcutaneous and intravenous injection of the monomethyl derivative of alicyclic tetrahydro-β-naphthylamine, the body temperature is raised in a few minutes. This rise occurs in the region of the cerebral ventricles within twenty seconds, and in the fore-brain in about forty to sixty seconds; the intestinal temperature rises next, and finally that of the skin (which falls during the first half minute). If death occurs, the intestine and skin remain warm after the temperature falls in the central nervous system. W. D. H.

Protozoan Protoplasm as an Indicator of Pathological Changes. I. In Nephritis. LORANDE LOSS WOODRUFF and FRANK P. UNDERHILL (*J. Biol. Chem.*, 1913, **15**, 385—400).—Extracts of normal kidneys from well-fed and starving animals exert no effect on the division rate of *Paramœcium*; but extracts of nephritic kidneys depress it. This is not due to accumulation of tartrate which was given to induce nephritis. The experiments were made on rabbits. W. D. H.

The Chemistry of the Leucocytozoon Syphilidis and of the Hirt's Protecting Cells. JAMES E. R. MCDONAGH and R. L. MACKENZIE WALLIS (*Biochem. J.*, 1913, **7**, 517—543).—Much of the work recorded relates to the properties of the colloidal dyes used for micro-chemically investigating the syphilis parasite. Basic stains are most suitable for work in vivo, and of these borax-methylene-blue is the best. The parasite has a lecithin-globulin envelope which stands out more clearly by adding dextrose to the stain. The varied affinity shown for methylene-violet and methylene-red is due to the prevalence of a substance which has

strong reducing properties (lecithin-globulin), and not to a change in the reaction. Details are given of the staining reactions of different parts of the parasite, but the whole subject is at present of subsidiary chemical interest. W. D. H.

(Pharmacological) Action of Bromine Salts. E. BERNOULLI (*Arch. expt. Path. Pharm.*, 1913, **73**, 355—397).—The theory of chlorine poverty is insufficient to explain the action of alkali bromides. For the neutralisation of the bromine action, the administration of chlorides is not necessary, but other salts (sodium sulphate and nitrate) act in the same way. Bromine salts cause changes in the colloïdal material of the central nervous system. The bromine ions which take the place of chlorine ions alter the aggregation state of the cell-colloids, probably in the direction of greater swelling, and thus is produced a functional change in the nerve-cells. W. D. H.

The Action of Leucocytes and Other Tissues on *dl*-Alanine. PHŒBUS A. LEVENE and GUSTAV M. MEYER (*J. Biol. Chem.*, 1913, **15**, 475—480).—Leucocytes under aseptic conditions form *d*-lactic acid from hexoses, regardless of the configuration of the hexose. The conversion of amino-acids into hydroxy-acids is analogous to the change of methyl-glyoxal into lactic acid; thus, alanine is transformed into lactic acid through the stage of pyruvic acid. Dakin, Dudley and Ringer found in diabetic dogs fed on pyruvic acid that the yield of sugar was smaller than from either alanine or lactic acid. Hence in the present research the action of leucocytes was tested on various forms of alanine. The unexpected result obtained was that neither leucocytes nor kidney tissue had any effect at all on *dl*-alanine. W. D. H.

The Behaviour of Pyruvic Acid in the Animal Body. II. GUSTAV EMBDEN and MAX OPPENHEIMER (*Biochem. Zeitsch.*, 1913, **55**, 334—340. Compare A., 1912, ii, 1075).—As pyruvic acid is a possible intermediate product in the conversion of alanine into lactic acid, it was of interest to ascertain whether the latter acid could be obtained directly from the former in the animal body. It was found that this change could be accomplished when pyruvic acid was perfused through a glycogen-poor liver of a dog which had been starved for four days. It was obtained in the *d*-form.

S. B. S.

The Behaviour of Pyruvic Acid in the Animal Body. III. The Formation of Sugar and Lactic Acid from Pyruvic Acid. PAUL MAYER (*Biochem. Zeitsch.*, 1913, **55**, 1—3).—The author recapitulates his former results, which indicate that pyruvic acid, on administration to rabits and dogs, causes hyperglycæmia and glycosuria, but that on administration to animals treated with phloridzin, it causes a diminution of the sugar and nitrogen output in the urine, owing apparently to a toxic action on the kidneys. He is not able to explain the difference between his results and those obtained by A. J. Ringer and by Dakin and Janney (this vol.,

i, 937), but rejects the explanation offered by the former. Animals to which pyruvic acid has been administered excrete in the urine both *dl*- and *d*-lactic acids. S. B. S.

The Degradation of Carboxylic Acids in the Animal Body. XV. The Behaviour of Benzaldehyde in the Animal Body. ERNST FRIEDMANN and WILHELM TÜRK (*Biochem. Zeitsch.*, 1913, **55**, 425—431).—After administration of benzaldehyde to dogs, only hippuric acid and small quantities of benzoic acid, but no cinnamic acid, could be isolated in the urine. The cinnamic acid found by Dakin after administration of phenylpropionic and phenylvaleric acid must be due therefore to degradation, and not to synthesis by condensation of an aldehyde with acetic acid. S. B. S.

The Degradation of Carboxylic Acids in the Animal Body. XVI. Behaviour of α-Phenylbutyric Acid in the Animal Body. ERNST FRIEDMANN and WILHELM TÜRK (*Biochem. Zeitsch.*, 1913, **55**, 432—435).—As γ-phenylbutyric acid undergoes in the animal body oxidation in the β-position to yield a keto-acid and finally phenylacetic acid, it was of interest to ascertain how the α-acid $CH_3\cdot CH_2\cdot CHPh\cdot CO_2H$ would behave. If oxidation were to take place in the β-position, phenylacetic and acetic acid should be expected as final products, according to the equations given by the authors. As a matter of fact, only unchanged α-phenylbutyric acid, and a neutral substance, which was not further investigated, could be isolated in the urine of dogs, to which this substance had been administered. S. B. S.

The Degradation of Carboxylic Acids in the Animal Body. XVII. Formation of Acetoacetic Acid from Acetic Acid in the Perfusion through the Liver. ERNST FRIEDMANN (*Biochem. Zeitsch.*, 1913, **55**, 436—442).—Adam Loeb has shown that the addition of sodium acetate to the blood perfused through the surviving liver of a dog causes a marked increase in the amount of acetoacetic acid formed. This is in contrast to the author's own results, where no such increase was found. It is now shown that this increase only results when the liver is poor in glycogen, as, for example, in the livers of animals which have been starved and tetanised by strychnine. In this case increase of acetoacetic acid only follows when acetate is added to the perfusing blood. Such an addition causes no increase when the livers used for experiment are rich in glycogen and taken from a well-fed animal. The mechanism of the formation of acetoacetic acid from acetic acid is discussed, and it is suggested that acetaldehyde is an intermediate product, which condenses with acetic acid to form crotonic acid, from which, by addition of water and oxidation, acetoacetic acid is formed. It is further suggested that in presence of carbohydrates, acetic acid is condensed in some other way. From the fact that acetoacetic acid is only formed from fatty acids with an even number of carbon atoms, the conclusion is drawn that acids do not always form β-keto-acids as intermediary oxidation products,

as in this case acetic acid should always be formed, and this is, as the experiment shows, an acetoacetic acid former. S. B. S.

The Degradation of Carboxylic Acids in the Animal Body. XVIII. Behaviour of Glycollic and Glyoxylic Acids in Perfusion through the Liver. JUNICHI MOCHIZUKI (*Biochem. Zeitsch.*, 1913, **55**, 443—445).—Friedmann has suggested (see preceding communication) that acetoacetic acid is formed from acetic acid in perfusion experiments by condensation of the latter with acetaldehyde to yield crotonic acid as an intermediate product. It follows, if this suggestion is correct, that no acetoacetic acid should be formed if the methyl group of acetic acid should have a hydrogen replaced by hydroxyl. As a matter of fact, it was found that neither from glycollic nor glyoxylic acid is acetoacetic acid formed. S. B. S.

The Degradation of Carboxylic Acids in the Animal Body. XIX. Acetoacetic Acid Formation in the Perfusion of Livers Rich in Glycogen. JUNICHI MOCHIZUKI (*Biochem. Zeitsch.*, 1913, **55**, 446—449).—It has been shown by Friedmann (this vol., i, 1276) that acetoacetic acid is formed from acetic acid only when perfused through livers poor in glycogen. It is now shown that butyric acid, β-hydroxybutyric acid, crotonic acid, and *iso*valeric acid yield acetoacetic acid when perfused through livers rich in glycogen, whence the conclusion is drawn that acetic acid is not an intermediary product of reaction. S. B. S.

The Degradation of Carboxylic Acids in the Animal Body. XX. Conversion of Crotonic Acid into *l*-β-Hydroxybutyric Acid by Liver Pulp. ERNST FRIEDMANN and C. MAASE (*Biochem. Zeitsch.*, 1913, **55**, 450—457).—Crotonic acid is converted into *l*-β-hydroxybutyric acid in the presence of liver pulp obtained from a fasting dog. Carbon dioxide inhibits the reaction. S. B. S.

The Fixation of the Digitalis Substances in the Animal Organism, Considered more Especially with Reference to their Behaviour in the Blood. ERNST OPPENHEIMER (*Biochem. Zeitsch.*, 1913, **55**, 134—152).—Various investigators have failed to detect these substances in the tissues after injection into animals, and researches were undertaken to ascertain the cause of this failure. It was found that the slightly soluble digitoxin is only slowly precipitated from its alcoholic solution. The solutions of both amorphous, slightly insoluble, digitalis glucosides are dialysable, and behave in this respect like the easily soluble crystalline glucosides, strophanthin and antiarin. As precipitation in the blood-stream does not account for the apparent absence of the substances in the blood-stream, the effect on their toxic action due to the admixture with serum was determined, Straub's method for estimating the toxicity (action on frog's heart) being employed. It was found that serum could diminish or destroy the toxicity of the following substances: digitoxin, gitalin, digitalin, oleandrin,

saponin, and methyl-violet. It increased the toxicity, on the other hand, of strophanthin and antiarin. This action of the serum cannot be replaced by either cholesterol, egg-white, or lecithin in Ringer's fluid. These experiments indicate that the failure to detect digitalis alkaloids after injection into the organism is not due to its fixation by cells of the tissues. S. B. S.

Action of Enzymes on Racemised Proteins and their Fate in the Animal Body. HENRY D. DAKIN and HAROLD W. DUDLEY (*J. Biol. Chem.*, 1913, **15**, 271—276).—"Racemised" casein and caseose are resistant to the action of pepsin, trypsin, and erepsin. On feeding the substances to a dog *per os*, they were excreted unchanged in the fæces, no absorption having taken place in the intestine. It appears as if this organ can take up only comparatively simple substances. Racemised caseose, when administered subcutaneously to a dog, produced no symptoms, and was excreted unchanged in the urine. "Racemised" casein remained unchanged in the presence of bacteria, but the caseose was slowly attacked, yielding indole and other products. S. B. S.

The Behaviour of Iodoprotein in the Organism. JULIUS WOHLGEMUTH and BRUNO REWALD (*Biochem. Zeitsch.*, 1913, **55**, 7—12).—The preparation of an iodine derivative from coagulated blood by means of an alcoholic solution of iodine is described, which contains about 15% of iodine and 0·25% of iron. Preliminary therapeutic experiments indicate that this preparation is well tolerated in relatively large doses by rabbits, dogs, and man. In the experiments on rabbits, it was shown that the iron accumulates in the liver. The preparation is readily absorbed, and about 70% of the iodine is excreted in the urine between the third and forty-eighth hours after administration. Little or no iodine is found in the fæces. S. B. S.

Degradation of the Naphthalene Ring in the Animal Body. ERNST FRIEDMANN and WILHELM TÜRK (*Biochem. Zeitsch.*, 1913, **55**, 463—476).—β-Naphthylalanine and β-naphthylpyruvic acid are degraded in the organism to benzoic acid. In order to study the influence of the side-chains on the degradation of the naphthalene nucleus, the degradation of the following products was studied: β-naphthoic acid, β-naphthylacetic acid, and (in greater detail) β-naphthylpyruvic acid. The former results with the last-named were confirmed, in that in the urine of dogs to which it had been administered an excess of hippuric acid was found. This did not happen in the case of either the naphthoic or naphthylacetic acids. The pyruvic acid derivative, however, yielded hippuric acid only when administered *per os*, but not when subcutaneously applied, and the conversion into benzoic acid is therefore possibly a putrefactive process in the intestines. After administration of β-naphthoic acid, in addition to unchanged product, naphthuric acid was found in the urine both after administration *per os* and after injection under the skin. A conjugation with glycine had

therefore taken place. After administration of β-naphthylacetic acid, a considerable amount of unchanged product was found in the urine. The fate of the remainder is still unknown. S. B. S.

The Influence of the Subsidiary Alkaloids of Opium on the Action of Morphine. RICHARD MEISSNER (*Biochem. Zeitsch.*, 1913, **54**, 395—429).—The experiments were carried out with a view to demonstrate the potentialising capacity of other alkaloids on the pharmacological action of morphine, as shown by Straub. The action on the respiratory centre of rabbits, the narcotic action on cats, and the action on the isolated intestine of rabbits were investigated. A larger diminution in the respiratory volume was produced by narcophine, but apart from this, no essential difference was found in the actions of narcophine, pantopone, or laudenone. The investigations appear to negative the conception of a potentialising action of narcotine on morphine. Nevertheless, the results must be accepted with some caution, in view of some quoted experiments of Zehbe on the action of various preparations on the human intestine. S. B. S.

Degradation of Phenylalanine in the Animal Organism. GUSTAV EMBDEN and KARL BALDES (*Biochem. Zeitsch*, 1913, **55** 301—322).—The general theory as to the relationship between the combustibility of amino-acids in the normal organism, their convertibility into homogentisic acid in alcaptonuric individuals, and their conversion into acetoacetic acid when perfused through the liver is discussed. Phenylpyruvic acid, a conceivable first oxidation product of phenylalanine, both of which substances are burnt up in the organism and converted into homogentisic acid in alcaptonuric cases, might be expected, like substances generally with this behaviour, to be convertible into acetoacetic acid by perfusion through the liver, especially as phenyl-lactic acid, and the keto-acid corresponding with tyrosine, undergo this change. This was found, however, not to be the case; on the contrary, phenylpyruvic acid even inhibits the acetoacetic acid formation from phenylalanine, tyrosine, leucine, and *p*-hydroxyphenylpyruvic acid when these are perfused in its presence. On the other hand, it does not inhibit acetoacetic acid formation from *iso*valeric or *n*-hexoic acids, and does not therefore act as a general inhibitor of oxidation processes in the liver. It possibly combines with the side-chains in the cell to which the amino-acids are normally attached when converted into acetoacetic acid. These facts suggest that phenylpyruvic acid is not the first oxidation product of phenylalanine, but oxidation takes place, probably, first in the benzene nucleus. It was found, in fact, that *dl*-phenylalanine, when perfused through the liver, gives rise to the normal *l*-tyrosine. From this, *p*-hydroxyphenylpyruvic acid could be formed, which is an acetoacetic acid former. It is suggested that when phenylpyruvic acid is burnt in the organism, it is converted first into phenylalanine, as it is known that the change of amino- into keto-acids in the body is a reversible one. S. B. S.

The Relations between Constitution and [Physiological] Action in Alicyclic Tetrahydro-β-naphthylamine and its Derivatives. MAX CLOETTA and ERNST WASER (*Arch. expt. Path. Pharm.*, 1913, **73**, 398—435).—From the substance mentioned, optically active *d*- and *l*-bases can be isolated, which resemble the racemic base in their action. From the latter a series of salts can be prepared with differing dissociation capacities, but no relation was found between this property and toxicity. The monomethyl derivative, like the original base, dilates the pupil, and raises body temperature and blood-pressure; the corresponding monoethyl compound acts in the same way, but is more toxic. If, however, the nitrogen is replaced by an acid residue (acetyl, formyl), the actions are reversed, the pupil is narrowed, and body temperature and blood-pressure fall. If an acid and alkyl group are both introduced there is a double action; for instance, in the frog, myosis is produced by the acid group, and in the rabbit, mydriasis by the alkyl group. In the case of derivatives that raise the blood-pressure, a second injection is not effective in the same way. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

The Fermentation of Pyruvic Acid by Bacteria. László Karczag and L. Móczár (*Biochem. Zeitsch.*, 1913, **55**, 79–87).—The bacteria which are capable of fermenting dextrose with evolution of gas are also able to ferment pyruvic acid. Amongst such bacteria are *B. coli*, *B. paratyphi-B.*, and Gaertner's bacillus. The gas evolution with bacteria follows more rapidly than with yeast, but there is a marked difference between the two classes of fermentations, for whereas with yeast the gas evolved is carbon dioxide, the pyruvic acid yielding this gas and formaldehyde, the gas evolved by bacteria consists for the most part of hydrogen. S. B. S.

Formation of Hydrogen Cyanide from Proteins. H. W. Emerson, Hamilton P. Cady, and E. H. S. Bailey (*J. Biol. Chem.*, 1913, **15**, 415—418).—Certain micro-organisms (*B. pyocyaneus*) evolve hydrogen cyanide when grown on protein media, especially if the medium is slightly acid to litmus and phenolphthalein. This is absent when free mineral acid is present. W. D. H.

Formation of Hydrogen Cyanide from Proteins. B. J. Clawson and C. C. Young, (*J. Biol. Chem.*, 1913, **15**, 419—422).—*B. pyocyaneus*, *B. fluorescens*, *B. violaceus*, and other bacteria the nature of which is still uncertain, produce hydrogen cyanide from protein material. W. D. H.

Chemistry of Bacteria. Sakae Tamura (*Zeitsch. physiol. Chem.*, 1913, **87**, 85—114).—Chemical investigations were made on large

quantities of the cells of *Bacillus tuberculosis* and *Mycobacterium lacticola perrugosum.* Extraction with ether failed to give any phosphatides, but treatment with warm alcohol showed the presence of a diaminomonophosphatide in each species of bacteria. Both cultures were found to contain an alcohol ($C_{29}H_{56}O$), for which the name *mycol* is suggested. This alcohol is present in the bacterial cell partly as an ester of a higher fatty acid, and it is to the alcohol or its ester that the acid- and alkali-resistance and gram-positiveness of the organisms are due. Adenine and hypoxanthine were present in each case, in addition to arginine, histidine, lysine, phenylalanine, proline, valine, tyrosine, and tryptophan. Bacterio-proteins are characterised by a high phenylalanine content.

H. B. H.

Fermentation of Cellulose by Thermophilic Bacteria. HANS PRINGSHEIM (*Centr. Bakt. Par.*, 1913, ii, **38**, 513—516).—Impure cultures of anaërobic, thermophilic, cellulose-decomposing bacteria were obtained from soil and horse manure. By means of a special apparatus the cultures were maintained at 55—60°, and samples of the decomposition gases were withdrawn from time to time. These were found to consist of 22—49% carbon dioxide, and the residue in all cases proved to be hydrogen.

Examination of the residual liquid cultures showed the presence of formic and acetic acids, but no butyric acid. This is significant, as the latter is the chief product of anaerobic cellulose decomposition at normal temperatures. Three grams of cellulose led to the production of 0·2125 gram of formic acid, 1·15 gram of acetic acid, a trace of lactic acid, and a mixture of carbon dioxide and hydrogen in the above proportions. H. B. H.

The Enrichment of the Invertase Content of Living Yeasts. LEOPOLD LICHTWITZ (*Biochem. Zeitsch.*, 1913, **56**, 160—162).—The author replies to certain criticisms of Meisenheimer, Gambarjan, and Semper (this vol., i, 1139), who found that the invertase content of yeast increases when the organism is kept in sugar solution. This is the direct contrary of what was found by the author. He calls attention to the fact, however, that yeast sown in large quantities in sugar solution, as was done by Meisenheimer and his collaborators, does not increase; on the contrary, it probably autolyses. This did not happen in the author's own experiments; hence, probably, the difference in the results. S. B. S.

Catalysts of Alcoholic Fermentation. HANS VON EULER (*Zeitsch. physiol. Chem.*, 1913, **87**, 142—144).—Earlier work has shown that the rapidity of fermentation by living yeasts is accelerated by the addition of alkali salts of organic and especially fatty acids, and dried yeast or yeast juice is not affected in a similar manner. Of the two possible interpretations of the results, particular attention has been paid to that which assumes that the activation is not directly connected with enzymes in the yeast cell, and experiments have been made to determine an alteration

of the protoplasmic layer of the cell or of the cell wall generally by the salts, with adsorption and an alteration of surface tension.

Preliminary experiments with sodium and ammonium salts of the acids having given negative results, an attempt was made to determine the action of various dye salts on the living cell. According to their behaviour towards the yeast cell, it was possible to divide the dye salts into three classes, namely, those without action on the cell, those which are clearly adsorbed, and others the entrance of which into the cell depends on the fermentative activity of the latter. These phenomena and the part played by an alteration of the surface tension are being further investigated.

H. B. H.

Influence of Certain Inorganic Salts, particularly Stannous Chloride and Bismuth Subnitrate, on Fermentation. GILBERT GIMEL (*Bull. Assoc. chim. Sucr. Dist.*, 1913, **31**, 128—129).—Results of further experiments confirm those obtained previously by the author (A., 1909, ii, 171). The activity of various yeasts in sweet worts is increased when the latter contain from 50 to 100 mg. of stannous chloride per litre. Bismuth subnitrate is soluble in acid liquids, such as musts, etc., and has a decided influence on the fermentation; it appears to inhibit acetic fermentation. The use of pure yeast cultures and different conditions of fermentation are probably the reason of the opposite opinion arrived at by Pozzi-Escot (this vol., i, 1139).

W. P. S.

Protein Degradation in Yeast. I. The Influence of Sugar Fermentation on the Protein Degradation of Yeast. W. ZALESKI and W. SCHATALOV (*Biochem. Zeitsch.*, 1913, **55**, 63—71).—Various views have been expressed to explain the fact that proteolysis is less in yeast that has been used for sugar fermentation than in unused yeast, the Ivanov has stated that acetaldehyde is the fermentation product which is responsible for the antiproteolytic action. This statement the authors have been unable to confirm, for they find that an appreciable inhibition of yeast autolysis only takes place in concentrations of this aldehyde which are far higher than those found in fermentation liquors. The same is also true for furfuraldehyde and for formaldehyde, which latter, however, has a much stronger inhibitory action than acetaldehyde. Although the distillates from fermentations possess antiproteolytic properties, the actual antiproteolytic substance has not been isolated. The conditions of nutrition of the yeast exert some action on the subsequent proteolysis. The addition of amino-acids to yeasts increases the autolytic degradation of their proteins; it cannot be claimed, however, that they antagonise the antiproteolytic properties of the fermentation products.

S. B. S.

Biochemical Conversion of Betaine into Glycollic Acid. FELIX EHRLICH and FRITZ LANGE (*Ber.*, 1913, **46**, 2746—2752).—In the course of their experiments on the behaviour of amino-acids towards micro-organisms, the authors have examined betaine, which is remarkably stable, not only to concentrated sulphuric acid or

aqua regia at high temperatures, but also during passage through the bodies of most animals except the ruminants. They find that betaine is not assimilated by brewers' and distillers' yeasts or by various kinds of *Saccharomyces*, but is extensively degraded by *Willia anomala*, *Pichia farinosa*, *Pichia membranefaciens*, and other yeasts rich in oxydases; also many moulds, such as *Penicillium*, *Aspergillus*, *Monilia*, *Oidium*, and *Dematium*, are able to employ betaine for the formation of their albumin. In most cases characteristic degradation products of betaine cannot be isolated, partly because the decomposition is too extensive, partly owing to the difficulty of separating the decomposition products of the sugar added as a source of carbon. In experiments on solutions containing betaine, nutrient salts, and ethyl alcohol as a source of carbon, the authors find that after the addition of a pure culture of *Willia anomala* and keeping for eight weeks, glycollic acid is present in quantity sufficient for isolation; the amount is small, because the acid is an intermediate, not the final, product of the assimilation of the betaine. This is proved by the fact that *Willia anomala* grows extensively in a solution containing nutrient salts, and glycollic acid and carbamide as the only sources of carbon, the glycollic acid disappearing completely after four months; in a similar experiment, in which carbamide is the only source of carbon, growth of the yeast cannot be detected.

In the preceding experiments with betaine, not a trace of trimethylamine can be detected. Probably it is converted into methyl alcohol and ammonia, the latter, which also cannot be detected, being utilised by the organism in the formation of albumin.

In conclusion, the authors reply to Stoltzenberg (this vol., i, 345; compare also Ehrlich, A., 1912, i, 835; Stoltzenberg, *ibid.*, i, 680) concerning the isolation of betaine from molasses residue.

C. S.

Protein Synthesis in Plants. I. Protein Synthesis in the Bulbs of Allium cepa. W. ZALESKI and W. SHATKIN (*Biochem. Zeitsch.*, 1913, **55**, 72—78).—Experiments confirm a former statement of Zaleski, that the proteins increase in quantity in the injured bulbs when left in a moist atmosphere or in intact bulbs when allowed to grow in the dark. Estimations were of the total nitrogen, proteins, peptones, ammonia, acid amides, organic bases, and monoamino-acids. It was found, as a result, that the proteins are formed at the expense of the monoamino-acids. The mono- and di-amino-acids and ammonia were also estimated in the various specimens after hydrolysis with acids. The results obtained indicate that the monoamino-acids pre-existing combine with the pre-existing proteins. There is no evidence that the acid amides, without further change, take any direct part in the protein synthesis.

S. B. S.

The Inulin Metabolism of Cichorium intybus (Chicory). III. VIKTOR GRAFE and VALENTIN VOUK (*Biochem. Zeitsch.*, 1913, **56**, 249—257. Compare A., 1912, ii, 977; this vol., i, 148).—It is shown

that by the freezing of the roots, the amount of inulin decreases, whereas the amount of reducing sugar increases; the amount of the latter returns to normal when the frozen roots are afterwards kept at normal temperature, whereas the amount of inulin remains unchanged. These results confirm the theory of Molisch, that the dissolved inulin acts as a "thermically active" protector against cold. The changes in the inulin and reducing sugar distribution in the roots which had wintered in a normal manner were also investigated. It was found that a hydrolysis of inulin takes place before new parts of the plants are visible; the reserve substances appear to be converted into building material, and this allows the further hydrolysis of the inulin reserves. A résumé of the results obtained by the authors up to the date of publication is also given. S. B. S.

The Colorimetric Method for Determining Hydrocyanic Acid in Plants with Special Reference to Kafir Corn. C. K. FRANCIS and W. B. CONNELL (*J. Amer. Chem. Soc.*, 1913, **35**, 1624—1628).—After examining the various methods for the estimation of small quantities of hydrocyanic acid, the authors decide in favour of a colorimetric process depending on the formation of ferric thiocyanate. This method indicates that Kafir corn contains minute quantities of combined hydrocyanic acid, the quantity apparently being greater in frost-bitten or stunted plants than in normal ones.

It is difficult to decide from the results whether the quantity of hydrocyanic present could prove fatal to an animal fed with this material. D. F. T.

Antitoxic Action of Chloral Hydrate on Copper Sulphate for Pisum sativum. R. P. HIBBARD (*Centr. Bakt. Par.*, 1913, ii, **38**, 302—308).—Water culture experiments in which garden peas were supplied with solutions of copper sulphate in concentrations varying from $M3 \times 10^{-4}$ to $M2{\cdot}5 \times 10^{-6}$, and with chloral hydrate, $M/165{\cdot}5$ to $M/16{,}550$, both together and separately. After forty-eight hours the roots of the plants were measured. Whilst in the single solutions growth was very slight, when both substances were supplied simultaneously the growth was distinctly better, especially when both substances are present in about equal amounts. The action of chloral hydrate in diminishing the toxicity of copper sulphate is similar, although less marked, to the influence of calcium over magnesium salts.

Several explanations are suggested, the most important of which is perhaps connected with the extent of ionisation which may be retarded when both substances are present. Or, changes may be brought about in the plasma membrane which will modify the permeability of the limiting layer. Then, again, the effect may be the result of changes in the cell itself. N. H. J. M.

Organic Chemistry.

Separation of Mixtures of a Saturated with an Unsaturated Hydrocarbon by means of Permanganate. S. S. NAMETKIN (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1423—1429).—Attempts to determine the proportions of the constituents of mixtures of (1) *cyclo*hexane and *cyclo*hexene, and (2) *n*-hexane and hexylene by oxidising the unsaturated hydrocarbon by means of permanganate were unsuccessful, owing to the saturated constituent reacting to some extent with the oxidising agent.

A similar method was then applied to analogous mixtures of gaseous hydrocarbons. For this purpose a special gas pipette was devised which permits the gaseous mixture to be passed repeatedly in small bubbles through the reagent, and in which the latter does not come into contact with mercury. After the reaction with saturated permanganate solution, the excess of oxidising agent was destroyed by means of saturated bisulphite solution, both this and the permanganate solution having been previously saturated with the saturated constituent of the gaseous mixture. With various mixtures of propane and ethylene, propane and propylene, and *cyclo*propane and propylene, the greatest error in the volume of the gas remaining after treatment with permanganate was 0·27%.

The unsatisfactory results obtained by Kishner (this vol., i, 153) are largely explained by the fact that, in most cases, the reaction was completed at 100°, and hence under conditions which should lead to attack of the saturated hydrocarbon. T. H. P.

Investigations on Polymerisation. I. Diethylene Hydrocarbons. SERGEI V. LEBEDEV and (in part) B. K. MERESHKOVSKI (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1249—1388. Compare A., 1911, i, 26, 774, 959; 1912, i, 173).—The vast majority of organic compounds are essentially unstable, and their great variety owes its existence to what the author terms passive resistance. It is quite conceivable that polymerisation, as a process directing molecules into more stable forms, is very widespread, and that most unsaturated organic compounds are able to polymerise under suitable conditions. No sharp line can be drawn between association and polymerisation, although with typical association no difference can be found between the chemical reactions of the monomeride and of the polymeride; it may be that, owing to ready dissociation of the latter, only the former reacts or that no sufficiently sensitive reagent for the polymeride has been discovered. The stability of the complex molecule depends on the particular type of polymerisation occurring, in addition to the properties of the individual compound.

In the great majority of cases polymerisation occurs with formation of a ring system, the ring having in all cases an even number of atoms. In studying polymeric changes, account must be taken of the isomerisa-

tion so common with unsaturated compounds, especially with rise of temperature.

Among the hydrocarbons the principal well-defined types of polymerisation are: (1) the styrene type, peculiar to ethylenic hydrocarbons with unsymmetrical substitution of the hydrogen atoms by definite groups (phenyl), and yielding polymerides of high molecular weight and structures not yet definitely established; (2) the stilbene type, exhibited by ethylene derivatives with symmetrical replacement of the hydrogen atoms by certain groups (phenyl); (3) the acetylene type, giving benzene derivatives; (4) the allene type, yielding *cyclo*butane derivatives; (5) the divinyl [$\Delta^{\alpha\gamma}$-butadiene] type, which forms *cyclo*hexane derivatives and polymerides of uncertain constitution. If it can be shown that stilbene forms a polymeride and styrene a dimeride of closed-chain structure, types (1) and (2) may have to be regarded as a single type; and, further, the resemblance between polymerides of the styrene and divinyl types (compare Ostromisslenski, A., 1912, i, 280) may lead to the fusion of these two types. Most cases of polymerisation of unsaturated compounds containing halogen, nitrogen, oxygen, or sulphur may be referred to one of the above types.

Polymerisation of the divinyl or $\Delta^{\alpha\gamma}$-butadiene type is first considered, an account being given of all such hydrocarbons studied in this respect. Experiments with isoprene and with di*iso*propenyl [$\beta\gamma$-dimethyl-$\Delta^{\alpha\gamma}$-butadiene] show that: (1) the relative proportions of dimeride and polymeride formed increase and diminish respectively as the temperature is raised; (2) at constant temperature, the ratio between the proportions of dimeride and polymeride does not change during the heating; (3) the reaction of polymerisation is sensitive to catalytic action, since replacement of the air in the tube by nitrogen results (with $\beta\gamma$ dimethyl-$\Delta^{\alpha\gamma}$-butadiene) in a fall of the relative amount of polymeride from 23% to 16·4%. It is further found that symmetrical hydrocarbons of this type, such as $\Delta^{\alpha\gamma}$-butadiene and its $\beta\gamma$-dimethyl derivative, yield a single dimeride, whereas the unsymmetrical isoprene gives two dimerides. In contradiction to the statement of Kondakov ("Synthetic Caoutchouc, its Homologues and Analogues," Yuriev, 1912, p. 101) and of Harries (A., 1911, i, 798), it is found that polymerisation of the pure hydrocarbons, without catalyst, yields no open-chain dimeride.

In general, it seems that no such equilibrium as that represented by dimeride $\rightleftarrows$ monomeride $\rightleftarrows$ polymeride exists, but that the processes of polymerisation are irreversible and proceed simultaneously in two directions, yielding dimeride and polymeride respectively. The existence of reversible processes of formation of dimeric and of polymeric forms renders it probable that such equilibria may yet be realised.

The possible methods of formation and structures of dimerides and polymerides are discussed in detail.

The dimeride of di*iso*propenyl [$\beta\gamma$-dimethyl-$\Delta^{\alpha\gamma}$-butadiene] is 4:6-dimethyldipentene or 4:6-dimethyl-$\Delta^{6,8(9)}$-menthadiene,

$$CMe{<}{\substack{CMe\cdot CH_2\\ CH_2\cdot CH_2}}{>}CMe\cdot CMe{:}CH_2,$$

which is a colourless liquid with an aromatic odour, b. p. 85°/13 mm.,

205°/750 mm., D_4^0 0·8741, D_0^{20} 0·8597, $n_C^{19·7}$ 1·47716, n_D 1·48074, n_F 1·48796, n_G 1·49491 (compare Richard, A., 1911, i, 733). Treatment with ozone in chloroform solution at −20° yields the *ozonide*, $C_{12}H_{20}O_6$, which is a froth-like, amorphous compound, exploding violently on heating, but failing to yield the triketone on decomposition with water. Oxidation of the dimeride in aqueous acetone by means of permanganate yields: (1) δ-*Methyl*-δ-iso*propenyl*-βη-*octandione*,

$$CH_3·CO·CH_2·CMe(·CMe{:}CH_2)·CH_2·CH_2·CO·CH_3,$$

which is a viscous liquid, b. p. 132—133°/8·5 mm., and yields the *semicarbazone*, $C_{14}H_{26}O_2N_6$, m. p. 228°; hydrogenation of the diketone at the ordinary temperature in presence of platinum black gives δ-*methyl*-δ-iso*propyl*-βη-*octandione*, $CH_3·CO·CH_2·CMePr^\beta·CH_2·CH_2·CO·CH_3$, as a colourless, viscous liquid, b. p. 133—135°/8 mm., D_4^{20} 0·9934, the corresponding *semicarbazone*, m. p. 202°, being also prepared. (2) A small proportion of an acid, m. p. 164—166°, containing 63·2% of carbon and 8·88% of hydrogen.

Oxidation of the dimeride of βγ-dimethyl-$\Delta^{\alpha\gamma}$-butadiene by means of benzoylhydroperoxide in ethereal solution (compare Prileschaev, A., 1911, i, 255) yields (1) a small proportion of the *monoxide*,

$$CMe{\lessdot}\begin{matrix}CMe·CH_2\\CH_2·CH_2\end{matrix}{>}CMe·CMe{<}\begin{matrix}CH_2\\|\\O\end{matrix},$$

b. p. 94—95°/10 mm., and (2) the *dioxide*, $C_{12}H_{20}O_2$, b. p. 110—112°/10 mm., which when heated in a sealed tube at 115° with water acidified with benzoic acid gives the tetrahydric alcohol (4 : 6-*limonetritol*), $OH·CMe{<}\begin{matrix}CMe(OH)·CH_2\\CH_2\text{———}CH_2\end{matrix}{>}CMe·CMe(OH)·CH_2·OH$, as a highly viscous liquid; oxidation of this by means of aqueous permanganate gave a small yield of the *keto-glycol*,

$$OH·CMe{<}\begin{matrix}CMe(OH)·CH_2\\CH_2\text{———}CH_2\end{matrix}{>}CMe·COMe,$$

m. p. 155—165°.

The action of dry hydrogen chloride on the dimeride in carbon disulphide yields 1 : 2 : 4-*trimethyl*-4-*chloro*iso*propyl*-Δ^1-cyclo*hexene*, $CMe{\lessdot}\begin{matrix}CMe·CH_2\\CH_2·CH_2\end{matrix}{>}CMe·CMe_2Cl$, which is a colourless liquid, b. p. 122—124°/17 mm.

The polymeride of di*iso*propenyl is shown by means of its ozonide to have the structure $(·CH_2·CMe{:}CMe·CH_2·CH_2·CMe{:}CMe·CH_2·)_x$. The *ozonide*, $C_6H_{10}O_3$, separates partly in a gelatinous form and yields acetonylacetone when heated with water (compare Harries, A., 1911, i, 798).

Further details are given of the results obtained with isoprene (compare A., 1911, i, 26). For obtaining pure isoprene use was made of the following method elaborated in Favorski's laboratory and not yet published. Crude isoprene, b. p. 30—40°, obtained by decomposition of turpentine, is poured into a cooled solution of hydrogen bromide in acetic acid, and the precipitated mixture of bromides washed and dried. Amyl bromide is distilled off at 52—53° under 100 mm. pressure, and the residual αγ-dibromo-γ-methylbutane, after distillation at 80—82° under 23 mm. pressure, heated at 150° with a large excess

of pounded potassium hydroxide in a flask provided with a dephlegmator and condenser; the dibromide and monobromide formed from it are arrested by the dephlegmator and fall back into the flask, whilst the isoprene passes over and is condensed. The isoprene thus obtained, distilled over sodium, has b. p. 34·5—35°, D_0^{20} 0·6803, n_D^{20} 1·42207, n_C 1·41787, n_F 1·43307, n_G 1·44280, optical exaltation (D) 1·07 (compare Harries and Neresheimer, A., 1911, i, 798).

Two dimerides of isoprene were obtained: (1) Dipentene, b. p. 58°/9·5 mm., 174—175°/760 mm., D_0^0 0·8607, D_0^{20} 0·8454, $n_D^{19·7}$ 1·47428, n_C 1·47069, n_F 1·48211, n_G 1·48887. (2) 1 : 3-Dimethyl-3-ethenyl-Δ^6-*cyclo*hexene (*loc. cit.*), D_0^0 0·8481, $n_D^{19·7}$ 1·46581, n_C 1·46230, n_F 1·47204, n_G 1·47964, which yields a liquid tetrabromide, not obtained pure, and combines with 2HBr in acetic acid solution, giving the *compound*, $C_{10}H_{18}Br_2$, softening at 25° and melting at 34—35°. 1 : 3-Dimethyl-3-ethyl*cyclo*hexane (*loc. cit.*), obtained by hydrogenation of this dimeride in presence of platinum black and under a pressure of 70 atmospheres, has D_4^0 0·8132, D_4^{20} 0·7990, n_D^{20} 1·44112. The *ozonide*, $C_{10}H_{16}O_6$, of this dimeride resembles those of di*iso*propenyl and dipentene and, on decomposition, gives an oil resolved on boiling into the *ketodialdehyde*, $COMe·CH_2·CMe(CHO)·CH_2·CH_2·CHO$, which yields α-methyl-α-acetonylglutaric acid on oxidation. Treatment of the dimeride with benzoylhydroperoxide yields (1) the monoxide, which is a liquid, b. p. 68—70°/15 mm., with a camphor-like odour, and (2) the *dioxide*, $O{<}{\begin{matrix}CMe{-\!\!-}CH_2\\CH·CH_2·CH_2\end{matrix}}{>}CMe·CH{<}{\begin{matrix}O\\CH_2\end{matrix}}$, which is a liquid with an aromatic odour, b. p. 108—109°/15 mm., and yields the *compound*, $C_{10}H_{20}O_4$, on hydration.

Two isomeric polymerides of isoprene are possible theoretically, and should give ozonides of the structures:

$$\text{(I)}\quad [\cdot CH_2\cdot\underbrace{CMe\cdot CH}_{O_3}\cdot CH_2\cdot CH_2\cdot\underbrace{CMe\cdot CH}_{O_3}\cdot CH_2\cdot]_x$$

$$\text{and (II)}\quad [\cdot CH_2\cdot\underbrace{CMe\cdot CH}_{O_3}\cdot CH_2\cdot CH_2\cdot\underbrace{CH\cdot CMe}_{O_3}\cdot CH_2\cdot]_x.$$

Of these, (I) corresponds with natural caoutchouc and should give, on decomposition, lævulinaldehyde and its peroxide, and lævulic acid; all these products were actually observed. Similarly, (II) should give succindialdehyde, succinic acid and acetonylacetone, none of which could be detected. Hence, only the former polymeride is formed; its *ozonide*, $C_5H_8O_3$, is an extremely viscous liquid, exploding when heated.

Piperylene should yield, not a dimeride of the structure,

$$CMe{<}{\begin{matrix}CH{-}CH_2\\CH_2\cdot CH_2\end{matrix}}{>}CH\cdot CH{:}CHMe$$

(compare Harries, this vol., i, 284), but two dimerides, formed thus:

$$(1)\quad CH_3\cdot\underset{|}{C}H\cdot\underset{|}{C}H\cdot\underset{|}{C}H\cdot CH_2\cdot \longrightarrow CH{<}{\begin{matrix}CH{-\!\!-}CH_2\\CHMe\cdot CH_2\end{matrix}}{>}CH\cdot CH{:}CHMe,$$

$$\text{and (2)}\quad \begin{matrix}CH_3\\|\\CH\cdot\underset{|}{C}H\cdot\underset{|}{C}H\cdot\underset{|}{C}H_2\end{matrix} \longrightarrow CH{<}{\begin{matrix}CH{-}CHMe\\CH_2\cdot CHMe\end{matrix}}{>}CH\cdot CH{:}CH_2;$$

the former should have the higher boiling point.

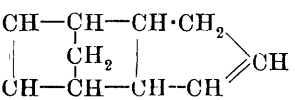
According to a private communication from Favorski, di*iso*crotyl [$\beta\epsilon$-dimethyl-$\Delta^{\beta\delta}$-hexadiene] undergoes spontaneous change into a waxy substance, but this was not observed by the author. This hydrocarbon undergoes polymerisation with great difficulty, only 50% of it being transformed after being maintained at 290° for ten days. The employment of such a high temperature causes partial isomerisation of the dimeride, of which only a single one should be formed from a symmetrical molecule, and also results in decomposition of the polymeride. The dimeride is 3 : 3 : 5 : 5 : 6 : 6-*hexamethyl*-4-*iso*crotyl-Δ^1-cyclo*hexene*, $CH{<}{\genfrac{}{}{0pt}{}{CH—CMe_2}{CMe_2{\cdot}CMe_2}}{>}CH{\cdot}CH{:}CMe_2$, b. p. 130—132°/24 mm., D_4^0 0·8634, D_4^{20} 0·8491, n_D^{20} 1·47751, n_C 1·47452, n_F 1·48757, n_G 1·49120. The polymeride was obtained only as an impure, yellow, viscous liquid containing decomposition products.

Myrcene, which probably consists of a mixture of two or more isomerides, was found to have the constants: b. p. 56—57°/12 mm., D_4^{20} 0·7982, n_D^{20} 1·47065, n_C 1·46675, n_F 1·48055, n_G 1·48905. When heated for twelve days at 150°, it yields (1) two cyclic isomerides of myrcene, (*a*) b. p. 60—61·5°/16 mm., D_4^{20} 0·8392, n_D^{20} 1·46611, n_C 1·46270, n_F 1·47334, n_G 1·47974, and (*b*) b. p. 65—65·5°/16 mm., D_4^{20} 0·8340, n_D^{20} 1·47133, n_C 1·46774, n_F 1·47922, n_G 1·48613; (2) a dimeride, b. p. 183—184°/10 mm., D_4^{20} 0·8763, $n_D^{20\cdot1}$ 1·49859, n_C 1·49568, n_F 1·50668, n_G 1·51606; (3) a viscous polymeride yielding a mixture of products when treated with ozone (compare Harries, A., 1902, i, 811).

α-Phenyl-$\Delta^{\alpha\gamma}$-butadiene polymerises with great ease. The dimeride was investigated by Riiber (A., 1904, i, 569), who suggested formulæ for it and for the tribasic acid yielded on oxidising it with permanganate. The author regards these formulæ as inaccurate, since, according to his scheme, the dimeride should have the structure

$$CH{<}{\genfrac{}{}{0pt}{}{CH—CH_2}{CHPh{\cdot}CH_2}}{>}CH{\cdot}CH{:}CHPh,$$

and the tribasic acid, $CO_2H{\cdot}CHPh{\cdot}CH_2{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2H$, the latter agreeing better with the analytical data than that proposed by Riiber.



As was shown by Stobbe and Reuss (A., 1912, i, 842), *cyclo*pentadiene polymerises so rapidly that intense cooling is necessary in order to obtain it in the monomeric form. If the type of polymerisation exhibited by open-chain hydrocarbons holds also for cyclic compounds, the dimeride should have the annexed structure (compare Kraemer and Spilker, A., 1896, i, 289). This case is under investigation.

Allene hydrocarbons polymerise with great ease and, unlike those of the divinyl type, with velocities varying only within narrow limits. The character of the polymerisation is also different, the polymerides being *cyclo*butane derivatives and forming an uninterrupted series from di- to hexa-merides. Actually, however, the polymerisation of allene hydrocarbons is complicated by transformation to the type shown by those of the divinyl series. This occurs in two ways: (1) the allene hydrocarbons undergo isomeric change into divinyl derivatives with

comparative ease, and (2) the dimerides are cyclic derivatives of divinyl; thus, that of allene has the structure

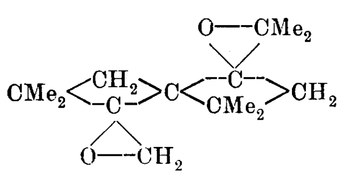
$$CH_2{:}C{<}\begin{matrix}-CH_2-\\C({:}CH_2)\end{matrix}{>}CH_2,$$

and readily polymerises giving a di-dimeride and a polymeride. At the ordinary temperature allene hydrocarbons polymerise so slowly that years elapse before the formation of an appreciable proportion of polymeride. But the temperature-coefficient of the velocity of the change is far greater than with divinyl derivatives, and at 150° the velocity is approximately the same as with isoprene and di*iso*propenyl. The author elaborates a scheme to explain the mechanism of the process, starting from the assumptions that the molecules combine initially at a single point and that the union is directed by two causes: the magnitude of the affinity with the unsaturated atoms and the polarity. The construction of models of the polymeric forms shows that two types of arrangement in space are possible: (1) the cyclic type, in which the central carbon atoms of allene are arranged in a ring in one plane, with the four-membered rings alternately on either side of this basal plane; and (2) the spiral type, in which the central atoms of the allene groups are arranged in a spiral so that the first, fourth, and seventh carbon atoms occupy analogous positions on the spiral, and so on; the four-membered rings lie in three mutually perpendicular planes, the first, fourth, and seventh rings also taking up similar positions on the spiral. The dimerides of the two types are identical, as also are the trimerides. Stereoisomerism is possible, beginning with the tetrameride, and assuming the formation of polymeric forms according to both types, two stereoisomerides may be expected for the tetra-, penta-, and hexa-meride. Higher degrees of polymerisation are possible only with the spiral type.

When heated to 130—140°, *as*-dimethylallene gives 3% of dimeride, b. p. 140—141°, 18% of dimeride, b. p. 149—150°, 40% of dimeride, b. p. 179—181°, 33% of trimeride, b. p. 100°/8 mm., and 60% of vaseline-like residue. The three dimerides, which are the only possible ones, have been already described (A., 1912, i, 173). The *trimeride*,

$$CMe_2{<}\begin{matrix}-CH_2-\\C({:}CH_2)\end{matrix}{>}C{<}\begin{matrix}C({:}CMe_2)\\-CMe_2-\end{matrix}{>}CH_2,$$

is a colourless, odourless liquid, b. p. 100°/8 mm., D_4^0 0·8723, D_4^{20} 0·8578, n_D^{20} 1·48724, n_C 1·48395, n_F 1·50260, n_G 1·51398, optical exaltation 2·28, and has the normal molecular weight in freezing benzene. Hydrogenation of the trimeride in presence of platinum black yields the *compound*, $CMe_2{<}\begin{matrix}-CH_2-\\CHMe\end{matrix}{>}C{<}\begin{matrix}CHPr^{\beta}\\-CMe_2-\end{matrix}{>}CH_2$, b. p. 116—118°/23 mm., D_4^0 0·8521, D_4^{20} 0·8380, $n_D^{19\cdot9}$ 1·46362, n_C 1·46101, n_F 1·47274, n_G 1·47827, optical exaltation 1·50.



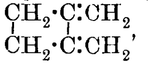
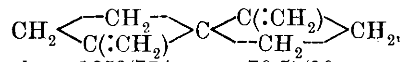
The ozonide of the trimeride is unstable, and was not obtained pure. Oxidation by means of benzoylhydroperoxide yields the *dioxide* (annexed formula), m. p. 49°, b. p. 137°/16 mm., which undergoes partial hydration to the *compound*, $C_{15}H_{26}O_3$, m. p. 136·5°,

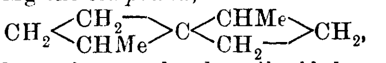
probably a glyco-oxide. Attempts to complete the hydration by heating with water containing a trace of acid resulted in the formation of a *diketone*, $C_{15}H_{24}O_2$, m. p. 86°, which yields a *semicarbazone*, $C_{17}H_{30}O_2N_6$, m. p. 170° (decomp.), but was not obtained in sufficient quantity to admit of the determination of its structure.

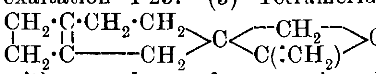
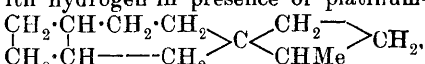
[With B. K. MERESHKOVSKI.]—When heated in a sealed tube at 150°, trimethylallene undergoes polymerisation and isomerisation, the mixture of dimerides consisting principally of 1 : 2-*dimethyl*-3 : 4-*di*iso*propylidene*cyclo*butane*, $\begin{matrix}CHMe\cdot C\colon CMe_2\\ |\qquad\quad |\\ CHMe\cdot C\colon CMe_2\end{matrix}$, which is a colourless liquid with the odour of kerosene, b. p. 69—70°/11 mm., 190—191°/754 mm., D_4^{20} 0·8247, n_D^{20} 1·48337, n_C 1·47946, n_F 1·49282, n_G 1·50297. The ozonide is unstable, and on distilling in a current of steam is decomposed into dimethylsuccinic acid, acetone peroxide, and 1 : 2-*dimethyl*-3 iso*propylidene*cyclo*butan*-4-*one*, $\begin{matrix}CHMe\cdot C\colon CMe_2\\ |\qquad\quad |\\ CHMe\cdot CO\end{matrix}$, which is a colourless liquid with the characteristic quinone-like odour common to all unsaturated ketones obtained from dimerides of allene hydrocarbons, b. p. 83—86°/20 mm., and was not obtained free from traces of the original dimeride; its *semicarbazone*, $C_{10}H_{17}ON_3$, m. p. 200—201° (decomp.), contained a small proportion of another semicarbazone, m. p. about 180°; oxidation of the ketone with permanganate yields the maleinoid form of dimethylsuccinic acid. Products of higher polymerisation are formed to the extent of 10%, but no individual compounds were isolated.

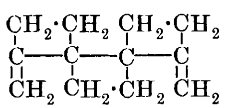
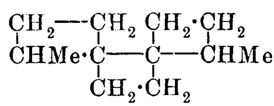
[With B. K. MERESHKOVSKI.]—At 150°, polymerisation of *s*-dimethylallene is complete in four to five days. The products contain (1) about 90% of the dimeride, 1 : 2-*dimethyl*-3 : 4-*diethylidene*cyclo*butane*, $\begin{matrix}CHMe\colon C\cdot CHMe\\ |\quad |\\ CHMe\colon C\cdot CHMe\end{matrix}$, which is a colourless liquid, b. p. 65°/22 mm., 163°/762 mm., D_4^{20} 0·8113, n_D^{20} 1·47850, n_C 1·47423, n_F 1·48913, n_G 1·49838, optical exaltation 2·25. When oxidised with permanganate, this dimeride yields the maleinoid form of *s*-dimethylsuccinic acid and acetic acid (?), whilst hydrogenation at ordinary temperature in presence of platinum black yields 1 : 2-*dimethyl*-3 : 4-*diethyl*cyclo*butane*, $\begin{matrix}CHEt\cdot CHMe\\ |\qquad |\\ CHEt\cdot CHMe\end{matrix}$, b. p. 155—156°/760 mm., D_4^{20} 0·7729, n_D^{20} 1·42447, n_C 1·42193, n_F 1·42950, n_G 1·43377, optical exaltation 0·24; (2) about 5% of the *trimeride*, $CHMe\negthinspace<\negthinspace\begin{matrix}-CHMe-\\ C(\colon CHMe)\end{matrix}\negthinspace>\negthinspace C\negthinspace<\negthinspace\begin{matrix}C(\colon CHMe)\\ -CHMe-\end{matrix}\negthinspace>\negthinspace CHMe$ (?), which is a colourless, odourless liquid, b. p. 108—110°/17 mm.

When heated at 140° for three and a-half days, allene yields 5% of dimeride, 15% of trimeride, 5% and 22% of tetramerides I and II, 18% of pentameride, 10% of hexameride, and 25% of residual polymeride. With the exception of the dimeride and tetrameride I, these polymeric forms all rapidly absorb atmospheric oxygen, and all without exception yield formic, oxalic, and succinic acids on oxidation, and give a dark brown coloration with tetranitromethane. The viscosity increases with the degree of polymerisation, the hexameride being somewhat more

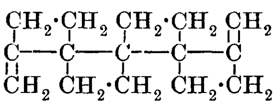
liquid than glycerol. (1) The dimeride, 1 : 2-*dimethylenecyclobutane*, , is a colourless liquid, b. p. 63—65°, D_4^{20} 0·7698, n_D^{20} 1·42317. (2) The *trimeride*, , is a liquid with a peculiar odour, b. p. 135°/774 mm., 70·5°/90 mm., 38°/21 mm., D_4^{20} 0·8624, n_D^{20} 1·48064, n_C 1·47677, n_F 1·48922, n_G 1·49694, optical exaltation 1·04. It readily absorbs hydrogen in presence of platinum-black giving the *compound*,



which is a colourless, almost odourless liquid, b. p. 132°/756 mm., D_4^{20} 0·7972, n_D^{20} 1·43459, n_C 1·43159, n_F 1·43950, n_G 1·44410, optical exaltation 1·23. (3) Tetrameride I is a *dimeride of the dimeride*, , and forms a colourless liquid with an odour of turpentine, b. p. 72—74°/9 mm., D_4^{20} 0·8955, n_D^{20} 1·50301, n_C 1·49905, n_F 1·51204, n_G 1·51999, optical exaltation 2·58. On prolonged heating in a sealed tube at 150°, it thickens and deposits an insoluble polymeride, which was obtained only in small amount. With hydrogen in presence of platinum-black, it gives the *compound*, , as a colourless liquid with a faint odour, b. p. 77—78°/13·5 mm., D_4^{20} 0·8679, n_D^{20} 1·46809, n_C 1·46448, n_F 1·47305, exaltation 1·51. (4) *Tetra-*

(I.)  (II.) 

meride II (I.) is a colourless liquid with an odour of kerosene, b. p. 101°/10 mm., D_4^{20} 0·9346, n_D^{20} 1·52624, n_C 1·52210, n_F 1·53579, n_G 1·54396, exaltation 2·33, and has the normal molecular weight in freezing benzene. On hydrogenation it yields the *compound* (II.), b. p. 95°/13·5 mm., D_4^{20} 0·8827, n_D 1·48289, n_C 1·47950, n_F 1·48941, n_G 1·49528, exaltation 2·02. On oxidation it yields formic, oxalic, and succinic acids.



(5) The *pentameride* (annexed formula) is a viscous, almost odourless liquid, b. p. 131—132°/10·5 mm., D_4^{20} 0·9498, n_D^{20} 1·52814, n_C 1·52422, n_F 1·53765, n_G 1·54591, exaltation 2·90. On hydrogenation it takes up sufficient hydrogen to saturate two double linkings, giving the *compound*, $C_{15}H_{24}$, as a colourless liquid with a faint odour, b. p. 123·5—124·5°/8 mm., D_4^{2} 0·9152, n_D^{20} 1·49623, n_C 1·49265, n_F 1·50241, n_G 1·50810, exaltation 2·40, and exhibits normal cryoscopic behaviour in benzene. (6) The *hexameride*, $C_{18}H_{24}$, of similar structure to the foregoing, is a viscous, almost odourless liquid, b. p. 170°/10 mm., D_4^{20} 0·9721, n_D^{20} 1·53869, n_C 1·53426, n_F 1·54817, n_G 1·55648, exaltation 3·64. Oxalic and succinic acids were found among its products of oxidation.

It has been shown by Favorski (A., 1891, 1330) that, when heated with alcoholic alkali hydroxide, hydrocarbons of the diallyl series undergo isomeric change to divinyl derivatives: C:C·C·C·C:C $\longrightarrow$ C·C:C·C:C·C; thus diallyl yields $\Delta^{\beta\delta}$-hexadiene. When heated at 250° for ten days, diallyl begins to isomerise, 10% of the monomeride boiling at a higher temperature than diallyl. The crude polymeride consists of (1) about 15% of a liquid of peculiar odour, b. p. 97—98°/20 mm., consisting of mixed dimerides, and (2) about 85% of colourless, insoluble, caoutchouc-like polymeride, which is converted into ozonide only with difficulty. At 150°, $\Delta^{\beta\delta}$-hexadiene yields a dimeride, b. p. 88—90°/20 mm., quite different from that of diallyl, but at 250° it gives a considerable proportion of the dimeride, b. p. 96—98°/20 mm.

The author has devised a method for determining the velocity at which polymerisation occurs. From 2 to 10 grams of the hydrocarbon were sealed in tubes and heated in a perfectly dark thermostat at 159 ± 0·1°. After definite intervals of time, the tubes were cooled and their contents introduced into tared distilling flasks connected with small condensers and tared receivers. Liquids with low boiling points were distilled at ordinary pressure and those with high boiling points under diminished pressure. A bath of Wood's metal was used for the heating, its temperature being at first below the boiling point of the monomeride, and finally about the boiling point of the dimeride. The monomeride, the residual polymeride, and sometimes also the dimeride were weighed to within 0·02 gram. In general, all the polymerised products were taken into account in calculating the velocity. The results obtained in this way were corrected for several errors inherent in the method. The numbers obtained with twelve hydrocarbons of the $\Delta^{\alpha\gamma}$-butadiene series show that: (1) With isomerides, the transference of a substituent from the extreme atom of a conjugated system of atoms to the middle atom is accompanied by increase in the velocity of polymerisation, and conversely. (2) The formation of a ring from a chain containing a conjugated system increases the velocity of polymerisation. (3) In homologous series, increase of the mass of a substituent at the middle (or extreme) atoms of a conjugated system increases (or lowers) the velocity of polymerisation, assuming that the heating occurs at corresponding temperatures. The results given by the four allene derivatives lead to the following conclusions: (1) The velocity of polymerisation of isomeric hydrocarbons of the allene series does not depend on the positions of the substituent groups. (2) In an homologous series of allene hydrocarbons, increase of the mass of the substituent results in increased velocity of polymerisation, the heating being at corresponding temperatures. T. H. P.

Polymerisation as a Method of Detecting the Allene Group, C:C:C. SERGEI V. LEBEDEV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1390—1391).—The polymerisation of allene hydrocarbons affords a simple and easy method of distinguishing them from diethylenic hydrocarbons of other types. At 150° allene hydrocarbons are polymerised almost completely in one to two days, part undergoing isomeric change to $\Delta^{\alpha\gamma}$-butadiene derivative. The crude polymeride consists principally

of dimeride or, with unsymmetrical allene hydrocarbons, of dimerides. The dimeride is separated by distillation; when several are present, the predominating one is obtained by fractionation. The dimeride is of the type $\begin{matrix} C\cdot C{:}C \\ | \quad | \\ C\cdot C{:}C \end{matrix}$, and, on oxidation by means of permanganate in acetone solution, gives a good yield of succinic acid or one of its substituted derivatives, these being well crystallised and readily transformed into anhydrides. Further, the dimerides of allene hydrocarbons exhibit marked optical exaltation, which is usually about, and greater than, 2; dimerides from diethylene hydrocarbons of other types are optically normal. T. H. P.

Isomeric Transformations of Diethylenic Hydrocarbons. I. Isomeric Transformation of Dimethylallene [γ-Methyl-$\Delta^{\alpha\beta}$-butadiene] into Isoprene. L. M. KUTSCHEROV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1634—1654).—When heated with quinoline hydrobromide (compare Favorski and Borgmann, A., 1908, i, 15), γ-methyl-$\Delta^{\alpha\beta}$-butadiene readily undergoes isomeric change into isoprene (50—55% yield) and a small proportion of *iso*propylacetylene [γ-methyl-Δ^{α}-butinene]. The reaction is irreversible, neither isoprene nor γ-methyl-Δ^{α}-butinene undergoing isomerisation under the above conditions; isoprene yields condensation products and combines with the pyridine, whilst γ-methyl-Δ^{α}-butinene partly remains unchanged and partly undergoes conversion into an unsaturated derivative according to the equation: $C_5H_8 + C_9H_7N,HX = C_5H_9X + C_9H_7N$. The formation from γ-methyl-$\Delta^{\alpha\beta}$-butadiene of isoprene is represented by the scheme: $CMe_2{:}C{:}CH_2 + C_9H_7N,HX \longrightarrow CMe_2X\cdot CH{:}CH_2 + C_9H_7N \longrightarrow CH_2{:}CMe\cdot CH{:}CH_2 + C_9H_7N,HX$, and that of γ-methyl-$\Delta^{\alpha}$-butinene by: $CMe_2{:}C{:}CH_2 + C_9H_7N,HX \longrightarrow CHMe_2\cdot CX{:}CH_2 + C_9H_7N \longrightarrow CHMe_2\cdot C{:}CH$; in the former case, the compound $CMe_2X\cdot CH_2\cdot CH_2X$ may also be formed as an intermediate product.

β-Bromo-γ-methyl-Δ^{α}-butene, $CH_2{:}CBr\cdot CHMe_2$, formed by treating γ-methyl-Δ^{α}-butinene either with hot quinoline hydrobromide or with hydrogen bromide in the cold, is a liquid, b. p. 100·5°/758 mm., D_4^{20} 1·2381 (1·2320), n_D^{20} 1·45093 (1·45033), and is reconverted into γ-methyl-Δ^{α}-butinene when heated in a sealed tube with alcoholic potassium hydroxide at 138°. When treated with aqueous hydrobromic acid it yields: (1) γδ-dibromo-β-methylbutane, b. p. 61—62°/12 mm.; (2) *γγ-dibromo-β-methylbutane*, $CMeBr_2\cdot CHMe_2$, m. p. 13—15°, b. p. 53·5—54°/12 mm., 44—45°/8 mm., D_4^0 1·6987, D_4^{20} 1·6695, n_D^{20} 1·50468, which is converted into methyl *iso*propyl ketone when heated in a sealed tube with water and lead hydroxide.

γγδ-Tribromo-β-methylbutane, $CH_2Br\cdot CBr_2\cdot CHMe_2$, obtained by the action of bromine on β-bromo-γ-methyl-Δ^{α}-butene, is a hygroscopic liquid, b. p. 100—101·5°/12·5 mm., D_4^{20} 2·07112, n_D^{20} 1·55448.

T. H. P.

Pyrogenic Acetylene Condensations. RICHARD MEYER and AUGUST TANZEN (*Ber.*, 1913, **46**, 3183—3199. Compare A., 1912, i, 525).—The previous experiments in which nine hydrocarbons present in coal tar were obtained synthetically by the condensation of acetylene

have been repeated in an enlarged apparatus which enabled 6000 grams of tar to be obtained, which has been completely investigated. Phenanthrene and acenaphthene and also, in small quantities, styrene and hexylene were identified. The last has previously only been found in boghead coal and in bituminous shale.

On heating acetylene diluted with coal gas with hydrogen cyanide, pyridine and its homologues were obtained. Mixtures of ammonia and benzene yield aniline when heated, the reaction being reversible. Further condensation of the aniline leads to carbazole and to benzonitrile, the latter being formed by the action of hydrogen cyanide on aniline.

In all, therefore, seventeen constituents of coal tar have been identified as formed by the pyrogenetic condensation of acetylene. The hexylene formed is *n*-hexylene, identical with that from mannitol.

The formation of pyridine requires a temperature of 800°, at which the mixture of acetylene, hydrogen, and hydrogen cyanide can be heated without catching fire. Apparently the hydrogen cyanide acts as a poison towards the catalytic changes which bring abont the sudden decomposition of acetylene and cause a mixture of acetylene and hydrogen to catch fire much below 800°.

The apparatus used is figured and described in detail. E. F. A.

Improvements in the Preparation of Dichlorinated Hydrocarbons in which the Chlorine is Combined with Different Carbon Atoms. WILLIAM H. PERKIN, CHARLES WEIZMANN, and HAROLD DAVIES (Fr. Pat. 452503, and 1st Addition).—If vaporised hydrocarbons or chlorohydrocarbons are treated with the required halogen with or without the addition of a catalyst or in the presence of light with subsequent fractionation under diminished pressure definite products are obtained, and the preparation of the following compounds as chief products of the reaction is described.

From *iso*amyl chloride: *δ-dichloro-β-methylbutane* (b. p. 142°), *γδ-dichloro-β-methylbutane* (b. p. 150°), and *βδ-dichloro-β-methylbutane* (b. p. 170—172°).

From α-chlorobutane: tetrachlorobutane: from *n*-heptane: chloroheptane, and from *iso*amyl bromide: βδ-dichloro-β-methylbutane (b. p. 72—75°/5 mm.).

Monochloroacetic acid can also be prepared from acetic acid in a similar manner. F. M. G. M.

Compounds of Aluminium Bromide with Hydrogen Sulphide and Organic Bromides. Synthesis of Mercaptans. VLADIMIR A. PLOTNIKOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1162—1173. Compare A., 1907, i, 580).—The following compounds have been prepared: $AlBr_3,H_2S$, obtained by passing hydrogen sulphide through aluminium bromide, either in a fused condition or in solution in carbon disulphide, forms colourless crystals, m. p. about 84°, and is decomposed immediately by the moisture of the air with liberation of hydrogen bromide and hydrogen sulphide.

$AlBr_3,EtBr,H_2S$, obtained by passing hydrogen sulphide through a solution of aluminium bromide in ethyl bromide, forms snow-white

crystals, m. p. (in sealed capillary) about 81°, is readily decomposed by water with formation of mercaptan (90% yield): $AlBr_3,EtBr,H_2S +$ aq. $= AlBr_3$,aq. $+ EtHS + HBr$, and in solution attacks aluminium or zinc with liberation of hydrogen. Electrolysis of a solution of the compound in ethyl bromide with platinum electrodes results in the development of hydrogen at the cathode and bromine at the anode.

$AlBr_3,CH_2Br\cdot CH_2Br,H_2S$ forms a pale yellow, crystalline powder decomposing at about 200°, and is also decomposed by the moisture of the air with formation of an oil with a garlic-like odour.

$AlBr_3,CHBr_3,H_2S$ is decomposed by water, apparently with formation of thioformic acid, which then undergoes condensation.

The structures of these compounds are considered in the light of Werner's co-ordination system. T. H. P.

Dipropyl*iso*amylcarbinol and the Action of Nickel Carbonate on its Chlorohydrin. IVAN VANIN (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1155—1162).—Zaicev (A., 1912, i, 777) has shown that the action of silver carbonate on 1-chloro-1-allyl*cyclo*hexane yields an unsaturated hydrocarbon, C_9H_{14}. The author finds that a similar change is effected by the action of nickel carbonate on ε-chloro-β-methyl-ε-propyloctane.

Dipropyl*iso*amylcarbinol (β-methyl-ε-propyloctan-ε-ol), obtained by the action of magnesium *iso*amyl bromide on butyrone, has properties agreeing well with those given by Murat and Amouroux (A., 1912, i, 527).

ε-Chloro-β-methyl-ε-propyloctane, $CPr_2Cl\cdot CH_2\cdot CH_2\cdot CHMe_2$, is a colourless, mobile liquid, b. p. 115—117°/30 mm., D_0^0 0·8901, D_0^{20} 0·8748. When heated with excess of nickel carbonate in a reflux apparatus in an oil-bath at 135—145° for four to five hours, it is converted into a *methylpropyloctene*, $CHEt{:}CPr\cdot CH_2\cdot CH_2\cdot CHMe_2$ or $CPr_2{:}CH\cdot CH_2\cdot CHMe_2$, b. p. 89—91°/20 mm., 189—191°/756·5 mm., D_0^0 0·7773, D_0^{20} 0·7610, which may be identical or isomeric with that obtained by Murat and Amouroux (*loc. cit.*) by catalytic dehydration of dipropyl*iso*amylcarbinol with alumina. T. H. P.

Transformation of *iso*Nitro-compounds into Ketones. S. S. NAMETKIN and (Mlle.) E. I. POZDNJAKOVA (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1420—1422).—Three methods exist for converting secondary nitro-compounds into ketones: (1) Reduction of nascent *iso*nitro-compounds by means of stannous chloride (compare Konovalov, A., 1899, i, 733); (2) action of acids on aqueous solutions of salts of *iso*nitro-compounds (compare Nef, A., 1895, i, 3); (3) heating of halogen-substituted nitro-compounds (compare Wislicenus and his collaborators, A., 1908, i, 973; 1909, i, 99; 1910, i, 621; 1912, i, 52). The last two methods are, however, only of theoretical interest. Nef's method yields, besides the ketone (or aldehyde), more or less free nitro-compound, which renders purification difficult, whilst method (3) is applicable only to those cases in which aggregation of several electro-negative groups to one carbon atom renders the halogen-

substituted nitro-compound unstable. Konovalov's method gives excellent results.

Investigation of the action of permanganate on nitro-compounds (compare A., 1910, i, 830; Konovalov, A., 1904, i, 499; 1905, i, 762) shows that, under the following conditions, almost quantitative yields of the corresponding ketones are obtained. A solution of the nitro-compound in potassium hydroxide solution (1 part to 2 of water) is mixed with five to six times its volume of water, and in the event of separation of insoluble nitro-compound, the latter is extracted by means of light petroleum. To the aqueous solution, mixed with pieces of ice in a large flask, is gradually added the theoretical quantity of 1·5% potassium permanganate solution, the ketone being subsequently distilled in a current of steam.

In this way, nitro*cyclo*hexane gave a 97% yield of *cyclo*hexanone, and nitrofluorene, a 96% yield of fluorenone. T. H. P.

Structure of *iso*Nitro-compounds. S. S. NAMETKIN (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1414—1420).—The author criticises the arguments advanced by Steinkopf and Jürgens (A., 1912, i, 152) in support of Hantzsch's formula for *iso*nitro-compounds.

Stress is laid on the unsaturated character of these compounds, which react with halogens and halogen hydracids, and in alkaline solution, even in the cold, instantly reduce 1—2% potassium permanganate solution, the nitro-compounds being converted almost quantitatively into ketones (compare preceding abstract). Such ready oxidisability is difficult to explain according to Hantzsch's ring constitution, but is easily understood if the presence of a double linking is assumed as is the case in the structure proposed by Michael and Nef. If oxidation at a double linking between carbon and nitrogen follows the same course as at one between two carbon atoms, the initial product of the reaction should be a compound exhibiting an accumulation of hydroxyl groups and hence possessing but slight stability; loss of the elements of water from this compound would yield ketone and a nitrite: $\text{=C:NO·OK} \longrightarrow \text{=C(OH)·NO(OH)(OK)} \longrightarrow \text{=CO} + KNO_2 + H_2O$.

The behaviour of salts of primary nitro-paraffins on acidification, which yields transitory nitroso-compounds and finally hydroxamic acids, is also readily accounted for on the basis of Michael and Nef's formula: $\text{CHR:NO·OH} \longrightarrow \text{CHR:O} + \text{:NOH} \longrightarrow \text{CHR(OH)·NO} \longrightarrow \text{CR(OH):NOH}$. When, however, the nitro-group is accompanied by a more or less electronegative group, this intermediate formation of nitroso-compound does not take place, as no blue or green coloration then makes its appearance. Such an essential variation in one and the same reaction leads the author to suggest that the first stage in the action of dry hydrogen chloride is most probably a direct combination, the unstable compound thus formed subsequently undergoing intramolecular rearrangement and loss of water: $\text{CHR:NO·OH} + \text{HCl} \longrightarrow \text{CHRCl·NH(OH):O} \longrightarrow \text{CHRCl·N(OH)}_2 \longrightarrow \text{CRCl:NOH}$. In those cases where the *iso*nitro-compound and the product of its union with the hydrogen haloid exhibit particularly slight stability,

the loss of water may partly precede the rearrangement; a nitroso-compound would then be formed as intermediate product:

$$CHR{:}NO{\cdot}OH \longrightarrow CHRCl{\cdot}NH(OH){:}O \longrightarrow CHRCl{\cdot}NO \longrightarrow CRCl{:}NOH.$$

Analogous interpretations suggest themselves for the formation of halogen-substituted nitro-products, nitrolic acids and ψ-nitroles. Further, Nef's reaction does not necessitate the intermediate formation of a ring compound, as it is expressed in all probability by the scheme: $:C{:}NO{\cdot}OH + H_2O \longrightarrow :C(OH){\cdot}NH(OH){:}O + H_2O \longrightarrow :C(OH)_2 + :NOH + H_2O$. T. H. P.

Nitrosites of the Aliphatic Series. K. V. SIDORENKO (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1585—1604).—The author has devised an improved method for preparing ethylene nitrosite (compare Demjanov, A., 1899, i, 845), a number of reactions of this compound being studied.

When heated in a sealed tube with dilute hydrochloric acid (1 : 1), it yields hydroxylamine, apparently according to the equation:

$$(C_2H_4O_3N_2)_2 + 4H_2O + 4HCl = 2CHO{\cdot}CO_2H + 4NH_2{\cdot}OH,HCl.$$

At the ordinary temperature it is dissolved by concentrated sulphuric acid, from which it is precipitated unchanged on dilution. Nitric acid seems to be without action on it in the cold, but in the hot yields oxalic acid.

With aniline in absolute alcoholic solution, it gives a basic compound, and this, with hydrochloric acid, yields a crystalline substance, which is difficult to purify and gives poor results on analysis. Under similar conditions, *p*-nitroaniline acts on it apparently as a catalyst, being obtainable unchanged from the products of the reaction.

With benzylamine it reacts in accordance with the equation:

$$(C_2H_4O_3N_2)_2 + NH_2{\cdot}CH_2Ph = (C_2H_4O_2N_2)_2{:}N{\cdot}CH_2Ph + N_2O + H_2O,$$

the unstable *compound* thus obtained crystallising in long, colourless, silky prisms and exhibiting normal cryoscopic behaviour in benzene.

With dibenzylamine it reacts thus: $(C_2H_4O_3N_2)_2 + 2NH(CH_2Ph)_2 = 2C_2H_4O_2N{\cdot}N(CH_2Ph)_2 + N_2O + H_2O$, the compound formed crystallising in long prisms, m. p. 74·6—75·2°, and possessing the normal molecular weight in freezing benzene. This compound exhibits feeble basic properties; it exerts a scarcely perceptible alkaline reaction on litmus, and yields no salts, even with strong acids. When reduced with tin and hydrochloric acid, it yields a sparingly soluble hydrochloride, which forms a platinichloride insoluble in alcohol. Accompanying the dibenzylamine derivative is a small quantity of a compound which separates in crystalline granules and possibly represents the result of combination between the amine and the nitrosite after the latter is resolved into two separate molecules.

From these results the conclusion is drawn that ethylene nitrosite has the structure $N_2O_2(CH_2{\cdot}CH_2{\cdot}NO_2)_2$, and thus belongs to the class of ψ-nitrosites (compare Wieland, A., 1904, i, 54). T. H. P.

The History of Alcohol. EDMUND O. VON LIPPMANN (*Chem. Zeit.*, 1913, **37**, 1313—1316, 1346—1347, 1358—1361, 1419—1422, 1428—1429. Compare A., 1912, i, 824; ii, 897).—A reply, with

historical quotations, to criticism by Diels of the author's view that alcohol and the process of distillation of readily volatile substances were unknown before the eleventh century. H. W.

Vapour Pressure of Glyceryl Trinitrate at the Ordinary Temperature. D. Chiaraviglio and O. M. Corbino (*Gazzetta*, 1913, **43**, ii, 390—398).—In certain circumstances the rate of cooling of a warm substance situated in a closed space containing a very attenuated gas or vapour is proportional to the concentration of the molecules of the gas or vapour. Applying this method, the authors find that at about 21° the vapour pressure of glyceryl trinitrate is less than 0·0001 mm., so that it is beyond the limits of measurement or even detection. The value for the vapour pressure given by Marshall (*J. Soc. Chem. Ind.*, 1904, **23**, 157; compare P., 1913, **29**, 157) they regard as untrustworthy, because it is based on the assumption that, since the vapour pressures of glyceryl trinitrate and mercury are equal at 70°, they are also equal at the ordinary temperature. R. V. S.

Preparation of Aluminium Ethoxide. Clément Berger (*Compt. rend.*, 1913, **157**, 717—718).—Aluminium amalgam acts but slowly on absolute alcohol, but if, prior to the addition of the amalgam, a little sodium is dissolved in the alcohol, then, on warming the mixture under a reflux condenser, a rapid action takes place. When a considerable precipitate has formed, it is filtered off rapidly, and the filtrate evaporated to dryness in a vacuum. The solid residue is *aluminium ethoxide*, $Al(OEt)_3$. It is readily decomposed in the solid state or in solution by water, giving alcohol and aluminium, the presence of small quantities of water stopping its preparation. In the solid state it is decomposed by heat. W. G.

Preparation of Epichlorohydrin. Jean Nìviere (*Bull. Soc. chim.*, 1913, [iv], **13**, 969—971).—A detailed account of a method already mentioned (compare this vol., i, 697) for the preparation of epichlorohydrin by the interaction of $\alpha\gamma$-dichlorohydrin and potassium hydroxide in the presence of small quantities of water. W. G.

Catalytic Preparation and Decomposition of Esters. Alphonse Mailhe (*Chem. Zeit.*, 1913, **37**, 777—778, 806—807).—The first paper contains a historical account of the work done on the catalytic preparation and decomposition of esters with particular reference to the more recent experiments of Sabatier and Mailhe on the use of metallic oxides. The second paper is a discussion of the behaviour of esters of aliphatic acids towards metallic oxide catalysts with special reference to formic acid and its esters. H. W.

Preparation of Sparingly Soluble Salts of Aluminium with Formic Acid Alone or with Formic together with Acetic Acid. Albert Friedländer (D.R.-P. 263865).—*Aluminium formate*, $Al(OH)(HCO_2)_2$, and *aluminium formoacetate*,

$$HCO_2\cdot Al(C_2H_3O_2)OH,2H_2O,$$

are respectively prepared by heating aluminium hydroxide with anhydrous formic acid or with a mixture of formic and acetic acids; they are of therapeutic value. F. M. G. M.

Ferri- and Chromi-formates. RUDOLF F. WEINLAND and HANS REIHLEN (*Ber.*, 1913, **46**, 3144—3150).—The compounds formed when a ferric salt is treated with sodium formate have been studied. In the deep red solution which results when equivalent quantities are mixed there is present the cation $[Fe_3(H{\cdot}CO_2)_6]$ of the hexaformato-triferri-base, of which only the monoformate has yet been isolated (Belloni, A., 1909, i, 283; Tower, 1910, ii, 900). By the addition of solid sodium formate to such a solution, the red colour gradually becomes pale, and *trisodium hexaformatoferrate*, $[Fe(H{\cdot}CO_2)_6]Na_3$, separates in pale green, microscopic, rectangular tablets. Thus, in presence of much sodium formate the anion $[Fe(H{\cdot}CO_2)_6]$ of hexaformatoferric acid is formed. This recalls the deep green of the trioxalatoferri-anion. By the action of water, the pale green solution or salt becomes red, the complex ions being in equilibrium.

The composition of the red formates, which are formed when ferric salts are mixed with sodium formate, varies, and the formic acid content rises with the concentration of that acid in the solution. It is therefore probable that in these substances there may be present salts of the hexaformatoferri-base with the hexaformatoferric acid Brick-red, microcrystalline *compounds* which agree with the formulæ $[Fe(H{\cdot}CO_2)_6][Fe_3(H{\cdot}CO_2)_6],8H_2O$ and

$$[Fe(H{\cdot}CO_2)_6]\left[Fe_3\begin{matrix}(H{\cdot}CO_2)_6\\(OH)_2\end{matrix}\right]_3,14H_2O$$

have been prepared.

Similar phenomena occur in the case of chromium salts. From a solution containing 30 mols. of sodium formate to one of chromium nitrate, *trisodium hexaformatochromate*, $[Cr(H{\cdot}CO_2)_6]Na_3,4{\cdot}5H_2O$, crystallises in greenish-violet rhombohedra, which are only decomposed by ammonia after prolonged boiling. J. C. W.

Two Isomeric Forms of Anhydrous Sodium Acetate. DANIEL VORLÄNDER and OTTO NOLTE (*Ber.*, 1913, **46**, 3199—3212).—An anhydrous form of sodium acetate is obtained on fusing sodium acetate trihydrate below 100°, and it also crystallises from fused sodium acetate. Intermediate hydrates do not exist. This modification is isomeric with that obtained on cooling the amorphous flux prepared by dehydrating above 200°. The new low temperature modification crystallises in the rhombic system and passes into the isomeride at 198°. The change is enantiotropic, the reverse change taking place so slowly that the two forms can exist side by side for months. The decomposition temperature of the trihydrate into water and anhydride is 58·2°.

Both anhydrous forms when crystallised from absolute ethyl or methyl alcohol yield the new rhombic form. This is an excellent condensation agent, absorbing water much more quickly than the ordinary fused form. For such purposes the trihydrate is best dehydrated at 120—160°.

The phenomena of polymorphism are explained on the assumption that within the molecule as a whole there is a difference in the intensity of the energy between the different parts. Further, in consequence of these intramolecular differences there are variable external differences in intensity between similar molecules, so that the molecules become united in different ways. Thus two sodium acetate molecules may be united.

$$\begin{array}{ccc} \mathrm{MeCO{\cdot}ONa} & \mathrm{MeCO{-}ONa} & \mathrm{CH_3{\cdot}CO{\cdot}ONa} \\ \vdots & \vdots \quad \vdots & \quad \vdots \\ \mathrm{MeCO{\cdot}ONa} & \mathrm{CH_3{\cdot}CO{\cdot}ONa} & \mathrm{NaO{\cdot}CO{\cdot}CH_3.} \end{array}$$

Such differences will explain the different crystalline structure of the polymorphic forms. E. F. A.

The Solidifying- and Melting-points of Mixtures of Stearic and Oleic Acids. ROBERT MELDRUM (*Chem. News*, 1913, **108**, 199—201).—The investigation was undertaken to confirm the degree of accuracy of Dalican's method of determining the solidifying point and the thermometer bulb method of determining the melting point of mixtures of fatty acids.

In the first series of experiments, the solidifying points were taken in a test-tube 7 inches by 1 inch filled three parts full, which was suspended in a glass jar. The mixtures of acids were melted and cooled to within 10° of their solidifying point. The thermometer was inserted and when crystallisation had commenced the whole was very slowly stirred until the thermometer ceased to fall, when the latter was fixed in the centre, $1\frac{1}{2}$ inches from the bottom, and the readings completed. The point at which the thermometer rose and remained stationary was taken as the solidifying point. The method yields very concordant results for any given mixture and, contrary to the general belief, indicates the composition of the mixture more accurately when the solidifying point is low than when it is high.

A second series of experiments was performed in the same apparatus, but without stirring. The results are concordant among themselves, but both rise and solidifying point are lower than indicated by the first method. The rise appears to be rather erratic, and is apparently governed by the amount of matter crystallised per given interval of time. When working with large quantities, it appears to be eliminated.

A series of determinations of m. p. has also been made (1) by covering the thermometer bulb with a thin layer of substance, and suspending it inside a test-tube which is gradually heated in a beaker of water; (2) by the closed capillary tube method; (3) with an open capillary, and (4) with a capillary U-tube both limbs of which are left open. One limb contains a column of solid fat 4 cm. long. The tube is heated in a water-bath, the thermometer being placed between the limbs. The temperature at which both columns of fat are at equal height is taken as the m. p. The conclusion is drawn that the bulb method is the most accurate, the chief difficulty in it lying in obtaining a uniform coating of the fat. In the methods which depend on the displacement of the column of solid (Nos. 3 and 4), movement occurs before the latter is completely molten. H. W.

The Reaction between Acetoacetic Esters and Phenyl Iododichloride. GEORG SACHS (*Monatsh.*, 1913, **34**, 1409—1415).—The application of phenyl iododichloride as a chlorinating agent has been studied in the case of methyl and ethyl acetoacetates. Reaction with the methyl ester commenced at 34—35° and slackened after slightly more than one molecular proportion of phenyl iododichloride had been added at 60°. On distillation, a constant boiling, inseparable mixture of approximately two molecules of iodobenzene with one molecule of the expected methyl α-chloroacetoacetate, b. p. 84°/30 mm., was obtained. When ethyl acetoacetate was warmed at 60—80° with two molecules of the agent, however, iodobenzene, b. p. 79°/23 mm., and ethyl α-dichloroacetoacetate, b. p. 99°/21 mm., 207°/753 mm., were obtained. J. C. W.

Optically Active Dimethylsuccinic Acid. ALFRED WERNER and M. BASYRIN (*Ber.*, 1913, **46**, 3229—3232).—It is shown that dimethylsuccinic acid may be resolved by means of optically active triethylenediaminecobaltic bromide. The modification of dimethylsuccinic acid, m. p. 195°, could not be resolved, and accordingly it represents the *meso*-form. The form m. p. 127° gives rise to d-*triethylenediaminecobaltic bromide* l-*dimethylsuccinate*, which is sparingly soluble, whereas the mother liquors contain the corresponding d-*dimethylsuccinate*. The optically active dimethylsuccinic acids have m. p. 135° and $[\alpha]_D$ +7·8° and −8·0.° E. F. A.

Ketonic Decomposition of β-Lactones and its Application to the Synthesis of Ketens. ERWIN OTT (*Annalen*, 1913, **401**, 159—177).—Somewhat similar to the behaviour of dialkylmalonic anhydrides by heating, whereby dialkylketens are formed (Staudinger and Ott, A., 1908, i, 602), is the behaviour of derivatives of Meldrum's β-lactone of β-hydroxy*iso*propylmalonic acid (T., 1908, **93**, 601). In these also, by heating, the 4-ring is broken and acetone and ketens are obtained. The β-lactone of β-hydroxy*iso*propylmalonic acid decomposes by heating into carbon dioxide, carbon suboxide, acetone, and acetic acid.

The *β-lactone* of *β-hydroxy-α-methyl*iso*propylmalonic acid*,

$$\begin{array}{l}\mathrm{O{-}{-}CMe_2}\\ \;|\quad\;\;|\\ \mathrm{CO\cdot CMe\cdot CO_2H}\end{array},$$

decomp. 110—113°, colourless leaflets, is obtained by treating methylmalonic acid with acetic anhydride and a little concentrated sulphuric acid, and keeping the product for many days with the calculated amount of acetone. The lactonic acid decomposes by heating into carbon dioxide, acetone, and viscous substances. It cannot be esterified directly, but the *methyl* ester, $C_8H_{12}O_4$, m. p. 59·5°, b. p. 71°/0·1 mm., is obtained, together with the β-lactones of β-hydroxy*iso*propylmalonic acid and of β-hydroxy-α-methyl*iso*propylmalonic acid, in a remarkable reaction between methyl iodide and the β-lactone of silver β-hydroxy*iso*propylmalonate. The methyl ester, which is remarkably stable and distils at 213°/723·4 mm., with only slight decomposition, yields, by heating in a current of hydrogen, carbon dioxide, acetone, and about 50% of dimethylketen.

The *β-lactone* of *α-bromo-β-hydroxy*iso*propylmalonic acid*,

$$\begin{array}{l}O\text{—}CMe_2\\ |\quad\ \ |\\ CO\cdot CBr\cdot CO_2H\end{array}$$

decomp. 87—92°, colourless needles, is prepared by exactly neutralising the β-lactone of β-hydroxy*iso*propylmalonic acid with 2*N*-sodium hydroxide in the cold and treating the solution slowly with the calculated amount of bromine. At 130° the brominated lactonic acid decomposes into acetone, carbon dioxide, and hydrogen bromide.

The *methyl* ester, $C_7H_9O_4Br$, m. p. 87°, colourless prisms, prepared from the silver salt and methyl iodide in benzene, is decomposed by slow distillation at 95° over a faintly glowing platinum spiral in a vacuum, whereby carbon dioxide, acetone, and *bromomethylketen*, $CBrMe\colon CO$, are obtained. Bromomethylketen is being fully examined; it polymerises with great readiness to a faintly yellow, resinous *substance*, $(C_3H_3OBr)_8$, m. p. 60—70°, and differs from all other ketens in not reacting with aniline.

Malonic acid and acetic anhydride in the presence of a little concentrated sulphuric acid yield, after removal of the excess of the anhydride and the acetic acid at 30—40°/1—2 mm., an extremely hygroscopic oil which is presumably the mixed malonic acetic anhydride, since it contains for each molecule of malonic acid, one acetyl group which cannot be removed without decomposition. The substance yields carbon suboxide by warming on the water-bath, and reacts with acetone to give an 87% yield of the β-lactone of β-hydroxy*iso*propylmalonic acid. Dimethylmalonic anhydride is obtained in 96% yield by treating dimethylmalonic acid with acetic anhydride and a little concentrated sulphuric acid, and removing by-products at 40°/1—2 mm., the operations being once repeated on the product. *Diethylmalonic anhydride*, prepared in a similar manner, is a liquid. C. S.

Synthesis of Formaldehyde from Carbon Dioxide and Water by Inorganic Colloids acting as Transformers of Light Energy. BENJAMIN MOORE and T. ARTHUR WEBSTER (*Proc. Roy. Soc.*, 1913, [*B*], **87**, 163—176).—The experiments of Bach, Euler, Usher, and Priestley (compare A., 1906, ii, 299, 881) have been confirmed and extended to show that formaldehyde is synthesised from carbon dioxide by means of inorganic colloidal uranic and ferric hydroxides in very dilute solution. The colloids act as catalysts for light energy, positive results being obtained only in strong, direct sunlight and in a "uviol" mercury arc. Under similar conditions, crystalloid uranium nitrate does not cause synthesis. The uranium catalyst is more powerful than the ferric catalyst. It is claimed that such a process occurring in nature forms the first step in the origin of life.

E. F. A.

Condensation of Aldol with Formaldehyde. V. P. KRAVEC (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1451—1453).—With the object of obtaining derivatives of pentaerythritol, from which the hydrocarbon, C_5H_8, regarded by Gustavson (A., 1896, i, 669) as vinyltrimethylene, has been obtained (compare Zelinski, this vol., i, 254), the author has investigated the condensation of aldol with formaldehyde under the

conditions laid down by Tollens and Wigand (A., 1892, 127); this reaction may be expected to give methylpentaerythritol.

Aldol may be readily prepared in good yield (30 grams) by a method devised by Zelinski and Volkonski, but not yet published. It consists in mixing acetaldehyde (100 grams), dissolved in an equal weight of water, with freshly precipitated, alkali-free lead hydroxide (30 grams) at a temperature not exceeding 5°, the mixture being left at the ordinary temperature for two hours and then gradually heated on the water-bath at 25°, 30°, and 35° during eighteen hours.

In presence of lead hydroxide, aldol and formaldehyde give pentaerythritol, so that resolution of the aldol molecule into 2 mols. of acetaldehyde precedes condensation with formaldehyde. The action of lead hydroxide on aldol is hence a typical, reversible reaction (compare de Bruyn and Alberda van Ekenstein, A., 1899, i, 850; Löb, A., 1909, i, 767; Löb and Pulvermacher, A., 1910, i, 95).

Pentaerythritol is also obtained from aldol and formaldehyde in presence of calcium hydroxide, but the latter is not able to effect the condensation of acetaldehyde to aldol. T. H. P.

Mechanism of Oxidative Changes. HEINRICH WIELAND (*Ber.*, 1913, **46**, 3327—3342).—The catalytic action of palladium or platinum is not due to the activation of molecular oxygen with intermediate formation of peroxide, but it is attributed to the activation of hydrogen. This theory is extended to biological oxidations, and it is shown that certain of these can take place in presence of palladium black and in the complete absence of oxygen, provided that the accumulated hydrogen is removed by the presence of other substances with an affinity for hydrogen such as *p*-benzoquinone or methylene-blue.

Dextrose can be dehydrogenated by shaking with palladium black at 40° in an atmosphere of nitrogen, carbon dioxide being formed from the beginning of the reaction as well as hydrogen. The change is accelerated on the addition of *p*-benzoquinone, which is converted into quinhydrone or of methylene-blue, which is decolorised. In presence of oxygen which forms water with the liberated hydrogen, the change is still more rapid. Gluconic acid is even more quickly dehydrogenated.

Lactic acid yields pyruvic acid under similar conditions. Phenol, *m*-cresol, guaiacol, pyrogallol and aniline can be dehydrogenated in the absence of oxygen. Tyrosine and uric acid are resistant, but in both these cases the action of the oxydase is known to be combined with that of a hydrolysing enzyme.

Alcohol in presence of methylene-blue or of *p*-benzoquinone is converted into acetic acid by an acetone preparation of acetic acid bacteria, all oxygen being excluded. Acetaldehyde behaves similarly, whereas methyl alcohol or formaldehyde are converted into formic acid. Dextrose is dehydrogenated by the acetic acid ferment in presence of methylene-blue, carbon dioxide being formed.

The reducing enzymes, for example, Schardinger's reductase, act in the same manner. Salicylaldehyde is converted into salicylic acid by the milk enzyme either in presence of oxygen or in presence of methylene-blue in the absence of oxygen. E. F. A.

Biochemical Synthesis of a Sugar of the Hexobiose Group, Gentiobiose. ÉMILE BOURQUELOT, HENRI HÉRISSEY, and J. COIRRE (*Compt. rend.*, 1913, **157**, 732—734; *J. Pharm. Chim.*, 1913, [vii], **8**, 441—449).—The authors have prepared and isolated gentiobiose in a pure state by the action of emulsin, from almonds, on a concentrated solution of dextrose at 15—20° for one month. The excess of dextrose was removed by fermenting it with top yeast, after destroying the emulsin by heat and diluting the solution. The fermented liquid was neutralised with calcium carbonate, filtered and evaporated to dryness under reduced pressure. The dry residue was extracted with 95% alcohol, from which extracts two crops of crystals were obtained, the first containing mineral matter, and the second being pure gentiobiose as shown by its physical and chemical properties. W. G.

Peculiarity in the Solubility Curve of Sugar in Water. PH. ORTH (*Bull. Assoc. chim. Sucr. Dist.*, 1913, **31**, 94—103).—A theoretical paper. It is shown that the equation $S = 28162/(157{\cdot}97 - t)$ gives the solubility of sucrose in water at a temperature t. The coefficient of supersaturation C_1 is obtained by the expression $C_1 = S(157{\cdot}97 - t_1)/28162$, in which S is the solubility at a temperature t and t_1, the lower temperature to which the solution is cooled without crystallisation. The constant 157·97 is shown to represent the temperature at which the solubility of sucrose in water becomes infinitely large, that is, the temperature at which sucrose and water are miscible in all proportions. A number of other empirical equations are given dealing with the freezing-point constant and the specific heat of aqueous solutions of sucrose, and also with the heat of solution.

J. F. S.

The Nitration of Cellulose, and the Decomposition of Nitrocellulose by Acids and Alkalis. G. MEISSNER (*Zeitsch. ges. Schiess. Sprengstoffwesen*, 1913, **8**, 252—254, 269—271).—An account of numerous experiments on the yields, stability, and variations in the products obtained by nitrating cellulose under different conditions, together with an account of the decomposition of these compounds by acids and alkalis. F. M. G. M.

Unstable Products in the Nitration of Cellulose. ERNST BERL and MAX DELPY (*Zeitsch. ges. Schiess. Sprengstoffwesen*, 1913, **8**, 129).—When water is removed from nitrocellulose by systematic treatment with alcohol, it gives rise to a brown powder, decomp. 162°, soluble in concentrated sulphuric acid; this when extracted with ether furnishes two *compounds*: (1) a yellowish-brown powder, decomposing at 174°, containing about 10% of nitrogen, and converted by concentrated alkalis into a compound soluble in water; and (2) a violet powder containing 9·45% of nitrogen and decomposing at 157°.

F. M. G. M.

Fatty Acid Esters of Hydrocellulose and their Hydrolysis. ALBRECHT STEIN (*Zeitsch. angew. Chem.*, 1913, **26**, 673—677).—Triacyl derivatives of hydrocellulose are prepared without difficulty by

acting on hydrocellulose with the anhydride of a fatty acid in the presence of concentrated sulphuric acid. The properties of the hydrocellulose esters of the homologues of acetic acid are similar to those of acetyl cellulose.

In order to obtain information as to the manner in which the catalyst acts in the esterification of hydrocellulose, the action of an acid anhydride on hydrocellulose in the presence of chloroacetic acid or trichloroacetic acid has been studied. It is found that the use of these catalysts leads to the production of an ester containing chlorine, in some cases to the extent of 2·8%. W. H. G.

The Preparation of Triethylamine. JITENDRA NATH RAKSHIT (*J. Amer. Chem. Soc.*, 1913, **35**, 1781—1783).—If 75 c.c. of ethyl bromide and 50 c.c. of ammonia solution (D 0·88) are heated together in a closed 750 c.c. flask in the steam-oven for three hours, subsequent distillation with sodium hydroxide solution into dilute hydrochloric acid gives a mixture of ammonium chloride and ethylamine hydrochloride which are most easily separated by filtering the latter in a molten condition from the solid ammonium chloride.

The ethylamine from 62 grams of the hydrochloride is then mixed with 44 c.c. of ethyl bromide and again heated in a closed flask for three hours in the steam-oven. After cooling, the liquid is decanted from the separated crystalline solid and is then evaporated with dilute hydrochloric acid, when the residue (approximately 19 grams) consists of pure triethylamine hydrochloride. D. F. T.

Resolution of α-Alanine into its Optical Antipodes by means of Active Acids. II. AMEDEO COLOMBANO and GIUSEPPE SANNA (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 292—298. Compare this vol., i, 1208).—In alcoholic solution, the ethyl ester of alanine and *d*-camphorsulphonic acid yield the *salt* of the *inactive* ester,

$$CO_2Et\cdot CHMe\cdot NH_2,C_{10}H_{15}O\cdot SO_3H,\tfrac{1}{2}H_2O,$$

m. p. 95—100°, $[\alpha]_D$ +11·49°. When water is used as solvent, crystalline fractions are obtained of gradually increasing melting point and specific rotation, but separation of the *d*- and *l*-alanines in this way is not easy.

Such resolution is, however, readily effected by means of *d*-bromocamphorsulphonic acid, mixing of the ammonium salt of this acid with alanine ester hydrochloride in aqueous solution resulting in the separation of *ethyl* d-*alanine* d-*bromocamphorsulphonate*,

$$CO_2Et\cdot CHMe\cdot NH_2,C_{10}H_{14}OBr\cdot SO_3H,1H_2O,$$

m. p. 145° or 192° (anhydrous), $[\alpha]_D^{26}$ +67·54° (hydrate), which corresponds with the dextro-ester and with *l*-alanine. Isolation of ethyl *l*-alanine *d*-bromocamphorsulphonate from the mother liquor is troublesome and gives only a small yield; possibly this ester could be more readily obtained by the use of *l*-bromocamphorsulphonic acid.

T. H. P.

Tetra-aminoadipic Acid and αδ-Dihydroxy-βγ-diaminoadipic Acid. WILHELM TRAUBE and ARTHUR LAZAR (*Ber.*, 1913, **46**, 3438—3450. Compare A., 1903, i, 76).—An account of the replacement of the bromine atoms in the monolactam of αδ-dibromo-βγ-di-

aminobutane-$\alpha\alpha\delta\delta$-tetracarboxylic acid (1) and the dilactam of $\alpha\delta$-dibromo-$\beta\gamma$-diaminoadipic acid (II) by the hydroxyl amino-, and dimethylamino-groups:

$$\text{(I.)}\quad \mathrm{CBr(CO_2H)_2{\cdot}CH}\left\langle\begin{matrix}\mathrm{CH(NH_2)}\\ \mathrm{NH{-}{-}CO}\end{matrix}\right\rangle\mathrm{CBr{\cdot}CO_2H}$$

$$\text{(II.)}\quad \mathrm{CO}\left\langle\begin{matrix}\mathrm{CHBr{\cdot}CH{-}{-}NH}\\ \mathrm{NH{-}{-}CH{\cdot}CHBr}\end{matrix}\right\rangle\mathrm{CO.}$$

When heated at 105° with alcoholic ammonia, the dilactam of dibromodiaminoadipic acid is converted into the *dilactam* of *$\alpha\beta\gamma\delta$-tetra-amino-adipic acid*, $\mathrm{CO}\left\langle\begin{matrix}\mathrm{NH{-}{-}{-}CH{\cdot}CH(NH_2)}\\ \mathrm{CH(NH_2){\cdot}CH{-}{-}{-}NH}\end{matrix}\right\rangle\mathrm{CO}$, which crystallises in stellar aggregates of short, stout needles, and forms a sparingly soluble *sulphate*, B,H_2SO_4 (solubility in water at 100° = 0·177 : 100), a *nitrate* (leaflets), *platinichloride* (hexagonal pyramids or rhombohedra), *hydrochloride* (colourless, prismatic needles), and *picrate* (fern-like aggregates).

The hydrochloride reacts with potassium cyanate in hot aqueous solution, yielding the *dilactam* of *$\beta\gamma$-diamino-$\alpha\delta$-dicarbamidoadipic acid*, $C_8H_{12}O_4N_6$, which crystallises with water (1 mol.) in colourless needles.

Attempts to prepare tetra-aminoadipic acid by acidifying solutions of the dilactam in aqueous alkalis were unsuccessful, the original dilactam being precipitated unchanged.

The *dilactam* of *α-bromo-$\beta\gamma\delta$-triamino-α*(or δ)*carboxyadipic* [*α-bromo-$\beta\gamma\delta$-triaminobutane-$\alpha\gamma\gamma$*(or $\alpha\alpha\gamma$)*-tricarboxylic*] *acid*, $C_7H_8O_4N_3Br$, obtained in the form of its *ammonium* salt by the action of alcoholic ammonia at 80—90° on the monolactam of $\alpha\delta$-dibromo-$\beta\gamma$-diaminobutane-$\alpha\alpha\delta\delta$-tetracarboxylic acid, crystallises with water ($1\frac{1}{2}$ mol.) in needles (decomp. 280°) and yields salts with both bases and acids; the *silver* salt (slender, colourless needles), *barium* salt, and *hydrobromide* (prisms) are described. The position of the free carboxyl group has not yet been determined. When kept in contact with an excess of aqueous dimethylamine (45%) for four or five days at the ordinary temperature, the dilactam of $\alpha\delta$-dibromo-$\beta\gamma$-diaminoadipic acid is converted into the *dilactam* of *$\beta\gamma$-diamino-$\alpha\delta$-tetramethyldiaminoadipic acid* (III), which is separated from the accompaning 3 : 4-*diaminotetrahydrofuran*-2 : 5-*dicarboxylic acid* (IV) by taking advantage of the sparing solubility of the latter compound in water.

$$\text{(III.)}\quad \mathrm{CO}\left\langle\begin{matrix}\mathrm{NH{-}{-}{-}CH{\cdot}CH(NMe_2)_2}\\ \mathrm{CH(NMe_2)_2{\cdot}CH{-}{-}{-}NH}\end{matrix}\right\rangle\mathrm{CO.}$$

$$\text{(IV.)}\quad \begin{matrix}\mathrm{CO_2H{\cdot}CH{\cdot}O{\cdot}CH{\cdot}CO_2H}\\ \mathrm{NH_2{\cdot}CH{-}{-}CH{\cdot}NH_2}\end{matrix}\,.$$

The furan compound crystallises in ill-defined tetragonal prisms which become yellow at 210°, and have m. p. 230° (decomp.). It forms with mineral acids very hygroscopic salts, of which the *nitrate* (decomp. 180°) is described. On treatment with fuming nitric acid, it yields 2-*nitro*-3 : 4-*diaminofuran*-5-*carboxylic acid*, $C_5H_5O_5N_3$, crystallising in stellar aggregates of slender needles (decomp. above 300°). The dilactam, III, separates with $2H_2O$ in

well developed rhombic crystals, which darken at 243° and have m. p. 252° (decomp.). It forms a *hydrochloride*, *B*,2HCl, long, slender needles; a *picrate*, hexagonal leaflets; *platinichloride*, rectangular plates; *sulphate*, rhombic prisms, and an *oxalate*, prismatic needles.

The monolactam of $\alpha\delta$-dibromo-$\beta\gamma$-diaminobutane-$\alpha\alpha\delta\delta$-tetracarboxylic acid reacts with silver nitrate in aqueous solution, yielding the *silver* salt, $C_8H_6O_7N_2Br_2Ag_2$, which is converted by boiling with water into the *monolactam* of *$\beta\gamma$-diamino-$\alpha\delta$-dihydroxybutane $\alpha\alpha\delta\delta$-tetracarboxylic acid*, $OH\cdot C(CO_2H)_2\cdot CH<\begin{matrix}CH(NH_2)\\NH\text{---}CO\end{matrix}>C(OH)\cdot CO_2H$. The latter compound could not be obtained crystalline, and, therefore, was isolated in the form of its *silver* salt, $C_8H_9O_9N_2Ag$.

When heated either alone at 180° or in aqueous solution, it loses carbon dioxide and water, yielding the *dilactam* of *$\beta\gamma$-diamino-$\alpha\delta$-dihydroxyadipic acid*, $CO<\begin{matrix}CH(OH)\cdot CH\text{------}NH\\NH\text{------}CH\cdot CH(OH)\end{matrix}>CO$, which crystallises in tetragonal prisms capped with pyramids.

Attempts to prepare tetrahydroxyadipic acid from the dilactams of tetra-aminoadipic and $\alpha\delta$-dihydroxy-$\beta\gamma$-diaminoadipic acids proved unsuccessful, the amino-groups in these compounds being stable towards the action of nitrous acid. F. B.

Preparation of Acetamide. E. F. Hitch and H. N. Gilbert (*J. Amer. Chem. Soc.*, 1913, **35**, 1780—1781).—Acetamide is conveniently prepared by heating a mixture of 42 grams of ammonium carbonate and 125 grams of acetic acid (compare Rosanoff, Gulick, and Larkin, A., 1911, i, 529) in a 250 c.c. round-bottomed flask in an air-bath. The flask is fitted with a Vigreux fractionating column carrying a thermometer and attached to a condenser. The mixture is boiled at such a rate that 20 to 30 drops distil per minute, and when the thermometer registers 223° the residue in the flask is almost pure acetamide.

The yield is 85—90% calculated on the ammonium carbonate, and the time required is four hours. D. F. T.

Synthesis of Amido-oxalylbiuret. Johan Th. Bornwater (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 198—200).—In a previous paper (A., 1911, i, 617) the author has shown that finely-powdered carbamide reacts with an ethereal solution of oxalyl chloride, yielding parabanic acid and, apparently, oxalyldiureide,

$$C_2O_2(NH\cdot CO\cdot NH_2)_2,$$

which is quite different from Grimaux's compound (A., 1880, 105) obtained by fusion of a mixture of carbamide and parabanic acid. Subsequently, the subject has been re-investigated by Biltz and Topp (this vol., i, 600, 602), who are led to the conclusion that the two substances are probably identical, although certain differences remain unexplained. The author points out that Grimaux's compound has been incorrectly described as oxalyldiureide in the German literature, since Grimaux calls it, "amide d'un acide oxalylbiurétique." He has further effected the synthesis of the latter compound.

Carbethoxyethoxalylcarbamide, $CO_2Et{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}CO_2Et$, needles, m. p. 152°, is obtained in 10% yield when ethyl oxamate and ethyl urethane are heated in dry benzene. When a solution of this substance in absolute alcohol is treated with dry, gaseous ammonia, amido-oxalylbiuret, $NH_2{\cdot}CO{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2$, is precipitated, which is identical with Grimaux's compound.

In effecting the biuret reaction, the author points out the desirability of first adding the highly diluted copper sulphate solution, and, subsequently, a solution containing at most 15% of potassium hydroxide. When the reagents are added in the reverse order and more concentrated solutions of potassium hydroxide are employed (compare Biltz and Topp, *loc. cit.*), there is a possibility that the substance is already undergoing partial decomposition before the copper sulphate is added.

The substance, $C_4H_5O_3N_3$, m. p. 272—273° (decomp.), obtained by the action of fuming hydriodic acid (D 1·96) on Grimaux's compound, is, possibly, uramil, the formation of which is explicable on the author's formulation of Grimaux's compound. H. W.

Simultaneous Reduction and Oxidation. I. Dichloropyruvic Acid, Nitrile and Ester from Trichlorolactic Acid, Nitrile and Ester. ARTHUR KÖTZ and K. OTTO (*J. pr. Chem.*, 1913, [ii], 88, 531—552. Compare Wallach, this Journ., 1875, 351; A., 1878, 285, 288; Pinner, this Journ., 1877, ii, 584; A., 1884, 1298).—With the object of throwing further light on the mechanism of the transformation of chloral into dichloroacetic acid under the influence of aqueous potassium cyanide, the authors have undertaken a systematic examination of similar cases of simultaneous reduction and oxidation occurring in compounds of the type $CCl_3{\cdot}CH(OH){\cdot}R$, the present paper dealing particularly with the transformation of $\beta\beta\beta$-trichlorolactic acid, and its nitrile and ester into the corresponding derivatives of dichloropyruvic acid.

They consider that the first stage in the reaction between chloral and potassium cyanide consists in the formation of $\beta\beta\beta$-trichlorolactonitrile (I), and that this loses hydrogen chloride, yielding the compounds (II) or (III), which are at once transformed into dichloropyruvonitrile (IV), the latter compound then undergoing hydrolysis to dichloroacetic and hydrocyanic acids:

$$\text{(I) } CCl_3{\cdot}CH(OH){\cdot}CN \longrightarrow \text{(II) } CCl_2{:}C(OH){\cdot}CN, \text{ or}$$

$$\text{(III) } \overset{\quad O \quad}{CCl_2{\cdot}CH}{\cdot}CN \longrightarrow \text{(IV) } CHCl_2{\cdot}CO{\cdot}CN \longrightarrow CHCl_2{\cdot}CO{\cdot}OH + HCN.$$

The following evidence is given in support of the view that $\beta\beta\beta$-trichlorolactonitrile is intermediately formed in the reaction: (1) Although potassium cyanide is hydrolysed to potassium hydroxide and hydrogen cyanide, the action of potassium cyanide on chloral does not give rise to chloroform, and therefore the chloral cannot be present as such in the mixture. (2) $\beta\beta\beta$-Trichlorolactonitrile, on treatment with potassium hydroxide, gives rise to potassium dichloroacetate, no chloroform being produced in the reaction.

βββ-Trichlorolactonitrile thus differs from chloral in not undergoing hydrolysis with the formation of chloroform. This difference is referred by the authors to the reactivating influence of the cyanogen group on the hydrogen atom directly attached to the central carbon of the nitrile; on account of this mobility of the hydrogen atom, the molecule readily loses hydrogen chloride, whilst at the same time the ability to yield chloroform by hydrolysis disappears.

A similar differance is shown by βββ-trichloroethyl alcohol, ethyl βββ-trichlorolactate, and other compounds of the type

$$CCl_3\cdot CH(OH)\cdot R.$$

On treatment with triethylamine, ethyl βββ-trichlorolactate and βββ-trichlorolactonitrile lose hydrogen chloride, yielding ethyl dichloropyruvate and dichloropyruvonitrile. The last-mentioned compound reacts with water and alcohol, yielding dichloroacetic acid and ethyl dichloroacetate.

The formation of dichloroacetamide, dichloroacetanilide, and ethyl dichloroacetate by the action of ammonia, aniline and alcohol on βββ-trichlorolactonitrile (Pinner and Wallach, *loc. cit.*) is considered by the authors to furnish additional support to their view that dichloropyruvonitrile is formed as an intermediate product in the action of potassium cyanide on chloral.

When heated with water or triethylamine, trichlorolactic acid decomposes, thus: $CCl_3\cdot CH(OH)\cdot CO_2H \longrightarrow HCl + CHCl_2\cdot CO\cdot CO_2H \longrightarrow CO_2 + CHCl_2\cdot CHO$.

The readiness with which this decomposition takes place affords an explanation of the fact that the interaction of trichlorolactic acid and ammonia, hydroxylamine, phenylhydrazine, or carbamide gives rise to derivatives of glyoxal or dichloroacetaldehyde.

Dichloropyruvonitrile is obtained (1) by the interaction of molecular proportions of trichlorolactonitrile and triethylamine in ethereal solution at the ordinary temperature, and (2) by heating dichloroacetyl chloride with silver cyanide. It forms a colourless liquid, b. p. 111—113°/12 mm.

ββ-Dichloro-α-benzyliminopropiobenzylamide,

$$CHCl_2\cdot C(:N\cdot C_7H_7)\cdot CO\cdot NH\cdot C_7H_7,$$

prepared by heating ethyl trichlorolactate with benzylamine (3 mols.) in ethereal solution, crystallises with water (1 mol.) and has m. p. 101° (not sharp). It may also be obtained by heating ethyl dichloropyruvate with benzylamine (2 mols.) in ethereal solution. When prepared by the second method, it crystallises with $2H_2O$ in lustrous, white leaflets, m. p. 220—221°, or slender needles, m. p. 104° and 150°.

Ethyl dichloropyruvate, prepared by heating ethyl trichlorolactate and triethylamine in alcoholic solution, is a colourless liquid, b. p. 115°/12 mm. It rapidly takes up water on exposure to air, and then has the composition $C_5H_6O_3Cl_2,2H_2O$.

Dichloropyruvic acid, $C_3H_2O_3Cl_2,H_2O$, obtained by hydrolysing the ester with hydrochloric acid, separates from a mixture of ether and light petroleum in white crystals, m. p. 119°, b. p. 215—220°, and after distillation has m. p. 110°. When boiled with water, it is converted into dichloroacetaldehyde. F. B.

Nitrogen Carbides. HERMANN PAULY and ERNST WALTZINGER (*Ber.*, 1913, **46**, 3129—3140).—It has already been shown (A., 1910, i, 639) that tetraiodoglyoxaline decomposes on heating to form the compounds C_3N_2I and then C_3N_2, the reaction recalling the formation of paracyanogen from cyanuric iodide (Klason, 1886, 1001). The fact that the decomposition takes place at a temperature which, according to experience, is not inimicable to the glyoxaline ring, suggests that the compounds formed still have ring structure, since a partial loss of nitrogen might be expected to ensue if the ring were opened. In order to test this point, and also to learn whether the preliminary decomposition into a monoiodo-compound was general, tri-iodo-5- and 2-methyl-glyoxalines and tetraiodopyrrole (iodole) have also been heated. In these cases, however, the compounds melt and enclose some of the liberated iodine, so that the formation of intermediate compounds was masked, and, in addition, the presence of hydrogen was disturbing and led to the production of a little ammonium iodide,

All the compounds obtained, C_3N_2, C_3N_2Me and C_4NH, are amorphous, charcoal-like products, and have, in common with paracyanogen, the following properties: they yield cyanogen on heating to redness in an indifferent atmosphere; they give up all their nitrogen as ammonia when heated with soda-lime; they dissolve in molten alkalis, forming ammonia, cyanides and carbonates. Animal charcoal has some of these properties, but does not dissolve in molten alkali. It may consist in part of such nitrogen carbides.

Quantitative studies on the decomposition of tetraiodoglyoxaline were carried out in a glass tube which was slightly bent downwards, so that it dipped below the surface of a metal bath. One end of the tube was attached to a U-tube and a flask containing potassium iodide solution for the absorption of iodine. The iodine was swept out by a stream of carbon dioxide. Since the tetraiodoglyoxaline cannot be purified by recrystallisation, it was analysed before use. It was found that, however carefully prepared, it contained about 1% of a by-product which could be removed by volatilisation at 105° in vacuum. The carbides obtained, readily absorbed gases and moisture, so that all analytical processes were carried out with the greatest expedition.

The formation of the soot-like, sepia-coloured *iodo-nitrogen carbide*, $(C_3N_2I)_x$, takes place at 180°. The substance forms a brown solution in nitric acid, iodine being liberated. The *carbide*, $(C_3N_2)_x$ is best obtained by heating tetraiodoglyoxaline, first at 180° and then at 420°. When heated at 800—900° in a current of carbon dioxide, cyanogen and a little carbon monoxide were formed, but in an atmosphere of nitrogen, the formation of cyanogen was quantitative. J. C. W.

Iron Salts which Combine with Carbon Monoxide. II. The Action of Amines on Sodium Nitroprusside. WILHELM MANCHOT and PIERRE WORINGER (*Ber.*, 1913, **46**, 3514—3521).—It has been shown previously (A., 1912, i, 955) that the action of ammonia on sodium nitroprusside is expressed by the equation:

$$Na_2[Fe(CN)_5NO] + 3NH_3 + H_2O = Na_2(NH_4)[Fe(CN)_5,NH_3] + NH_4\cdot NO_2.$$

It has now been found possible to replace the NO-group by alkylamines instead of ammonia, and the compounds thus formed give similar reactions to the ammonia compound, and also possess the property of combining with carbon monoxide and oxygen. Methylamine, dimethylamine, trimethylamine, and ethylenediamine react very readily, but aromatic amines, such as aniline, toluidine, etc., have no action on sodium nitroprusside.

Trisodium ferropentacyanomethylamine, $Na_3[Fe(CN)_5,NH_2Me]$, was obtained in the form of yellow crystals from sodium nitroprusside and methylamine in aqueous methyl-alcoholic solution, dilution with the alcohol being necessary to moderate the reaction. The reaction mixture also contained sodium acetate, to prevent the formation of a disodium methylamine salt.

The *disodium ethylenediamineferropentacyanoethylenediamine*,

$$Na_2[Fe(CN)_5],C_2H_4(NH_2)_2,$$

was not obtained pure, although the product was well crystallised, and appeared homogeneous under the microscope. The addition of sodium acetate to the reaction mixture did not give a trisodium salt.

Although sodium nitroprusside does not react with pyridine, the salt *trisodium ferropentacyanopyridine*, $Na_3[Fe(CN)_5,C_5H_5N]$, can be obtained by the action of pyridine on an aqueous-methyl alcoholic solution of trisodium ammonium ferropentacyanoammine. It crystallises as a felted mass of long, yellow needles, and possesses properties similar to those of the alkylamine compounds.

Experiments to prepare the ferric compounds corresponding with the ferropentacyanocarbon monoxide salts have not hitherto been successful. T. S. P.

Action of Organomagnesium Compounds on Ethyl Diazoacetate. Ernst Zerner (*Monatsh.*, 1913, **34**, 1609—1630).—By means of the reaction between organomagnesium compounds and ethyl diazoacetate or diazomethane, the author hoped to be able to throw some light on the constitution of aliphatic diazo-compounds. No direct proof of the ring or open-chain structure could be obtained, but the results offer more support to the latter view than to the former. The author critises the Angeli-Thiele formula, R:N⋮N, however, and proposes instead the type R:N·N, making the active nitrogen atom univalent.

Although Thiele has suggested that certain reactions of nitrous oxide agree with the constitution O:N⋮N, it was found that the gas has no action whatever on magnesium methyl iodide. When ethyl diazotate was added to magnesium methyl iodide at 0°, however, a vigorous reaction occurred, and a crystalline solid and an oil were obtained. The former was most probably the *methylhydrazone* of *ethyl glyoxylate*, $CO_2Et·CH:N·NHMe$. It formed long, colourless needles, m. p. 91—92°, responded to Molisch's thymol reaction and Tollens's naphtharesorcinol test, and reduced ammoniacal silver and Fehling's solutions. It was hydrolysed by warm dilute sulphuric acid, and methylhydrazine sulphate and ethyl glyoxalate were obtained. An *acetyl* derivative, $C_7H_{12}O_3N_2$, was also prepared, in freely soluble white needles, m. p. 67—69°. The oily product also gave methyl-

hydrazine on hydrolysis. It was probably impure methylhydrazone of hydroxy*iso*butaldehyde, $OH\cdot CMe_2\cdot CH{:}N\cdot NHMe$. The crystalline compound might also have been ethyl *N*-methylhydraziacetate, $CO_2Et\cdot CH<\begin{matrix}NH\\|\\NMe\end{matrix}$, but this would assume that the diazo-compound reacts differently from the fatty azoimides, which, under the influence of organomagnesium haloids, yield fatty diazoamino-compounds, as Dimroth has shown.

To elucidate this point the action of ethyl diazoacetate on magnesium phenyl bromide was investigated, since it was expected that either the known phenylhydrazone of ethyl glyoxylate or an isomeride would be obtained. However, the only crystalline product was one in which the ester group had also been attacked. It was most probably the *phenylhydrazone* of *hydroxydiphenylacetaldehyde*, $OH\cdot CPh_2\cdot CH{:}N\cdot NHPh$. It crystallised in large, rectangular plates, m. p. 132°, and yielded a red, crystalline *product*, $C_{20}H_{16}N_2$, m. p. 69—70°, on boiling with dilute sulphuric acid, water being eliminated. The red compound gave intense, red solutions in concentrated mineral acids. On evaporating the solution in hydrochloric acid in a desiccator over lime, a snow-white, additive *product*, $C_{20}H_{17}N_2Cl$, was obtained. This was very sparingly soluble in water, but gave a turbidity with silver nitrate. It was freely soluble in organic media, and exhibited a fine blue fluorescence in alcohol. Here again the crystalline product might have been the hydrazi-compound, $OH\cdot CPh_2\cdot CH<\begin{matrix}NPh\\|\\NH\end{matrix}$, but this did not give a condensation product with any chromophoric groups.

Magnesium ethyl iodide and ethyl diazoacetate were also brought together, and ethylhydrazine sulphate was obtained by hydrolysing the unpleasant smelling, brown syrup which resulted.

When diazomethane was distilled into magnesium benzyl chloride, an oily product which contained crystals of either the benzylhydrazone of formaldehyde, or benzylhydrazimethylene, was obtained. The *compound*, $C_8H_{10}N_2$, formed stable, white plates, m. p. 124°, whereas a crystalline product obtained by mixing 40% formaldehyde and benzylhydrazine was very unstable. J. C. W.

Organic Silicon Compounds which Liberate Hydrogen from Silicon Hexachloride and Magnesium Methyl Bromide or Iodide. GEOFFREY MARTIN (*Ber.*, 1913, **46**, 3289—3295. Compare this vol., i, 961).—By the action of magnesium methyl bromide on silicon hexachloride, a compound, $Si_6H_6O_{12}Me_2$, is obtained, which yields 102—118 c.c. of hydrogen per gram of substance when decomposed with potassium hydroxide. Under other experimental conditions, compounds $Si_6H_2O_{12}Me_4$, $Si_6HO_{11}Me_5$, and $Si_6H_2O_7Me_8$ are obtained; these yield less and less hydrogen on decomposition as the number of methyl groups increases.

Hexamethylsilicoethane, Si_2Me_6 (Bygden, A., 1912, i, 341), does not yield hydrogen on decomposition, although containing the linking Si—Si. Evidently the characteristic decomposition of silicon

compounds with alkali hydroxide is due to the association of oxygen complexes with the silicon atoms. E. F. A.

The Isolation and Properties of Some Electropositive Groups and their Bearing on the Problem of the Metallic State. CHARLES A. KRAUS (*J. Amer. Chem. Soc.*, 1913, **35**, 1732—1741).—When solutions of mercury alkyl salts in liquid ammonia are electrolysed, the free mercury alkyl group is deposited at the cathode, except in the case of members of the series above C_4H_9Hg, when no deposition takes place. The electrolytic cell used contained small platinum wires as electrodes, the cathode being situated at the bottom of the cell. The free groups deposited as an attenuated, opaque mass, which, by means of pressure, could be brought into a fairly coherent form. They are good conductors of electricity and do not amalgamate with mercury to any extent.

The *mercury methyl group*, $HgCH_3$, was obtained pure from the compound MeHgCl by washing it free from salt with liquid ammonia. Decomposition takes place at ordinary temperatures, with the formation of mercury and mercury methyl, $HgMe_2$; there is appreciable decomposition at $-33°$. The ethyl derivative behaves similarly, but the propyl derivative is less stable. The ethyl mercury group, when compressed, exhibits metallic reflection of a copper colour, whereas the mercury methyl group is black.

Attempts to isolate groups by the electrolysis of liquid ammonia solutions of the following salts were not successful: Me_4SbI, Me_3SI, Ph_2II, $C_5H_{11}HgI$, $C_8H_{17}HgI$, PhHgI, and Me_3SnI.

The bearing of the above results on the metallic state is discussed, and the conclusion drawn that the electrons to which conduction is due in metals are the same electrons which are involved in the common chemical combination of metals with other elements.

T. S. P.

The Optical Activity of Petroleum and its Significance. FRANK W. BUSHONG (*Science*, 1913, **38**, 39—44).—Attention is drawn to the optical activity of the heavy oils. Since the naphthenic acids derived from the petroleum by treatment with alkali during refining are optically active, the activity of the original oil might be attributed to these acids. It does not necessarily follow, however, that the optically active constituents present in these naphthenic acids are identical with those originally present in the petroleum, and there seems good evidence that this is not the case, as both the author and others have found that the heavy oils retain most of their optical activity after treatment with alcoholic potash; still, the optical activity may be due to some extent to these acids. It is probable that the oils contain active hydrocarbons (naphthenes), and it is generally held that the naphthenic acids are oxidation products of these.

[The author's views as to the cause of the activity of petroleum were somewhat misrepresented in an earlier abstract (this vol., i, 969).]

J. C. W.

Distillation of Coal under Reduced Pressure. AMÉ PICTET and MAURICE BOUVIER (*Ber.*, 1913, **46**, 3342—3353; *Compt. rend.*, 1913, **157**, 779—781).—In an earlier paper (Pictet and Ramseyer, A., 1911, i, 850) it has been shown that extraction of coal (Montrambert) with boiling benzene gives a mixture of hydroaromatic hydrocarbons, from which a hexahydrofluorene, $C_{13}H_{16}$, could be isolated; it was also mentioned that distillation of the same coal under reduced pressure produced a similar mixture in which the same hydrocarbon could be detected. As the latter procedure was more rapid and gave better yields, it has now been applied more carefully.

The method was to heat 2—5 kilograms of the coal in a vertical iron retort of approximately 10 litres capacity; the temperature was slowly raised to 450°, whilst the pressure was maintained at a few centimetres of mercury by means of water-pumps. The experiment generally occupied about five hours.

Of the products of the decomposition, the tar only was carefully investigated; the gases were not collected, but were observed to resemble butadiene and isoprene in odour; the water had an acid reaction and contained no ammonium salts; the coke was found to yield still further quantities of combustible gas when heated more strongly. The tar, which amounted to approximately 4% of the coal, was lighter than water, had a brown colour with feeble green fluorescence, and resembled petroleum in odour; it contained no phenols, but a considerable quantity of bases which appeared to be mainly of the secondary type. Careful fractionation under reduced pressure failed to disclose the presence of any solid substances, and oxidation yielded only aliphatic acids, indicating the absence of aromatic hydrocarbons. It is therefore probable that the tar is a mixture of hydroaromatic compounds of the naphthene class.

Decomposition of the crude tar by distillation at ordinary pressure through a red-hot iron tube packed with coke produced a considerable quantity of gas resembling coal gas in odour, and consisting mainly of hydrogen and paraffin hydrocarbons together with water containing much free ammonia and a dark-coloured tar resembling coal-tar in odour. This tar, unlike the original product, contained phenols, bases recalling the odour of pyridine, and aromatic hydrocarbons, amongst which benzene, naphthalene, and anthracene could be identified. It is tentatively suggested that in coal distillation the methane, ammonia, phenols, and aromatic hydrocarbons are not primary products, but are formed by the decomposition of intermediate products represented by the above "vacuum tar."

Treatment of certain fractions of the "vacuum tar" with sodium removes certain hydroxy-compounds (the presence of which had already been indicated by the results of analysis) which exhibit the usual behaviour of alcohols towards alkalis and acyl chlorides. The natural supposition that these alcohols form the origin of the phenolic substances during subsequent decomposition by further heat received no confirmation when they were passed in the vapourous condition through a red-hot tube, the only products being unsaturated hydrocarbons.

The hydrocarbon residues after extracting various fractions with

sodium immediately decolorise cold potassium permanganate solution, and consequently must contain unsaturated hydrocarbons. The latter were removed by the action of fuming sulphuric acid, and the residue again heated with sodium. By repeated fractional distillation the liquid was separated into various portions in the hope of identifying some of the constituents. Decahydronaphthalene was definitely proved to be absent, and a comparison of the compositions and densities of the various fractions with those of corresponding fractions from Caucasian petroleum clearly demonstrated their distinct character. A similar comparison with fractions from Canadian petroleum (which is also known to contain hydrocarbons of the general formula C_nH_{2n}) proved the identity of the fractions containing the hydrocarbons $C_{10}H_{20}$ and $C_{11}H_{22}$. The former of these is very sensitive to most reagents, and generally gives complex reaction products, but by the action of bromine vapour, dibromodurene (?), m. p. 202°, could be obtained; also by distillation over iron oxide at a dull red heat a distillate is obtained, which on nitration yields dinitrodurene (?), m. p. 202°. Although this evidence is not regarded as final, the authors consider themselves justified in identifying the hydrocarbon, $C_{10}H_{20}$, with hexahydrodurene (*s*-tetramethyl*cyclo*hexane), whilst to the hydrocarbon, $C_{11}H_{22}$, they ascribe the structure of a pentamethyl*cyclo*hexane. D. F. T.

Electrolytic Oxidation of Toluene. FRITZ FICHTER (*Zeitsch. Elektrochem.*, 1913, **19**, 781—784).—A suspension of toluene in 2*N*-sulphuric acid is placed in a large cylindrical lead vessel which serves as anode; a cathode consisting of a lead spiral is used. The suspension is vigorously stirred, and a current of 0·01 ampere per sq. cm. of anode is passed through until one-half of the toluene has disappeared. Stopping the process at this point, prevents the destruction of some of the products by further oxidation. The toluene layer on allowing it to settle contains after the oxidation toluquinone and a little benzaldehyde, whilst the aqueous layer contains quinol and phenol.

The process of the reaction proceeds as indicated:

$$CH_3{\cdot}C_6H_5 \begin{array}{l} \nearrow HO{\cdot}C_6H_4{\cdot}CH_3\ (1:2) \longrightarrow \\ \rightarrow HO{\cdot}C_6H_4{\cdot}CH_3\ (1:4) \longrightarrow \\ \searrow C_6H_5{\cdot}CHO \end{array}$$

$$(HO)_2C_6H_3{\cdot}CH_3\ (1:2:5) \longrightarrow CH_3{\cdot}C_6H_3O_2$$

$$HO{\cdot}C_6H_3{\cdot}CHO\ (1:4) \begin{array}{l} \nearrow C_6H_4(OH)_2\ (1:4). \\ \searrow C_6H_5{\cdot}OH \end{array}$$

It is thus obvious that the oxidation occurs mainly in the nucleus (compare also T. Kempf, A., 1901, i, 728; R. Kempf, A., 1911, i, 464). J. F. S.

Transformations of Unsaturated Haloid Compounds. II. Cinnamaldehyde and Phenyl Vinyl Ketone. FRITZ STRAUS and ABRAHAM BERKOW (*Annalen*, 1913, **401**, 121—159. Compare Straus, A., 1912, i, 989).—It has been shown (*loc. cit.*) that the changes R·CO·CH:CHR′ ⟶ R·CH:CH·CO·R′ ⟶ R·CO·CH:CHR′ can be effected by a series of substitutive reactions. The present paper deals with a simple case in which R′ is hydrogen. The conversion of cinnamaldehyde into phenyl vinyl ketone has been accomplished, but the reverse change of the ketone to the aldehyde has revealed unexpected and important peculiarities.

Cinnamaldehyde and phosphorus pentachloride readily yield the normal keto-chloride, cinnamylidene dichloride (*loc. cit.*), an ethereal solution of which reacts with a slight excess (over 1 mol.) of sodium methoxide to form *α-chloro-γ-methoxy-γ-phenyl-Δ^{α}-propene*,

CHCl:CH·CHPh·OMe,

b. p. 111°/18 mm., D_4^{15} 1·0959. The latter is converted in petroleum solution in the presence of calcium chloride into cinnamylidene dichloride by hydrogen chloride, yields cinnamaldehyde by hydrolysis, and is oxidised to α-methoxyphenylacetic acid by potassium permanganate in acetone. *α-Chloro-γ-ethoxy-γ-phenyl-Δ^{α}-propene*, $C_{11}H_{13}OCl$, b. p. 120·5°/12 mm., is prepared similarly. An ethereal solution of cinnamylidene dichloride and *N*-sodium hydroxide ($1\frac{1}{2}$ mols.) yields after a hundred and twenty hours a substance which loses water by distillation in a vacuum, and is converted into *γ-chloro-α-phenylallyl ether*, $(CHCl:CH·CHPh)_2O$, b. p. 127°/18 mm.

The *acetal* of phenyl vinyl ketone, CH_2:CH·CPh$(OMe)_2$, b. p. 85—86°/12 mm., D_4^{15} 0·9887, is obtained by boiling α-chloro-γ-methoxy-γ-phenyl-Δ^{α}-propene with 5% methyl-alcoholic sodium methoxide (2 mols.) for four days. The constitution of the acetal is proved by reduction by colloidal palladium and hydrogen at 2 atmospheres, whereby the *acetal*, b. p. 206—208° or 92—93°/18 mm., of phenyl ethyl ketone is obtained. The hydrolysis of the unsaturated acetal to phenyl vinyl ketone is difficult on account of the instability of the ketone, and has only been effected by means of 5% sulphuric acid at 60—70° in the absence of light.

Phosphorus pentachloride ($1\frac{1}{2}$ mols.) reacts with phenyl vinyl ketone in benzene to form *αγ-dichloro-α-phenyl-Δ^{α}-propene*, CPhCl:CH·CH_2Cl, b. p. 124—125°/16 mm., the constitution of which is proved by the action of ozone, followed by that of water, on the substance in carbon tetrachloride, whereby, amongst other products, benzoic and chloroacetic acids are obtained. The substance reacts with a slight excess (over 1 mol.) of methyl-alcoholic sodium methoxide to form quantitatively *α-chloro-γ-methoxy-α-phenyl-Δ^{α}-propene*, CPhCl:CH·CH_2·OMe, b. p. 131—132°/27 mm., D_4^{22} 1·146, which is reconverted into αγ-dichloro-α-phenyl-Δ^{α}-propene by hydrogen chloride in petroleum in the presence of calcium chloride, and yields benzoic acid by oxidation in acetone with potassium permanganate. By reduction in acetone with colloidal palladium and hydrogen at 2 atmospheres, α-chloro-γ-methoxy-α-phenyl-Δ^{α}-propene is converted into *methyl γ-phenylpropyl ether*,

CH_2Ph·CH_2·CH_2·OMe,

b. p. 207—208° or 92—94°/12 mm., D_4^{15} 0·9990, which has also been prepared from γ-phenylpropyl chloride and an excess of boiling 5% sodium methoxide; *methyl α-phenylpropyl ether*, OMe·CHPhEt, prepared from α-phenylpropyl chloride in a similar manner, has b. p. 183—185° or 76—77°/14 mm., D_4^{15} 0·9216, and a quite different odour.

By boiling for four and a-half to five days with 5% sodium methoxide, α-chloro-γ-methoxy-α-phenyl-Δ^{α}-propene is converted, unexpectedly, into *αγ-dimethoxy-α-phenyl-Δ^{α}-propene*,

$$OMe\cdot CPh\colon CH\cdot CH_2\cdot OMe,$$

b. p. 100—102°/11 mm., D_4^{17} 1·0412, which yields benzoic acid by oxidation in acetone by potassium permanganate, and is reduced by hydrogen and colloidal palladium to *αγ-dimethoxy-α-phenylpropane*, $OMe\cdot CHPh\cdot CH_2\cdot CH_2\cdot OMe$, b. p. 215—217° (decomp.) or 94—95°/15 mm., D_4^{10} 0·9829. The last substance has also been prepared from γ-chloro-α-phenylpropyl alcohol (Fourneau, A., 1907, i, 762); the chlorohydrin in benzene in the presence of calcium bromide is converted by hydrogen bromide into *γ-chloro-α-bromo-α-phenylpropane*, $CHPhBr\cdot CH_2\cdot CH_2Cl$, b. p. 118—120°/20 mm., which is converted by sodium methoxide successively into *γ-chloro-α-methoxy-α-phenylpropane*, $C_{10}H_{13}OCl$, b. p. 110—112°/12 mm., and αγ-dimethoxy-α-phenylpropane. C. S.

p-Nitrophenylethyl Chloride [β-Chloro-4-nitroethylbenzene]. JULIUS VON BRAUN and B. BARTSCH (*Ber.*, 1913, **46**, 3050—3055).—The product obtained by nitrating β-chloroethylbenzene can be separated into two portions, of which one is solid, the other liquid. The former, which may constitute 50% of the mixture, has been shown to be β-chloro-4-nitroethylbenzene (A., 1912, i, 498). The latter is now shown to have a similar constitution, since, on nitration, each substance yields *β-chloro-2-nitro-4-aminoethylbenzene*, which can be further reduced to *β-chloro-2:4-diaminoethylbenzene*, whilst, under the influence of sodium acetate and glacial acetic acid, each substance is transformed into a mixture of *4-nitro-β-acetoxyethylbenzene*, $NO_2\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot OAc$ and *4-nitro-α-acetoxyethylbenzene*,

$$NO_2\cdot C_6H_4\cdot CHMe\cdot OAc,$$

from which, on saponification, the corresponding alcohols are obtained. The formation of the latter substance probably depends on the intermediate production of 4-nitrostyrene, $NO_2\cdot C_6H_4\cdot CH\colon CH_2$. A similar reaction is not observed to any extent with β-chloroethylbenzene or γ-chloronitropropylbenzene.

β-Chloro-2-nitro-4-aminoethylbenzene, m. p. 84°, is obtained by the action of nitric and sulphuric acids on the hydrochloride of β-chloro-4-aminoethylbenzene obtained from solid β-chloro-4-nitroethylbenzene (compare A., 1912, i, 498). The *hydrochloride*, m. p. 190°, and the *benzoyl* derivative, m. p. 130°, have been prepared. Identical products are obtained from liquid β-chloro-4-nitroethylbenzene. Reduction of β-chloro-2-nitro-4-aminoethylbenzene (whether obtained from solid or liquid β-chloro-4-nitroethylbenzene) by means of stannous chloride gives *β-chloro-2:4-diaminoethylbenzene hydrochloride*, m. p. 256°, after darkening at 250°. The colour reactions of this salt greatly

resemble those of tolylenediamine. The free base has not been isolated.

When solid β-chloro-4-nitroethylbenzene is heated with sodium acetate and glacial acetic acid and the product fractionated under diminished pressure, two substances are obtained, b. p. 189°/16 mm. and 161—163°/16 mm. respectively. The former consists of 4-nitro-β-acetoxyethylbenzene [4-nitrobenzylcarbinyl acetate], and is converted by saponification into *4-nitro-β-hydroxyethylbenzene* [*4-nitrobenzylcarbinol*], $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot OH$, b. p. 177°/16 mm. (*benzoyl* derivative is oily; m-*nitrobenzoyl* derivative, m. p. 64—65°; *phenylurethane*, m. p. 127—128°), the constitution of which is proved by its conversion into β-chloro-4-nitroethylbenzene, 66% of which is obtained in the solid form. The fraction of lower b. p., consisting of α-acetoxy-4-nitroethylbenzene, yields the corresponding *alcohol*, b. p. 158°/16 mm. (m-*nitrobenzoyl* derivative, m. p. 152—153°; *phenylurethane*, m. p. 205—206°), which, on oxidation, gives p-nitrobenzoic acid. If the above operations are repeated with liquid β-chloro-4-nitroethylbenzene, the same products result and in the same yields.

β-Chloroethylbenzene, when treated with sodium acetate and acetic anhydride, gives an 85% yield of benzylcarbinyl acetate, b. p. 232°, which, on saponification, regenerates the alcohol. About 15% of *α-acetoxyethylbenzene*, b. p. 222°, is simultaneously produced, which loses some acetic acid on distillation and is saponified to phenylmethylcarbinol, b. p. 204°.

γ-Acetoxy-4-nitropropylbenzene, b. p. 210—212°/21 mm. (slight decomp.), is obtained as sole product of the action of acetic acid and sodium acetate on γ-chloro-4-nitropropylbenzene. H. W.

Spectrochemical Notes. I. Hydrated Naphthalenes. II. Spectrochemical Behaviour of Acenaphthene Derivatives. III. Haworth's Dimethyl*cyclo*hexadiene. KARL VON AUWERS (*Ber.*, 1913, **46**, 2988—2995).—Δ^1-Dihydronaphthalene and Δ^2-dihydronaphthalene (Straus and Lemmel, this vol., i, 256) have $D_4^{18 \cdot 2}$ 0·9982, $n_D^{18 \cdot 1}$ 1·58326, and $D_4^{32 \cdot 7}$ 0·9928, $n_D^{32 \cdot 7}$ 1·55489 respectively.

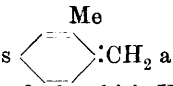
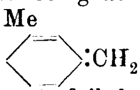
The 1 : 2 : 3 : 4-tetrahydronaphthalene obtained by von Braun and Deutsch (A., 1912, i, 435) is apparently not a homogeneous product, but the specimens obtained by Willstätter and King (this vol., i, 353) and by Straus and Lemmel (*loc. cit.*) agreed together in their properties, namely, $D_4^{17 \cdot 6}$ 0·9738, $n_D^{17 \cdot 6}$ 1·54529.

Decahydronaphthalene (Willstätter and King, *loc. cit.*) gave $D_4^{18 \cdot 1}$ 0·8951, $n_D^{18 \cdot 0}$ 1·48035.

A comparison of the refractive indices for various wave-lengths indicates that, of the above substances, Δ^1-dihydronaphthalene alone has high exaltation of specific refraction and dispersion; *cyclo*-hexadiene is remarkable for showing a slight depression, a phenomenon which has also been observed with *cyclo*hexene. Tetrahydronaphthalene gives results in accord with those expected for a di-substituted benzene derivative, and decahydronaphthalene is approximately normal.

In connexion with the work of Crompton and Smyth (T., 1913, **103**, 1302), who come to the decision that acenaphthene and its

mono-halogen derivatives are optically normal, attention is drawn to the fact that their calculations are made with the molecular refraction of naphthalene as a standard. As this substance exhibits a marked exaltation, it follows that the acenaphthene compounds are also optically exalted.

In reference to the two compounds described as dimethyl*cyclo*-hexadienes (Haworth, T., 1913, **103**, 1242), one of which has already been prepared (Murawski, *Diss.*, Greifswald, 1911), the author, on optical and also chemical grounds (compare Auwers and Peters, A., 1910, i, 826), regards the substances as being at least mainly composed of the substances  and  respectively. 1 : 3-*Dimethyl*cyclo-Δ^1-*hexen*-3-*ol*, which Haworth failed to isolate as the intermediate product in the preparation of the latter of the above two substances, can be obtained from 1-methyl*cyclo*-Δ^1-hexen-3-one by the action of magnesium methyl iodide; it has b. p. 75°/15 mm., $D_4^{16\cdot4}$ 0·9336, $n_D^{17\cdot5}$ 1·47711. D. F. T.

Organic Radicles. XVIII. Ditertiary Hydrazines. Heinrich Wieland and Carl Müller (*Annalen*, 1913, **401**, 233—243).—The dissociation of tetra-anisylhydrazine in solution into the free radicles $\cdot N(C_6H_4\cdot OMe)_2$ (A., 1912, i, 907) is found to be in harmony with Piccard's colorimetric dilution law (A., 1911, ii, 561).

An interesting contribution to the chemistry of triphenylmethyl is recorded. When heated in boiling *m*-xylene, triphenylmethyl is converted into triphenylmethane and *p*-benzhydryltetraphenylmethane. In boiling *o*-xylene in an atmosphere of carbon dioxide, however, the products are triphenylmethane and a *triphenyl*-o-*xylylmethane*, $CPh_3\cdot C_6H_3Me_2$, m. p. 165—168°, colourless leaflets. In boiling *p*-xylene, similar results are obtained, triphenylmethane and *triphenyl*-p-*xylylmethane*, m. p. 158—159°, long prisms, being formed. These two hydrocarbons do not exhibit halochromy and, like tetraphenylmethane itself, develop intense yellow colorations with concentrated sulphuric acid and a trace of potassium dichromate.

Triphenylmethyl in benzene and triphenylmethyl peroxide in glacial acetic acid are reduced to triphenylmethane by hydrogen and palladium black. Triphenylmethyl and diphenylketen do not react in benzene at 60—70°. C. S.

Constitution and Colour. III. Friedrich Kehrmann (*Ber.*, 1913, **46**, 3036—3040. Compare A., 1908, i, 699, 993).—The author gives a further explanation of his views on this subject. In the formation of salts from phenazine, phenanthraquinone and similar substances, where the change is accompanied by a marked change in colour, the author is of opinion that the chromophore undergoes modification, for example, by an increase in the valency of one of the elements (nitrogen, oxygen, etc.), or by a change from the ortho- to the para-configuration or vice-versâ.

In reference to the views of Willstätter and Piccard (A., 1908, i, 475), the author draws attention to a constitutive characteristic common

to the coloured salts of the triphenylmethane class and to Wurster's salts; both classes have the auxochrome outside the quinonoid portion of the molecule, so that both may, in a wide sense, be regarded as of meriquinonoid type. D. F. T.

Double Chlorides of Ferric and Ferrous Chloride with Some Aromatic Bases. RAPHAEL MONROE MCKENZIE (*Amer. Chem. J.*, 1913, **50**, 308—335).—A number of double chlorides of ferrous and ferric iron with the hydrochlorides of aniline *o*-toluidine, *m*-toluidine, and *p*-toluidine have been prepared by adding the constituent substances together in hydrochloric acid solution, and evaporating over sulphuric acid and solid potassium hydroxide.

The following compounds are described: $FeCl_3.2NH_3PhCl$, crystallising in stout, green needles; $FeCl_3,2NH_3PhCl,H_2O$, crystallising in long, thin, very dark green needles; $FeCl_3,6NH_3PhCl$, crystallising in long, thin, orange-yellow, silky needles; $FeCl_3,6NH_3PhCl,2H_2O$, crystallising in orange needles; $FeCl_3,6NH_3(C_7H_7)Cl,3H_2O[1:2]$, forming brownish-yellow needle clusters; $FeCl_3,2NH_3(C_7H_7)Cl[1:3]$, forming shining yellow plates; $FeCl_3,3NH_3(C_7H_7)Cl[1:3]$: this substance is a viscid, fuming mass which is very deliquescent and could not be crystallised; $FeCl_3,3NH_3(C_7H_7)Cl[1:4]$: forming lustrous, red prisms or plates; $FeCl_2,2NH_3PhCl,2H_2O$, separates from hydrochloric acid in light yellow needles; $FeCl_2,3NH_3(C_7H_7)Cl,6H_2O[1:2]$, crystallising in long, fine, yellow needles, and $FeCl_2,6NH_3(C_7H_7)Cl,HCl,xH_2O[1:2]$: this salt was prepared in the absence of air. J. F. S.

Quaternary Ammonium Salts from Trimethylamine and Arylsulphonyl Chlorides. DANIEL VORLÄNDER and OTTO NOLTE (*Ber.*, 1913, **46**, 3212—3228. Compare Kauffmann and Vorländer, A., 1910, i, 822).—When trimethylamine in aqueous solution is shaken with benzenesulphonyl chloride, a quaternary salt is formed, characterised by forming a sparingly soluble platinichloride which allows of the separation from trimethylammonium platinichloride (compare A., 1910, i, 822). *Benzenesulphonyltrimethylammonium chloride*, $SO_2Ph\cdot NMe_3Cl$, obtained by saturating the platinichloride with hydrogen sulphide, crystallises in long, flat colourless prisms, m. p. 185° (decomp.), which are optically anisotropic. The *platinichloride*, $(PhSO_2\cdot NMe_3)_2PtCl_6$, forms doubly refractive platelets or small, flat prisms, m. p. 215—220° (decomp.). The *aurichloride*, $SO_2Ph\cdot NMe_3\cdot AuCl_4$, yields yellow, doubly refractive needles, m. p. 194—200°. The *picrate* crystallises in splendid, yellow, anisotropic plates and stellate aggregates, m. p. 137°. The *dichromate* is characterised by doubly refractive, orange-yellow crystals, m. p. 202°. The *perchlorate* forms colourless needles, m. p. 145°. The colourless needles of the *stannichloride* have decomp. 245°. The *thallichloride* likewise forms colourless, double refractive needles.

*Toluene-*p*-sulphonyltrimethylammonium platinichloride* separates in optically anisotropic platelets and pointed needles. The *dichromate* forms doubly refractive, orange-red plates, decomp. 195°.

Cryptocrystalline α- and β-*naphthalenesulphonyltrimethylammonium platinichlorides* were obtained.

Similar salts were not obtained from triethyl- or tripropyl-amine or from dimethyl- or diethyl-aniline.

The existence of these neutral benzenesulphonylammonium salts stable towards water, which yet contain the very strongly acid benzenesulphonyl radicle, proves that the salt-forming function of the ammonium does not depend on the positive and negative nature of the radicles. E. F. A.

Catalysis on the Basis of Work with Imino-esters. The Problem of Saponification and Esterification. JULIUS STIEGLITZ (*J. Amer. Chem. Soc.*, 1913, **35**, 1774—1779).—A theoretical consideration of the mode of action of acids in accelerating the formation or hydrolysis of esters (compare A., 1908, ii, 29, 167, 472; this vol., ii, 396). Although purely mathematical considerations fail to decide with which oxygen compound (for example, acid or alcohol in esterification) the complex oxonium ion is produced, some decision can be drawn by analogy to the conversion of imino-esters by ammonia or amines into amidines which is also accelerated by acid. In this case the change may occur by interaction of the ammonium ion with the free imino-ester or of the imino-ester cation with free ammonia, according to the alternative schemes: $CPh(:NH)\cdot OMe + H\cdot NH_3^+ \longrightarrow$
$CPh\cdot C(NH_2)(OMe)\cdot NH_3^+ \longrightarrow CPh(:NH)\cdot NH_3^+ + MeOH$
or $CPh(OMe):NH_2^+ + HNH_2 \longrightarrow CPh(NH_2)(OMe)NH_3^+ \longrightarrow$
$CPh\cdot C(:NH)NH_3^+ + MeOH$. According to the latter scheme the salts of tertiary amines should be unable to form amidines from imino-esters, and according to Pinner this is actually the case.

The conclusion is therefore to be drawn that in the formation of amidines from imino-esters and amines in the presence of acids, action occurs between the amine (or ammonia) and the ion resulting from the additive compound of the imino-ester with the acid. Extending this analogy to the hydrolysis or formation of esters, it is in these cases most probable that the action is of a hydroxide, water, or alcohol on the oxonium ion of the ester or of the organic acid. D. F. T.

Hydrates of Calcium Oxide and their Molecular Compounds. IV. Compounds of Hydrated Calcium Oxide with Phenols. FEDOR F. SELIVANOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1535—1556. Compare this vol., ii, 214, 406, 407).—The following compounds of calcium hydroxide with phenol have been prepared.

The *diphenolate*, $CaO,H_2O,2PhOH$, apparently analogous to the barium compound obtained by Laurent (*Ann. Chim. Phys.*, 1841, [iii], **3**, 203), is a colourless, hygroscopic compound, and is decomposed by carbon dioxide, although it remains unchanged in a sealed, exhausted tube. It is decomposed by water, with liberation of phenol and calcium hydroxide, a similar action being brought about by ether, benzene, alcohol, etc. On this ground the compound is regarded as possessing the constitution $Ca(OH)_2,2Ph\cdot OH$, which is confirmed by the mode of dissociation of the diphenolate in a vacuum; the phenol is hence present as phenol of crystallisation, the water possessing a constitutional character. When heated

at 105—110°, the diphenolate is decomposed into phenol, water, and the *monophenoxide*, HO·Ca·OPh, in which the acid properties of the phenol are very faint, so that water effects decomposition into calcium hydroxide and phenol.

The diphenolate forms various hydrates, which may be expressed by the general formula $2Ca(OH)_2,4PhOH,(2n+1)H_2O$, where $n=$ 0, 1, 2, 3 or 4.

The diphenolate is capable of combining with phenol, giving the *tetraphenolate*, $Ca(OH)_2,4PhOH$, and the *hexaphenolate*,

$$Ca(OH)_2,6PhOH.$$

Calcium hydroxide and phenol are also able to form hygroscopic solid solutions, which separate in needles apparently of the rhombic system, and do not dissolve in water, but give with it an oily and an aqueous layer (compare Runge, *Ann. Phys. Chem.*, 1834, **31**, 69; **32**, 308) exhibiting an alkaline reaction. Similar solid solutions are formed by calcium hydroxide and thymol and by magnesium hydroxide and phenol. T. H. P.

Introduction of Selenium into Organic Compounds. EMIL FROMM and KARL MARTIN (*Annalen*, 1913, **401**, 177—188).—Selenium, unlike sulphur, does not react with stilbene or ethyl cinnamate even by prolonged heating at high temperatures. Contrary to Bauer's statement (this vol., i, 263), 1-phenylbenzoselenazole is obtained in 15—20% yield by vigorously boiling benzanilide and selenium. It is not ruptured by fusion with potassium hydroxide, and forms a *tetrabromide*, $C_{13}H_9NBr_4Se$, m. p. 134°, brick-red powder, and a *tetraiodide*, $C_{13}H_9NI_4Se$, m. p. 84°, greenish-black, metallic crystals, with bromine and with iodine in cold and in boiling chloroform respectively. The four halogen atoms are very easily removed, so the substances probably have the constitution: $C_6H_4<\begin{matrix}NX_2\\SeX_2\end{matrix}>CPh$.

Equivalent quantities of potassium selenocyanate and *o*-nitrobenzyl chloride in boiling alcohol yield *o-nitrobenzyl selenocyanate*, $C_8H_6O_2N_2Se$, m. p. 77°, decomp. 215°, pale yellow crystals. *o*- and *p*-Chloronitrobenzenes do not react similarly, but 1-chloro-2:4-dinitrobenzene rapidly yields 2:4-*dinitrophenyl selenocyanate*, m. p. 163°, yellow crystals, which can be crystallised from concentrated nitric acid. 2:4-Dinitrophenyl selenocyanate and boiling aqueous alkalis yield a brownish-red solution containing the 2:4-dinitrophenylselenol, from which by atmospheric oxidation *di*-2:4-*dinitrophenyl diselenide*, $C_{12}H_6O_8N_4Se_2$, m. p. 264—265°, yellow crystals, is precipitated.

Dibenzyl diselenide, like dibenzyl disulphide (this vol., i, 357), reacts additively with bromine and iodine in chloroform to form a *tetrabromide*, $C_{14}H_{14}Br_4Se_2$, m. p. 137°, red powder, and *tetraiodide*, m. p. 98°, dark green, metallic crystals; the additive compounds react with silver oxide or acetate, but are thereby extensively changed, and, unlike the corresponding disulphides (*loc. cit.*), do not yield the diselenoxide.

Seleno-ethers are readily obtained by boiling dibenzyl diselenide with alcoholic sodium ethoxide (2 equiv.) and treating the resulting brownish-red solution of the selenol with an alkyl haloid. Thus

benzyl chloride yields Jackson's dibenzyl selenide, m. p. 45·5°, whilst methyl iodide, ethyl iodide, and ethylene dibromide yield respectively benzyl methyl selenide, benzyl ethyl selenide, and *dibenzyl ethylene selenide*, $C_2H_4(Se\cdot C_7H_7)_2$, m. p. 68—69°, pale yellow needles. Dibenzyl selenide reacts in chloroform with bromine or iodine to form the *dibromide*, $SeBr_2(C_7H_7)_2$, m. p. 84°, red powder, and *di-iodide*, m. p. 97°, violet crystals, from which, however, the selenoxide cannot be obtained by the action of alkalis, or silver oxide or acetate.

The so-called dibenzyl selenide nitrate obtained by Jackson in 1875 by the action of nitric acid on dibenzyl selenide proves to be *tribenzylselenonium nitrate*, $(C_7H_7)_3Se\cdot NO_3$, decomp. 102—103°; the corresponding *chloride*, $C_{21}H_{21}ClSe$, has m. p. 92°. C. S.

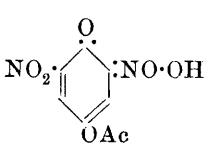
Nitroquinhydrones. M. M. RICHTER (*Ber.*, 1913, **46**, 3434—3438).—The author has previously pointed out (A., 1911, i, 136) that the introduction of negative groups into the quinone molecule diminishes the basic properties of the oxygen atom, and thus reduces the tendency to quinhydrone formation. In agreement with this view it is found that nitroquinol combines with *p*-benzoquinone to form an unstable quinhydrone, whilst in the case of 2 : 6-dinitroquinol the ability to give rise to quinhydrones has completely disappeared.

Nitroquinhydrone, $C_6H_4O_2,C_6H_3(OH)_2\cdot NO_2$, prepared by evaporating an ethereal solution of *p*-benzoquinone and nitroquinol in the absence of moisture, crystallises in small needles or stout, obliquely cut prisms. It is almost black, and has m. p. 89—90°, with slight previous decomposition at 84°. On exposure to air, it loses *p*-benzoquinone, yielding nitroquinol.

By nitrating the diacetyl derivative of quinol, Hesse (A., 1880, 317) and Nietzki (A., 1883, 465) have obtained a dinitro-derivative, m. p. 96°, which they consider to be the diacetyl derivative of 2 : 6-dinitroquinol. The author finds, however, that the substance is not a diacetate, but a monoacetyl derivative, one of the acetyl groups being removed during the nitration.

A similar elimination of an acetyl group occurs during the nitration of the diacetyl derivative of toluquinol.

On account of its yellow colour, the monoacetate is considered to be an aci-2 : 6-*dinitro*-4-*acetoxyphenol* of the annexed constitution. It has m. p. 95·6°, and on treatment with metallic nitrites in aqueous solution yields salts, which decompose explosively when heated. The *sodium* salt forms red needles, containing water (3 mols.), which is lost on exposure to sunlight, the anhydrous salt being orange in colour. The golden-yellow *barium* salt and red *potassium* salt (needles) are also described.



2 : 6-*Dinitro*-1 : 4-*diacetoxybenzene*, $C_6H_2(NO_2)_2(OAc)_2$, prepared by heating the preceding monoacetyl derivative or its sodium and potassium salts with acetic anhydride, crystallises in slender, colourless needles, m. p. 135°.

2 : 6 - *Dinitro* - 1 - *benzoyloxy*-4-*acetoxybenzene*, $OAc\cdot C_6H_2(NO_2)_2\cdot OBz$, obtained by the action of benzoyl chloride on the monoacetate in

benzene solution in the presence of pyridine, forms small, white needles, m. p. 128—129°.

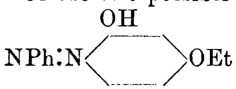
2 : 6-Dinitroquinol and its monoacetyl derivative possess pronounced acid properties, and combine with aniline, toluidine, benzidine, diphenylformamidine, carbamide hydrazine and pyridine to form coloured additive compounds.

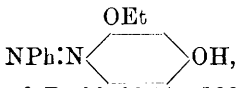
The additive *compound* of aniline with 2 : 6-dinitroquinol crystallises in dark red needles, m. p. 102—103° (decomp.).

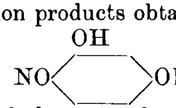
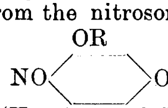
The additive *compound* of aniline with *aci*-2 : 6-dinitro-4-acetoxyphenol forms orange needles, m. p. 120° (decomp.). F. B.

The Constitution of the Monomethyl and Monoethyl Ethers of Aminoresorcinol from the Monomethyl and Monoethyl Ether of Benzeneazo-4-resorcinol.

FERDINAND HENRICH and H. BIRKNER (*Ber.*, 1913, **46**, 3380—3384).—The constitution of the ethyl ether obtained by the action of ethyl iodide on the potassium salt of benzeneazo-4-resorcinol has never been finally settled (Will and Pukall, A., 1887, 660). Of the two possible formulæ,



and , the former is rendered more probable by the work of Bechhold (A., 1889, 1155) on the corresponding methyl ether, but the evidence is far from satisfactory.

The reduction products obtained from the nitrosoresorcinol ethers of the structure  and , where R represents the methyl or ethyl radicle (Henrich and Rhodius, A., 1902, i, 447), will by comparison with the reduction products of the above azo-compounds fix definitely the constitution of the latter. Experiment shows that it is the *o*-amino-ether which is identical with the corresponding ether above, so that the first of the two possible formulæ for the ethyl (and methyl) ether is the correct one, alkylation having occurred in the para-position.

Improved methods are described for the methylation (by methyl sulphate) and ethylation of the benzeneazoresorcinol. D. F. T.

Action of Organomagnesium Derivatives on Trialkylacetophenones.

(Mme.) PAULINE RAMART-LUCAS (*Ann. Chim. Phys.*, 1913, [viii], **30**, 349—432).—The reaction between magnesium methyl, ethyl, phenyl, or benzyl haloid and trimethylacetophenone proceeds normally and leads to the formation of the tertiary alcohol,

$$CMe_3\cdot CPhR\cdot OH.$$

Such carbinols do not exhibit ordinary alcoholic functions, and are readily dehydrated, yielding an unsaturated hydrocarbon. The individual compounds have been described (A., 1910, i, 378; 1911, i, 636; 1912, i, 351, 449). Magnesium propyl or *iso*propyl iodide acts

as a reducing agent to trimethylacetophenone and converts it into the corresponding secondary alcohol.

α-Phenyl-α-anisyl-ββ-dimethylpropan-α-ol,

$$\mathrm{CMe_3{\cdot}CPh(OH){\cdot}C_6H_4{\cdot}OMe},$$

m. p. 67—68°, b. p. 210—215°/15 mm., and *α-phenyl-α-phenetyl-ββ dimethylpropan-α-ol*, b. p. 215—220°/15 mm., have been prepared from trimethylacetophenone and magnesium anisyl or phenetyl bromide. The following alcohols have been obtained in a similar manner from αα-diethylpropiophenone or triethylacetophenone; the yields are generally smaller than those obtained with trimethylacetophenone. *β-Phenyl-γ-methyl-γ-ethylpentan-β-ol*, $\mathrm{CMeEt_2{\cdot}CPhMe{\cdot}OH}$, b. p. 83—84°/3 mm., D_4^{25} 0·9781, n_α 1·51692, n_D 1·52061, n_β 1·52986; *αα-diphenyl-β-methyl-β-ethylbutan-α-ol*, $\mathrm{CMeEt_2{\cdot}CPh_2{\cdot}OH}$, b. p. 200—205°/13 mm., D_4^{25} 0·95005, n_α 1·56573, n_D 1·57206; by distillation at the ordinary pressure, the latter decomposes into benzophenone and γ-methylpentane. *αβ-Diphenyl-γ-methyl-γ-ethylpentan-β-ol*,

$$\mathrm{CMeEt_2{\cdot}CPh(OH){\cdot}CH_2Ph},$$

b. p. 200—202°/15 mm., D_4^{25} 0·9791, n_α 1·55249, n_D 1·55696, n_β 1·57944, yields deoxybenzoin and γ-methylpentane by distillation under atmospheric pressure. *β-Phenyl-γγ-diethylpentan-β-ol*,

$$\mathrm{CEt_3{\cdot}CPhMe{\cdot}OH},$$

b. p. 160°/18 mm., and *αα-diphenyl-ββ-diethylbutan-α-ol*,

$$\mathrm{CEt_3{\cdot}CPh_2{\cdot}OH},$$

m. p. 47—48°, b. p. 215—220°/17 mm., are described; the latter decomposes quantitatively into benzophenone and γ-ethylpentane by distillation at the ordinary pressure.

The preceding tertiary alcohols have been dehydrated by heating them with formic, oxalic, or dilute sulphuric acid, or, best, with a mixture of acetic anhydride and acetyl chloride; in some cases, the constitutions of the resulting hydrocarbons have been established by the examination of their products of oxidation. Alcohols which contain the group $\mathrm{OH{\cdot}\dot{C}Ph{\cdot}CH{<}}$ yield hydrocarbons of the type $\mathrm{{\cdot}CPh{:}C{<}}$, whilst alcohols which contain the group $\mathrm{{>}CMe{\cdot}CPh_2{\cdot}OH}$ apparently yield a mixture of hydrocarbons of the types $\mathrm{{>}C\overset{CH_2}{\diagup\!\!—\!\!\diagdown}CPh_2}$ and $\mathrm{{>}CPh{\cdot}CPh{:}CH_2}$; hydrocarbons of the latter type are produced owing to an intramolecular transformation preceding dehydration. β-Phenyl-γγ-dimethyl-Δ^α-butene, $\mathrm{CMe_3{\cdot}CPh{:}CH_2}$, b. p. 88—92°/15 mm., D_4^{25} 0·8839, n_α 1·49708, n_D 1·50133, n_β 1·51185, n_γ 1·52106, yields acetophenone or trimethylacetophenone by oxidation by chromic and acetic acids or by acidified potassium permanganate respectively. *γ-Phenyl-δδ-dimethyl-Δ^β-pentene*, $\mathrm{CMe_3{\cdot}CPh{:}CHMe}$, b. p. 91—93°/12 mm., D_4^{25} 0·9064, n_α 1·51100, n_D 1·51550, n_β 1·52710, n_γ 1·53776, yields trimethylacetophenone by oxidation. The dehydration of αα-diphenyl-γγ-dimethylpropan-α-ol yields a *substance*, b. p. 159—160°/11 mm., D_4^{25} 1·0031, n_D 1·57589, which is probably a mixture of 1 : 1-diphenyl-2 : 2-dimethyl*cyclo*propane and 1 : 2-diphenyl-1 : 2-dimethyl*cyclo*propane or βγ-diphenyl-γ-methyl-Δ^α-butene, since it yields both acetophenone and benzophenone by oxidation (A., 1912, i, 449). *αβ-Diphenyl-γγ-dimethyl-Δ^α-butene*, $\mathrm{CMe_3{\cdot}CPh{:}CHPh}$, b. p. 164—165°/11 mm., yields benzoic

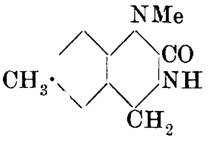
acid, trimethylacetophenone, and a *substance*, $C_{20}H_{20}O$, m. p. 131°, by oxidation. The dehydration of α-phenyl-α-anisyl-ββ-dimethylpropan-α-ol yields a liquid, b. p. 188—189°/15 mm., which is probably a mixture, since its products of oxidation contain *p*-anisic acid and *p*-methoxybenzophenone. Similar remarks apply to the liquid, b. p. 198—200°/15 mm., obtained by the dehydration of α-phenyl-α-phenetyl-ββ-dimethylpropan-α-ol. *αβ-Diphenyl-γ-methyl-γ-ethyl-Δ^{α}-pentene*, $CMeEt_2$·CPh:CHPh, b. p. 175—180°/12 mm., D_4^{25} 0·9791, n_{α} 1·56110, n_D 1·56671, n_{β} 1·58131, n_{γ} 1·59467, yields benzoic acid, deoxybenzoin, and αα-diethylpropiophenone by oxidation. *β-Phenyl-γγ-diethyl-Δ^{α}-pentene*, CEt_3·CPh:CH_2, b. p. 130—132°/15 mm., yields acetophenone and triethylacetophenone by oxidation. αα-Diphenyl-ββ-diethylbutan-α-ol is the only alcohol of the whole series which is not dehydrated by heating with acetic anhydride and acetyl chloride; the effect of this reagent, like that of boiling, is to decompose the alcohol into benzophenone and γ-ethylpentane.

Further attempts have been made to ascertain the constitution of the acid, $C_{17}H_{18}O_2$, m. p. 173° (*chloride*, $C_{16}H_{17}$·COCl, m. p. 95—96°; *amide*, m. p. 149°), obtained ultimately from diphenyl-ψ-butylcarbinol (A., 1912, i, 623). From its method of formation the acid might be αβ-diphenyl-α-methylbutyric acid, ββ-diphenyl-αα-dimethylpropionic acid, or αα-diphenyl-β-methylbutyric acid; it is certainly not the first acid (*loc. cit.*). The last acid has been synthesised by the action of sodamide, followed by that of *iso*propyl iodide, on diphenylacetonitrile in boiling benzene; the resulting *αα-diphenyl-β-methylbutyronitrile*, CPh_2Pr^{β}·CN, b. p. 193—195°/15 mm., is hydrolysed by acetic and hydrochloric acids at 180°, whereby are produced *αα-diphenyl-β-methylbutyric acid*, $CPh_2Pr^{\beta}\cdot CO_2H$, m. p. 166°, its *anhydride*, $C_{34}H_{34}O_3$, m. p. 162—163°, and a *substance*, $C_{16}H_{16}O_2$, m. p. 109—110°. The acid, $C_{17}H_{18}O_2$, m. p. 173°, therefore, is not αα-diphenyl-β-methylbutyric acid, neither is it ββ-diphenyl-αα-dimethylpropionic acid, m. p. 134—135°, which has been synthesised by Nef. C. S.

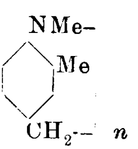
Tertiary Derivatives of *o*- and *p*-Aminobenzyl Alcohol. II. JULIUS VON BRAUN, O. KRUBER, and E. AUST (*Ber.*, 1913, **46**, 3056—3069).—It has been previously shown (A., 1912, i, 968) that the group $-CH_2$·OH can be introduced into tertiary aromatic amines by the use of an excess of formaldehyde. The present communication deals (1) with the reactivity of the tertiary, basic groups; (2) the possibility of replacing the hydrogen atoms of the benzene nucleus, and (3) the capacity for condensation of the hydroxyl group present in the side-chain.

I. Tertiary aminobenzyl alcohols cannot be de-alkylated by means of cyanogen bromide, since the hydroxy-group is also affected. If the latter is protected, however, dealkylation is readily effected. Thus, when 6-dimethylamino-3-methylbenzyl acetate is treated with cyanogen bromide at the ordinary temperature during several days, *6-cyanomethylamino-3-methylbenzyl acetate*, CN·NMe·C_6H_3Me·CH_2·OAc, b. p. 210°/10 mm., is obtained, whilst, in the same manner, the corresponding *cyano*-compound, b. p. 213—216°/11 mm., is prepared from

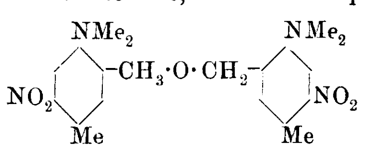
4-dimethylamino-3-methylbenzyl acetate. Secondary aminobenzyl alcohols cannot be prepared by saponification of these compounds when the $-CH_2 \cdot OH$ is in the ortho- or para-position to the cyano-group. When 6-cyanomethylamino-3-methylbenzyl acetate is boiled with aqueous alcoholic sulphuric acid, a *base*, $C_{10}H_{12}ON_2$, b. p. 166—168°/8 mm., m. p. 59—60°, is obtained (*platinichloride*, m. p. 214°), which is probably a quinoxaline derivative of the annexed formula.



Under similar conditions, the cyano-group of 4-cyanomethylamino-3-methylbenzyl acetate is not replaced; concentrated hydrochloric acid at 120°, however, forms an amorphous *product*, which softens at 70°, and has m. p. 76—80°. It appears to be an anhydro-product of the secondary base (annexed formula), since it combines with dimethylaniline in hot, faintly acid solution to form *trimethyldiaminophenyltolylmethane*, m. p. 55°. That 4-*methylamino*-3-*methylbenzyl alcohol* is capable of existence in the free state (unlike methyl amino- and ethylamino-benzyl alcohols) is proved by its isolation from the products of the action of a large excess of formaldehyde on monomethyl-*o*-toluidine. It is a yellow oil, b. p. 130—132°/8 mm., which yields a *picrate*, m. p. 112°, and a platinichloride, reddish-yellow crystals, m. p. 173°.

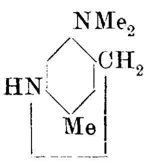


II. 4-*Nitro*-6-*dimethylamino*-3-*methylbenzyl alcohol*, b. p. 191—192°/8 mm., m. p. 51° (*platinichloride*, m. p. 198°; *picrate*, m. p. 153°), is formed when a mixture of nitric and sulphuric acids is slowly added to a solution of 6-dimethylamino-3-methylbenzyl alcohol in concentrated sulphuric acid, the temperature being kept at 0° during two hours and the mixture subsequently being allowed to remain for three hours at the ordinary temperature. Should the temperature be allowed to rise, considerable quantities of a substance are formed which can be isolated in the form of its sparingly soluble *sulphate*. The free *base* (annexed formula) has m. p. 136°, and is not hydrolysed by prolonged warming with $2N$-sulphuric acid. The *picrate* has m. p. 154°. 6-*Nitro*-4-*dimethylamino*-3-*methylbenzyl alcohol*, b. p. 204—208°/11 mm. (slight decomp.), m. p. 64—65° (*platinichloride*, reddish-yellow, crystalline powder), is similarly prepared from 4-dimethylamino-5-methylbenzyl alcohol.



4-Nitro-6-dimethylamino-3-methylbenzyl alcohol is readily reduced by stannous chloride and hydrochloric acid to 4-*amino*-6-*dimethylamino*-3-*methylbenzyl alcohol*, white crystals, m. p. 103—104°. The base is completely decomposed by distillation, yields a *picrate*, m. p. 179°, a viscous *acetyl* compound, and a *monobenzoyl* compound, m. p. 135°. It is slowly diazotised by nitrous acid. It combines with allylthiocarbimide, yielding the crystalline *compound*, $NMe_2 \cdot C_6H_2Me(CH_2 \cdot OH) \cdot NH \cdot CS \cdot NH \cdot C_3H_5$, m. p. 178°, and with salicylaldehyde, yielding the *salicylidene* compound, m. p. 70°.

Although the composition of the base seems, therefore, to be firmly established, certain indications lead the authors to consider that there is some tendency for it to pass into the *anhydro*-compound (annexed formula) in the presence of aqueous mineral acids; thus the base, in itself colourless, dissolves in aqueous acid with a



n reddish-yellow coloration, whilst the colourless *hydrochloride* becomes yellow on exposure to moist air; further, the base, like the readily dehydrated *p*-aminobenzyl alcohol and its monoalkyl derivatives and unlike the tertiary amino-alcohols in which dehydration is impossible, readily condenses with aromatic compounds in faintly acid solution to form derivatives of diphenylmethane. So with dimethylaniline, it yields 4-*amino*-2 : 4′-*tetramethyldiamino*-3-*methyldiphenylmethane*, m. p. 92° (*benzoyl* derivative, m. p. 134°), whilst the corresponding *compound* from aniline is oily and gives a *diacetyl* derivative, m. p. 207°.

III. The condensation of dimethylaminobenzyl alcohol and its homologues with dimethylaniline and its homologues, which does not occur to an appreciable extent with aqueous acid solution, can be effected at higher temperatures by the help of zinc chloride. The authors have already shown that a derivative of diphenylmethane is thus formed in the case of 4-dimethylaminobenzyl alcohol and dimethylaniline (A., 1912, i, 970), and now show by a series of examples that the reaction takes a similar course with their homologues containing methyl groups. Thus 4-dimethylaminobenzyl alcohol and dimethyl-*m*-toluidine yield 4 : 4′-*tetramethyldiaminophenyl*-o-*tolylmethane*, $NMe_2 \cdot C_6H_4 \cdot CH_2 \cdot C_6H_3Me \cdot NMe_2$, b. p. 240—244°/8 mm. (*platinichloride*, m. p. 188—190° after darkening from 150°; *picrate*, m. p. about 70°), the constitution of which follows from its identity with the product obtained by the action of dimethyl-*m*-toluidine on 4-dimethylaminobenzyltoluidine in hydrochloric acid solution (compare Cohn and Fischer, A., 1900, i, 690).

Trimethyldiaminophenyl-*m*-tolylmethane (see above) is difficultly converted by exhaustive methylation into a pure di-quaternary iodide. When heated at 120° during three hours with methyl iodide and methyl alcohol, it yields a mono-*methiodide*, $C_{19}H_{27}N_2I$, m. p. 152°, which, when distilled in a vacuum, gives 4 : 4′-tetramethyldiaminophenyl-*m*-tolylmethane (obtained from 4-dimethylamino-3-methylbenzyl alcohol and dimethylaniline, A., 1912, i, 970), which is further identified by means of its picrate, m. p. 183°.

The statement of the D.R.-P. No. 107712, that aminobenzylaniline and its homologues only condense with amines which do not contain a substituent in the para-position is incorrect, at any rate as far as *p*-toluidine is concerned; when dimethylaminobenzyltoluidine is treated with *p*-toluidine in hydrochloric acid solution, 2′-*amino*-4-*dimethylaminophenyl*-m-*tolylmethane*, $NH_2 \cdot C_6H_3Me \cdot CH_2 \cdot C_6H_4 \cdot NMe_2$, b. p. 240—245°/10 mm., m. p. 87°, is obtained in poor yield. The *picrate* has m. p. 180—181°. When heated with methyl iodide and methyl alcohol, the base yields a di-quaternary iodide, m. p. 204° (previously obtained from 2-dimethylamino-5-methylbenzyl alcohol and dimethyl-

aniline), which, when heated in a vacuum, yields 4 : 6′-tetramethyldiaminophenyl-*m*-tolylmethane, m. p. 84°.

4-Dimethylamino-3-methylbenzyl alcohol condenses with dimethyl-*o*-toluidine to form *s-tetramethyldiaminodi*-m-*tolylmethane*,

$$CH_2(C_6H_3Me{\cdot}NMe_2)_2.$$

yellow oil, b. p. 228—229°/11 mm.; *picrate*, m. p. 187°; *platinichloride*, needles, m. p. 224° after darkening at 222°; *methiodide*, m. p. 199° after softening at about 190°. The constitution of the base is proved by its identity with the product obtained by the methylation of *s*-dimethyldiaminodi-*m*-tolylmethane prepared by Gnehm and Blumer by the condensation of formaldehyde with methyl-*o*-toluidine.

The liquid nature of many of the basic derivatives of diphenylmethane and the frequently indistinct melting point of their salts has led the authors to investigate the suitability of their nitro-derivatives in characterising them. They seem to be generally well adapted for this purpose. According to the quantity of nitric acid used, mono- or di-nitro-derivatives can be obtained which are crystalline, and can readily be reduced by stannous chloride to the corresponding mono- and di-amino-compounds. In this connexion, the following substances have been prepared: 2 : 2′-*dinitro*-4 : 4′-*tetramethyldiaminodi*-m-*tolylmethane*, $CH_2[C_6H_2Me(NO_2){\cdot}NMe_2]_2$, yellow leaflets, m. p. 125°; 4 : 4′-dinitro-2 : 2′-tetramethyldiaminodi-*m*-tolylmethane, m. p. 102°, which, on reduction, yields the corresponding *di-amino*-compound; 2′ : 4-*dinitro*-2 : 4′-*tetramethyldiaminophenyl*-m-*tolylmethane*,

$$NMe_2{\cdot}C_6H_2Me(NO_2){\cdot}CH_2{\cdot}C_6H_3(NO_2){\cdot}NMe_2,$$

dark red crystals, m. p. 187°, which is reduced to the *diamino*-derivative, colourless crystals, m. p. 140°; 2′-*nitro*-2 : 4′-*tetramethyldiaminophenyl*-m-*tolylmethane*, $NMe_2{\cdot}C_6H_3Me{\cdot}CH_2{\cdot}C_6H_3(NO_2){\cdot}NMe_2$, red crystals, m. p. 94°; corresponding *amino*-compound, m. p. 97—98°.

According to Biehringer (A., 1897, i, 73), 2 : 2′-diamino-4 : 4′-tetramethyldiaminodiphenylmethane loses ammonia when heated with hydrochloric acid with formation of an acridine ring. The authors find that a similar ring formation does not occur when the hydrogen atoms of the amino-group are replaced by methyl. When heated with hydrochloric acid at a temperature not exceeding 180°, the bases are unchanged; under more drastic treatment, formaldehyde is eliminated, but the liberation of methyl-, dimethyl- or trimethyl-amine could not be detected. H. W.

Tertiary Derivatives of *o*- and *p*-Aminobenzyl Alcohol. III. JULIUS VON BRAUN and OTTO KRUBER (*Ber.*, 1913, **46**, 3460—3470).—In previous papers (A., 1912, i, 968; preceding abstract), the authors have shown that tertiary aromatic amines of the dialkylaniline type readily condense with formaldehyde, either alone or in the presence of hydrochloric acid, yielding derivatives of 2 : 2′- and 4 : 4′-tetra-alkyldiaminodiphenylmethane, $CH_2(C_6H_4{\cdot}NMe_2)_2$, and of *o*- and *p*-dialkylaminobenzyl alcohols. The reaction has now been extended to the following amines in order to ascertain the effect of nuclear substituents on the course of the condensation: (1) dimethyl-*m*-toluidine, (2) diethyl-*m*-toluidine, (3) dimethyl-*m*-chloroaniline, (4) phenylbenzylmethylamine, (5) dimethylcumidine, (6) dimethyl-*p*-chloroaniline,

(7) dimethyl-*p*-bromoaniline, (8) dimethyl-*p*-bromo-*m*-toluidine, and (9) dimethyl-*o*-chloroaniline.

The meta-substituted amines, (1) and (3), resemble the unsubstituted dimethylaniline in that they are almost quantitatively converted by the theoretical amount of formaldehyde ($\frac{1}{2}$ mol.) into the corresponding diphenylmethane derivatives, whilst, with excess of formaldehyde, only small yields of the dialkylaminobenzyl alcohols are obtained. The behaviour of the para-substituted amines (5)—(8) is similar to that of dimethyl-*p*-toluidine. They do not form diphenylmethane derivatives, but, with excess of the aldehyde, give rise to the dialkylaminobenzyl alcohols in good yield.

In the case of the amines 6, 7 and 8, containing a halogen atom in the para-position to the dimethylamino-group, the prolonged action of formaldehyde in the presence of hydrochloric acid causes partial oxidation of the alcohol to the corresponding acid.

It is also found that dimethyl-*o*-chloroaniline condenses with formaldehyde much more readily than dimethyl-*o*-toluidine, and the conclusion is, therefore, drawn that the inhibiting effect of ortho-substituents on the reactivity of the para-hydrogen atoms of the dialkylanilines is not always the same (compare Friedländer, A., 1899, i, 350), but may vary considerably with the nature of the substituent.

Dimethyl-*m*-toluidine condenses with formaldehyde ($\frac{1}{2}$ mol.), yielding 4 : 4′-tetramethyldiaminodi-*o*-tolylmethane, b. p. 253—256°/12 mm., m. p. 82° (*picrate*, m. p. 150°) ; with excess of formaldehyde it yields 4-*dimethylamino*-3-*methylbenzyl alcohol* as a yellow, almost odourless oil, b. p. 138—142°/10 mm., which forms a *picrate*, felted needles, m. p. 145—146°, an oily *methiodide*, a *platinichloride*, needles, m. p. 178°, and m-*nitrobenzoyl* derivative, m. p. 64°.

4 : 4′-*Tetraethyldiaminodi-*o*-tolylmethane*, $CH_2(C_6H_3Me{\cdot}NEt_2)_2$, b. p. 260—266°/10 mm., m. p. 54—55°, and 4-*diethylamino*-3-*methylbenzyl alcohol*, b. p. 160—170°/18 mm. (decomp.) are formed by condensing diethyl-*m*-toluidine with formaldehyde. The alcohol is very resistant towards reducing agents and forms a *picrate*, m. p. 100—103° ; the *platinichoride* and *methiodide* are oils.

m-Chlorodimethylaniline condenses with formaldehyde ($\frac{1}{2}$ mol.) in the presence of hydrochloric acid, yielding 4 : 4′-*tetramethyldiaminodi-*o-*chlorodiphenylmethane*, b. p. 272—276°/9 mm., m. p. 96—97° [*picrate*, m. p. 130—133° ; *platinichloride* (decomp. 230°)], which on oxidation with lead dioxide is converted into 4 : 4′-*tetramethyldiamino*-2 : 2′-*dichlorobenzhydrol*. This forms colourless crystals, m. p. 121°, yields blue solutions in glacial acetic acid, and condenses with dimethylaniline in acid solution to form 4 : 4′ : 4″-*hexamethyltriamino*-2 : 2′-*dichlorotriphenylmethane*, $NMe_2{\cdot}C_6H_4{\cdot}CH(C_6H_3Cl{\cdot}NMe_2)_2$, which separates from alcohol in lustrous crystals, m. p. 193°, and is oxidised to a blue *dye* of extraordinary fastness to light.

2-*Chloro*-4-*dimethylaminobenzyl alcohol*, obtained in poor yield (2%) from *m*-chlorodimethylaniline and excess of formaldehyde, forms a yellow oil, b. p. 156—160°/9 mm. ; the *picrate* has m. p. 150°, the *platinichloride*, m. p. 184°.

p-*Benzylmethylaminobenzyl alcohol*, $C_7H_7{\cdot}NMe{\cdot}C_6H_4{\cdot}CH_2{\cdot}OH$, prepared from benzylmethylaniline, distils with decomposition at 230°

under diminished pressure, and, therefore, could not be isolated in a pure condition.

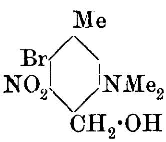
Dimethylcumidine gives rise to 6-*dimethylamino*-3-iso*propylbenzyl alcohol*, a yellow oil, b. p. 140—144°/8 mm. (*picrate*, m. p. 118—119°; *methiodide*, m. p. 147°; *platinichloride*, reddish-yellow leaflets, m. p. 187°), which condenses with 1-phenylpiperidine in the presence of zinc chloride, yielding 4-*piperidino*-6′-*dimethylamino*-3′-iso*propyldiphenylmethane*, $NMe_2 \cdot C_6H_3Pr^{\beta} \cdot CH_2 \cdot C_6H_4 \cdot NC_5H_{10}$, as a viscid oil, b. p. 260—266°/9 mm. (*picrate*, m. p. 100—105°; *platinichloride*, m. p. 219—220°).

Dimethyl-*p*-chloroaniline very readily condenses with formaldehyde, yielding 5-*chloro*-2-*dimethylaminobenzoic acid* (*hydrochloride*, m. p. 172—173°; *platinichloride*, m. p. 190°) and 5-*chloro*-2-*dimethylaminobenzyl alcohol*, a yellow oil, b. p. 158—160°/10 mm. (*picrate*, m. p. 152°; *methiodide*, m. p. 137°), which condenses with *p*-chlorodimethylaniline and dimethylaniline, yielding 5 : 5′-*dichloro*-2 : 2′-*tetramethyldiaminodiphenylmethane*, $CH_2(C_6H_3Cl \cdot NMe_2)_2$, b. p. 240—260°/14 mm., m. p. 151°, and 5-*chloro*-2 : 4′-*tetramethyldiaminodiphenylmethane*, b. p. 242—246°/12 mm., m. p. 144° (*picrate*, yellow leaflets, m. p. 165°; *methiodide*, m. p. 195°), respectively.

The behaviour of dimethyl-*p*-bromoaniline is similar, 5-*bromo*-2-*dimethylaminobenzoic acid* (not isolated) and 5-*bromo*-2-*dimethylaminobenzyl alcohol*, b. p. 160—170°/13 mm. (*picrate*, m. p. 153°) being produced.

By brominating dimethyl-*m*-toluidine, Wurster and Riedel (A., 1880, 109) obtained a bromo-compound of m. p. 98°, b. p. 276°. The authors find, however, that the bromination of pure dimethyl-*m*-toluidine in glacial acetic acid solution yields a bromo-derivative, m. p. 55°, b. p. 146—148°/17 mm., which decomposes completely on distillation under ordinary pressure. It forms a methiodide, m. p. 177°, identical with that described by Fischer and Windaus (A., 1900, i, 484), and accordingly must be a p-*bromodimethyl*-m-*toluidine*.

5-*Bromo*-2-*dimethylamino*-4-*methylbenzyl alcohol*, obtained together with the corresponding *acid* by the condensation of the preceding bromodimethyltoluidine with formaldehyde, has b. p. 168—172°/14 mm., forms a *picrate*, crystallising in leaflets, m. p. 150°, and on nitration in concentrated sulphuric acid solution yields a yellow, crystalline *nitro*-derivative, m. p. 83°, of the annexed constitution.



3-*Chloro*-4-*dimethylaminobenzyl alcohol*, b. p. 168—170°/11 mm. (*picrate*, m. p. 130°; *platinichloride*, m. p. 168°; *methiodide*, m. p. 119°; *nitro*-derivative, $C_9H_{11}O_3N_2Cl$, m. p. 80°), prepared from *o*-chlorodimethylaniline and excess of formaldehyde in the presence of hydrochloric acid, condenses with dimethylaniline and *o*-chlorodimethylaniline to form 3-*chloro*-4 : 4′-*tetramethyldiaminodiphenylmethane*, $NMe_2 \cdot C_6H_3Cl \cdot CH_2 \cdot C_6H_4 \cdot NMe_2$, a liquid, b. p. 248—250°/12 mm. (*picrate*, m. p. 166—167°; *dimethiodide*, m. p. 201°), and 3 : 3′-*dichloro*-4 : 4′-*tetramethyldiaminodiphenylmethane*, $CH_2(C_6H_3Cl \cdot NMe_2)_2$, which forms a viscid oil, b. p.

258—260°/10 mm., yields a deep yellow *dinitro*-derivative, m. p. 144°, and is also obtained by the direct condensation of *o*-chlorodimethylaniline with the calculated amount of formaldehyde. F. B.

Steric Hindrance with Tertiary Aromatic Amines. JULIUS VON BRAUN and OTTO KRUBER (*Ber.*, 1913, **46**, 3470—3479).—In preparing the methiodides of the tetramethyldiaminodiarylmethanes, tabulated below, the authors found that the bases 5, 7, and 8, containing a substituent in the ortho-position to one of the dimethylamino-groups, combined rapidly with two molecules of methyl iodide, whilst in the case of the amines 2, 4, and 9, in which substituents occur in the ortho-position to both the dimethylamino-groups, the addition of methyl iodide proceeded very slowly. It would thus appear that the occurrence of the reaction at the sterically unhindered dimethylamino-group induces the same reaction at the sterically hindered group.

(1) 4 : 4′-Tetramethyldiaminodiphenylmethane.
(2) 4 : 4′-Tetramethyldiaminodi-*m*-tolylmethane.
(3) 4 : 4′-Tetramethyldiaminodi-*o*-tolylmethane.
(4) 6 : 6′-Tetramethyldiaminodi-*m*-tolylmethane.
(5) 4 : 4′-Tetramethyldiaminophenyl-*m*-tolylmethane.
(6) 4 : 4′-Tetramethyldiaminophenyl-*o*-tolylmethane.
(7) 4 : 6′-Tetramethyldiaminophenyl-*m*-tolylmethane.
(8) 4 : 4′-Tetramethyldiamino-*o* : *m*-ditolylmethane.
(9) 6 : 4′-Tetramethyldiaminodi-*m*-tolylmethane.
(10) 4 : 6′-Tetramethyldiamino-*o* : *m*-ditolylmethane.

The addition of methyl iodide to tertiary aromatic amines is, however, not particularly subject to steric influences, and the authors have, therefore, examined the behaviour of the above amines towards cyanogen bromide and iodoacetonitrile.

With respect to the action of cyanogen bromide on tertiary aromatic amines, it has already been shown that whilst sterically unhindered amines react with extreme ease at the ordinary temperature yielding compounds of the type $R\cdot NMe_3Br$ and $R\cdot NMe\cdot CN$, amines containing an ortho-substituent enter into reaction with great difficulty. In the case of iodoacetonitrile, the presence of an ortho-substituent completely suppresses the reaction.

In agreement with the results obtained by the addition of methyl iodide, it was found that the di-*o*-substituted amines 2, 4, and 9 do not react with either cyanogen bromide or iodoacetonitrile, whilst the amines 5, 7, 8, and 10, containing a substituent in the ortho-position to only one of the dimethylamino-groups, enter into reaction as readily as the amines 1, 3, 6 in which steric influences are completely absent, the reactions proceeding according to the following scheme:

$$CH_2(C_6H_4\cdot NMe_2)_2 \xrightarrow{CN\cdot Br} CH_2(C_6H_4\cdot NMe_3Br)_2 \text{ and } CH_2(C_6H_4\cdot NMe\cdot CN)_2.$$

$$CH_2(C_6H_4\cdot NMe_2)_2 \xrightarrow{CH_2I\cdot CN} NMe_3I\cdot C_6H_4\cdot CH_2\cdot C_6H_4\cdot NMe\cdot CH_2\cdot CN + CH_2(C_6H_4\cdot NMe\cdot CH_2\cdot CN)_2 \text{ and } CH_2(C_6H_4\cdot NMe_3I)_2$$

That the presence of meta-substituents has little effect on the inter-

action of tertiary amines and cyanogen bromide or iodoacetonitrile has been shown by the behaviour of *m*-chlorodimethylaniline and dimethyl-*m*-toluidine, both of which react with these compounds almost as readily as dimethylaniline and dimethyl-*p*-toluidine.

m-*Tolyltrimethylammonium bromide*, obtained together with m-*tolylmethylcyanamide*, $C_6H_4Me\cdot NMe\cdot CN$, a yellow oil, b. p. 142—144°/8 mm., by the action of cyanogen bromide on dimethyl-*m*-toluidine, volatilises at about 200° without melting.

m-Chlorodimethylaniline and cyanogen bromide give rise to m-*chlorophenylmethylcyanamide*, $C_6H_4Cl\cdot NMe\cdot CN$. This has m. p. 72°, and is readily hydrolysed to *m*-chloromethylaniline, which is thus obtained more readily and in better yield than by the direct methylation of *m*-chloroaniline, Iodoacetonitrile reacts with dimethyl-*m*-toluidine, yielding m-*tolyltrimethylammonium iodide*, m. p. 177°, and *methylcyanomethyl*-m-*toluidine* [N-*methyl*-m-*toluidinoacetonitrile*],

$$C_6H_4Me\cdot NMe\cdot CH_2\cdot CN,$$

a yellow oil, b. p. 158°/8 mm. With *m*-chlorodimethylaniline it yields m-*chlorophenyltrimethylammonium iodide*, m. p. 187°, and *methylcyanomethyl*-m-*chloroaniline* [N-*methyl*-m-*chloroanilinoacetonitrile*],

$$C_6H_4Cl\cdot NMe\cdot CH_2\cdot CN,$$

b. p. 175—180°/9 mm.

4 : 4′-*Tetramethyldiamino*-o : m-*ditolylmethane*,

$$CH_2(C_6H_3Me\cdot NMe_2)_2,$$

prepared by condensing 4-dimethylamino-3-methylbenzyl alcohol with dimethyl-*m*-toluidine in the presence of zinc chloride, is a yellow oil, b. p. 244—246°/10 mm., and readily combines with methyl iodide to form a *dimethiodide*, m. p. 232—234°.

6 : 4′-*Tetramethyldiaminodi*-m-*tolylmethane*, obtained from 2-dimethylamino-5-methylbenzyl alcohol and dimethyl-*o*-toluidine in a similar manner, has b. p. 218—222°/11 mm., yields a *picrate*, m. p. 95°, and forms a *dimethiodide*, lustrous leaflets, m. p. 195°.

4 : 6′-*Tetramethyldiamino*-o : m-*ditolylmethane*, prepared from 2-dimethylamino-5-methylbenzyl alcohol and dimethyl-*m*-toluidine, has b. p. 230—235°/12 mm., and forms a *dimethiodide*, m. p. 209°.

Of the compounds produced by the action of cyanogen bromide and iodoacetonitrile on the 10 amines enumerated above, the following are described: the *dicyano*-compound,

$$CH_2(C_6H_3Me\cdot NMe\cdot CN)_2$$

(lustrous leaflets, m. p. 130°), derived from 6, together with the corresponding *dicyanomethyl* compound,

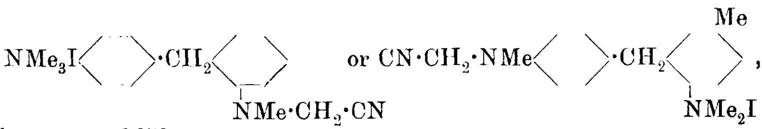
$$CH_2(C_6H_3Me\cdot NMe\cdot CH_2\cdot CN)_2,$$

needles, m. p. 134°, and the *cyanomethyl-methiodide*,

$$NMe_3I\cdot C_6H_3Me\cdot CH_2\cdot C_6H_3Me\cdot NMe\cdot CH_2\cdot CN,$$

lustrous leaflets, m. p. 143°; the *dimethiodide* from 6 has m. p. 243°. The *dicyano*-compound from 3 has m. p. 125°; the *dimethiodide*, m. p. 205°.

The *dicyano*-derivative from 7 forms long needles, m. p. 151°; the *dicyanomethyl* derivative, leaflets, m. p. 104°; the corresponding *cyanomethyl-methiodide*,



has m. p. 165°.

Of the derivatives formed by the action of iodoacetonitrile on the amines 5, 8 and 10, only the *dimethiodides* and the *dicyanomethyl* compound derived from 8 were isolated.

The action of cyanogen bromide on 5, 8 and 10 yields the corresponding *dicyano*-derivatives, which have m. p. 96—97°, 90—91°, and 120° (with previous softening at 115°) respectively.

The behaviour of 4 : 4′-tetramethyldiamino-3-chlorodiphenylmethane and 2 : 4′-tetramethyldiamino-5-chlorodiphenylmethane towards cyanogen bromide and iodoacetonitrile is similar to that of the analogously constituted methyl compounds 5 and 7. The first-named base yields a *dicyano*-derivative, m. p. 157°; the corresponding *dicyanomethyl* compound and *cyanomethyl-methiodide* have m. p. 105° and 141°. F. B.

Oxonium Compounds. III. GEORGE L. STADNIKOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1391—1414. Compare A., 1912, i, 971).—The greater part of this paper has been already abstracted (this vol., i, 1183).

The author further shows experimentally that, in the action of 3 mols. of diphenylmethyl ethyl ether on magnesium propyl iodide under the conditions employed by Tschelincev and Pavlov (this vol., i, 461), part of the etherate passes into solution. During distillation, this etherate is subjected to a very high temperature (280°), and it is hence not surprising that it decomposes with formation of tetraphenylethane. Other results obtained by these authors are also criticised.

Gorski's results (this vol., i, 462) are not new (see Oddo, A., 1911, i, 443). T. H. P.

Triphenylthiocarbinol. DANIEL VORLÄNDER and ERNST MITTAG (*Ber.*, 1913, **46**, 3450—3460).—Although triphenylcarbinol contains three phenyl groups its acid properties are no greater than those of an aliphatic alcohol. It has, however, more pronounced basic properties than any other tertiary alcohol, and shows a marked tendency to lose its hydroxyl group.

This behaviour is in accordance with the rules laid down by Vorländer (A., 1902, i, 309), according to which the reactivating influence of unsaturated groups on adjacent atoms or groups attains a maximum in the 3 : 4-position. The unsaturated phenyl groups in triphenylcarbinol occupy the 3 : 4-position with respect to the oxygen atom, which, therefore, is very mobile and readily separates from the molecule in the form of hydroxyl: $(\overset{4}{C}{=}\overset{3}{C})\cdot\overset{2}{C}\cdot\overset{1}{O}\cdot H$. In order to ascertain the effect of substituting sulphur in place of oxygen in the above system, the authors have examined the behaviour of triphenylcarbinyl-

mercaptan, and find that, in accordance with the above rule, it shows a marked tendency to rupture between the sulphur and central carbon atoms. Its acid properties are scarcely more pronounced than those of hydrogen sulphide or methyl mercaptan. It dissolves in alkali hydroxides, but the salts thus formed are readily hydrolysed by water. It comparison with other thio-alcohols it shows a marked tendency to lose the thiol group. On treatment with concentrated sulphuric acid or perchloric acid it evolves hydrogen sulphide and is transformed into triphenylcarbinol. A similar decomposition occurs when the thiocarbinol is heated with acetic acid or acetic anhydride. With hydrogen chloride in benzene solution it yields hydrogen sulphide and ω-chlorotriphenylmethane. When boiled with dilute aqueous alkali hydroxides it slowly forms the corresponding alkali sulphides.

The behaviour towards silver salts is very characteristic. It instantly reacts with silver nitrate in alcoholic solution, yielding silver sulphide and triphenylcarbinol; in this respect it resembles the hydrosulphides of the alkali-metals or metals of the alkaline earths. With silver perchlorate in benzene solution it forms silver sulphide and triphenylmethyl perchlorate.

The benzoyl and acetyl derivatives, and also the methyl ether, resemble the parent substance in being readily ruptured between the sulphur and central carbon atoms. Thus, the methyl ether on treatment with alcoholic silver nitrate yields the silver salt of methyl mercaptan, whilst with concentrated sulphuric acid or dilute hydrochloric acid, the mercaptan itself is produced; with alcoholic silver nitrate the benzoyl derivative yields silver thiobenzoate.

The readiness with which triphenylcarbinylmercaptan suffers rupture between the sulphur and central carbon atoms indicates that the union between these atoms is very similar to that between the chlorine and carbon atoms in ω-chlorotriphenylmethane. On the other hand, the union between the cyano-group and central carbon atom in triphenylacetonitrile is much more stable, for this compound does not react with silver nitrate, and is unattacked by sulphuric or perchloric acids.

Attempts to prepare triphenylcarbinyl mercaptan and triphenylacetonitrile by the action of hydrogen sulphide and hydrogen cyanide on triphenylcarbinol were unsuccessful.

By passing hydrogen sulphide into ω-chlorotriphenylmethane at 120—150°, triphenylmethane, sulphur, and hydrogen chloride were produced.

Reduction of the thiocarbinol with sodium and alcohol yields triphenylmethane and sodium sulphide, whilst the action of chlorine in carbon tetrachloride solution gives rise to ω-chlorotriphenylmethane.

The behaviour of triphenylmethyl disulphide, $(CPh_3)_2S_2$, has also been investigated. On treatment with perchloric acid it liberates hydrogen sulphide, but not so readily as the thiocarbinol. It is transformed by chlorine into ω-chlorotriphenylmethane.

Triphenylcarbinyl mercaptan [*ω-thioltriphenylmethane*], $CPh_3\cdot SH$, prepared by saturating a solution of sodium ethoxide in ethyl alcohol with hydrogen sulphide and heating the resulting solution of sodium

hydrosulphide with ω-chlorotriphenylmethane, separates from alcohol in long, white, prismatic crystals, m. p. 107°. The *sodium* salt is obtained by shaking an ethereal solution of the thiocarbinol with concentrated aqueous potassium hydroxide. The *lead* and *mercuric* salts are also described.

The acetyl and benzoyl derivatives, prepared by the action of the acid chlorides on the carbinol in pyridine solution, have m. p. 139—141° and 185° respectively, and are decomposed by sulphuric acid with the evolution of hydrogen sulphide (compare Wheeler, A., 1902, i, 28; Meyer and Fischer, 1911, i, 120).

Triphenylmethyl disulphide is obtained in colourless needles by the addition of sulphuryl chloride to an ice-cold, alcoholic solution of the sodium salt of the thiocarbinol; it becomes yellow, and begins to decompose at 140°, m. p. about 155°.

Triphenylmethyl methyl sulphide, prepared by the action of methyl sulphate on a solution of the thiocarbinol in methyl-alcoholic sodium methoxide, or by heating the carbinol with methyl iodide and potassium hydroxide in methyl-alcoholic solution, has m. p. 105—106° (compare Meyer and Fischer, *loc. cit.*). F. B.

Action of Dimethylamine on the Iodohydrins of Styrene; Study of the Two Phenyldimethylaminoethanols. MARC TIFFENEAU and ERNEST FOURNEAU (*Bull. Soc. chim.*, 1913, [iv], **13**, 971—981).—The authors have confirmed Krassusky's views that the formation of an amino-alcohol from a chloro- or iodo-hydrin takes place through the intermediate formation of an ethylene oxide (compare A., 1908, i, 139). The two isomeric styrene iodohydrins, $OH\cdot CHPh\cdot CH_2I$ and $CHPhI\cdot CH_2\cdot OH$, both react with dimethylamine to give the same β-dimethylamino-α-phenylethanol, $OH\cdot CHPh\cdot CH_2\cdot NMe_2$, which is also obtained by the interaction of styrene oxide and dimethylamine. It is a liquid, b. p. 132—133°/15 mm., D_4^0 1·021 (compare Tiffeneau, *Ann. Chim. Phys.*, 1907, [viii], **10**, 342). It yields a *hydrochloride*, m. p. 147°; a *picrate*, m. p. 35—40°; a benzoyl hydrochloride, m. p. 210° (compare *loc. cit.*); a *morpholone hydrochloride*, m. p. 229°, from interaction in benzene solution with ethyl chloroacetate; a *methiodide*, m. p. 225°; a *methochloride*, m. p. 199—200°, by the action of silver chloride on the methiodide. This methochloride, which is the hydrochloride of secondary phenylcholine, gives an *aurichloride*, m. p. 154°, soluble in water, and a *picrate*, prismatic needles, m. p. 195°.

Styrene methyliodohydrin reacts similarly with dimethylamine, yielding *β-dimethylamino-α-methoxy-α-phenylethane*, $OMe\cdot CHPh\cdot CH_2\cdot NMe_2$, b. p. 105—107°/15 mm., 229—230°/760 mm.; D_4^0 1·0013, which gives a *hydrochloride*, m. p. 228°; a *hydriodide*, m. p. 205°, and a *methiodide*, m. p. 180°. Styrene ethyliodohydrin similarly yields *β-dimethylamino-α-ethoxy-α-phenylethane*, b. p. 118—119°/19 mm., 229—230°/760 mm., D_4^0 0·9623, giving a *hydrochloride*, m. p. 134°, a *hydriodide*, m. p. 153°, and a *methiodide*, m. p. 157°.

In further proof that the styrene iodohydrin, $CHPhI\cdot CH_2\cdot OH$, does not yield the corresponding dimethylaminoethanol,

$$NMe_2\cdot CHPh\cdot CH_2\cdot OH,$$

but the isomeric ethanol, the former has been prepared by other methods and characterised as follows:

Phenylacetyl chloride was brominated by direct addition of bromine to the acid chloride at 80°, the product being finally boiled with excess of alcohol, giving *ethyl α-bromophenylacetate*, b. p. 145°/15 mm. This substance reacts with dimethylamine in benzene solution to give *ethyl α-dimethylaminophenylacetate*, $NMe_2\cdot CHPh\cdot CO_2Et$, b. p. 135°/13 mm., which is readily reduced by sodium in absolute alcohol to *α-dimethylamino-α-phenylethanol*, $NMe_2\cdot CHPh\cdot CH_2\cdot OH$, b. p. 135—138°/15 mm. and 248—250°/760 mm, solidifying at −5°. The following derivatives have been prepared: *hydrochloride*, m. p. 114°; *picrate*, m. p. 115°; *gold* salt, m. p. 110°, decomposed on boiling with water, reduced gold being deposited; *benzoyl* derivative, m. p. 165°; *morpholone hydrochloride*, m. p. 220°, sparingly soluble in alcohol; *methiodide*, difficult to crystallise; *methochloride* [primary *phenylcholine hydrochloride*], $NMe_3Cl\cdot CHPh\cdot CH_2\cdot OH$, yielding a crystalline *gold* salt and a *picrate*, m. p. 165°. W. G.

Electrolysis in Non-Aqueous Solvents. *o*-Nitrobenzoic Acid Solutions of Potassium *o*-Nitrobenzoate. CARL SCHALL (*Zeitsch. Elektrochem.*, 1913, **19**, 830—833).—Berl (A., 1904, i, 282) showed that the electrolysis of fused organic salts led to results which differed from those obtained from the electrolysis of aqueous solutions of these salts. In the case of the sodium salt of *o*-nitrobenzoic acid melted with its free acid, the product was nitrobenzene, and not 2 : 2′-dinitrodiphenyl as was expected. The author has electrolysed a 15% solution of potassium *o*-nitrobenzoate in *o*-nitrobenzoic acid at 160—170°, using a small porous pot as anode vessel and a beaker as cathode vessel. The anode consisted of 6—7 cms. of platinum wire wound into a spiral, and the cathode was a platinum foil 3 cms. × 7 cms. The electrolysis was carried out by a current of 5 amperes and 50 volts. During the electrolysis an odour of aniline was noticed. On allowing the fusion to cool, the cathode material contained a small quantity of a liquid with an *iso*nitrile odour, and a black substance which dissolved in alkali and acid. The anode vessel contained a little *o*-nitrophenol, a little 2 : 2′-dinitrodiphenyl, and a brown powder of undetermined composition. The experiment of Lilienfeld (D.R.-P. 1902, 147943) was repeated; by this 2 : 2′-dinitrodiphenyl should be obtained by the electrolysis of copper *o*-nitrobenzoate in aqueous solution. The author is unable to obtain any of this compound either under the specified or any other conditions. J. F. S.

Nitro-*o*-sulphobenzoic Acid and Some of its Derivatives. MARTIN BELL STUBBS (*Amer. Chem. J.*, 1913, **50**, 193—204. Compare Taverne, A., 1906, i, 273).—If *o*-sulphobenzoic acid is treated with a mixture of fuming nitric and concentrated sulphuric acids, the mixture heated until all the nitric acid has been eliminated, and water added to the cooled product, *5-nitro-2-sulphobenzoic anhydride*,

$$NO_2\cdot C_6H_3{<}^{SO_2}_{CO}{>}O,$$

m. p. about 212° (uncorr.), separates in white crystals. *Potassium*

hydrogen 5-nitro-2-sulphobenzoate crystallises with $1H_2O$, the *lead* salt with $2H_2O$, the *barium* salt with $3H_2O$, and the *copper* salt with $2H_2O$; the *calcium* salt also contains water of crystallisation, whilst the *potassium* salt is anhydrous. On treating the *chloride*,

$$NO_2\cdot C_6H_3(SO_2Cl)\cdot COCl,$$

a yellow oil, with dry ammonia, the *sulphinide*,

$$NO_2\cdot C_6H_3{<}^{SO_2}_{CO}{>}NH,$$

is produced; its *sodium* salt crystallises with $1H_2O$. When the *ethyl* ester of the *chloride*, $NO_2\cdot C_6H_3(SO_2Cl)\cdot CO_2Et$, obtained as an oil by the action of alcohol on the chloride, is neutralised with barium carbonate, *barium ethyl* 5-*nitro-2-sulphobenzoate*,

$$[NO_2\cdot C_6H_3(CO_2Et)\cdot SO_3]_2Ba,3H_2O,$$

is produced, which forms colourless needles. E. G.

Characterisation of 3 : 5-Dibromotyrosine. CARL TH. MÖRNER (*Zeitsch. physiol. Chem.*, 1913, **88**, 124—137).—In view of its importance as a product of hydrolysis of a natural protein (gorgonin), 3 : 5-dibromotyrosine has been studied in detail.

Dibromo-*l*-tyrosine crystallises anhydrous in long, slender needles grouped in voluminous bundles or balls, or with $2H_2O$ in thin plates similar to benzoic acid. It has $[\alpha]_D^{20}$ + 1·3°.

Dibromo-*dl*-tyrosine crystallises $+ H_2O$ in transparent, four-edged prisms or thick plates. It is nearly twice as soluble in water as the *l*-isomeride. Both forms have m. p. about 245° (much decomp.). They are stable to concentrated sulphuric and hydrochloric acids even on heating. The bromine atoms are removed quantitatively on heating with zinc dust. E. F. A

Ketens. XXIV. Mixed Diphenylacetic Anhydrides and their Decomposition. HERMANN STAUDINGER, E. ANTHES, and H. SCHNEIDER (*Ber.*, 1913, **46**, 3539—3551).—It has been previously shown (Staudinger and Ott, A., 1908, i, 602) that anhydrides of malonic acid decompose when heated, yielding carbon dioxide and ketens. The scope of this method of preparation is greatly limited by the difficulty of preparing such anhydrides, and the authors have therefore investigated the behaviour of mixed anhydrides of malonic and other acids (compare Staudinger and Bereza, A., 1909, i, 83) which can be readily prepared by the action of ketens on malonic acid.

The authors have prepared a series of mixed anhydrides by the action of diphenylketen on derivatives of malonic acid. These are stable, well-crystallised substances which appear to be unimolecular, and thus differ remarkably from the amorphous, polymerised dimethyl- and diethyl-malonic anhydrides (A., 1908, i, 939). An anhydride could not, however, be obtained from malonic acid itself, decomposition occurring in this case at a low temperature with formation of diphenylacetic anhydride and brown, resinous products.

The action of heat on the mixed anhydrides causes a primary dissociation into diphenylacetic anhydride and the corresponding malonic anhydride; the latter then loses carbon dioxide to yield the keten. Dimethylketen and diethylketen can be obtained in this

manner from dimethyl- and diethyl-malonic diphenylacetic anhydrides respectively. In the latter case, however, small quantities of diphenylketen are also produced. This is attributed to the partial decomposition of diphenylacetic anhydride into diphenylketen and diphenylacetic acid, the latter substance also uniting with a portion of the diethylketen and thus reducing the yield of the latter. A similar secondary decomposition occurs quantitatively during the decomposition of benzylidenemalonic diphenylacetic anhydride, so that the product of the reaction is diphenylketen instead of the expected benzylideneketen, whilst the desired ketens were also not obtained from *iso*propylidenemalonic diphenylacetic anhydride and dichloromalonic diphenylacetic anhydride. Ethylchloroketen, on the other hand, was readily obtained from ethylchloromalonic diphenylacetic anhydride.

The mixed anhydrides are prepared by the addition of diphenylketen to very concentrated solution or suspension of the malonic acid in absolute ether, reaction being allowed to proceed in an atmosphere of carbon dioxide. After a period which depends on the derivative of malonic acid employed, the mixed anhydride separates in the crystalline state. The m. p.'s of the products depend somewhat on the manner of heating.

Dimethylmalonic diphenylacetic anhydride, $CMe_2(CO{\cdot}O{\cdot}CO{\cdot}CHPh_2)_2$, has m. p. 91° (decomp.). When heated at the ordinary pressure, it yields only small quantities of dimethylketen; when decomposed in a vacuum, however, the yield of the latter amounts to 50%. The liquid, polymeric compound (Staudinger and Klever, A., 1907, i, 424) of dimethylketen appears to be formed in small quantity, whilst the residue consists of almost pure diphenylacetic anhydride.

Diethylmalonic diphenylacetic anhydride, m. p. 94°, when heated in a vacuum gives a 64% yield of diethylketen; at a somewhat higher temperature, diphenylketen is evolved, which is identified by conversion into diphenylacetanilide.

Diphenylacetic anhydride is obtained by the action of diphenylketen on an ethereal solution of ethylmalonic acid. The products of the decomposition of ethylmalonic anhydride have not yet been investigated.

Benzylidenemalonic diphenylacetic anhydride, m. p. 103°, is more stable than the preceding compounds. When heated to 180° in a vacuum, it yields diphenylketen. Cinnamic and diphenylacetic acids are obtained by saponification of the residue from the distillation.

iso*Propylidenemalonic diphenylacetic anhydride*, m. p. 101°, decomposes slowly at its melting point. When distilled in a vacuum it yields diphenylketen; the residue consists of dark brown, pasty mass, which is probably formed by the rapid polymerisation of the keten and subsequent decomposition of the polymerisation product.

Dichloromalonic diphenylacetic anhydride, m. p. 74° (decomp.), is an unstable substance, which slowly decomposes at the ordinary temperature. When heated, it yields more than the calculated quantity of carbon dioxide, and, at a higher temperature, evolves hydrogen chloride. Dichloroketen has not been isolated.

Ethylchloromalonic acid, m. p. 101—102°, is obtained by boiling an absolute ethereal solution of ethylmalonic acid with sulphuryl chloride

(compare Conrad and Reinbach, A., 1902, i, 529). It combines with diphenylketen, yielding *ethylchloromalonic diphenylacetic anhydride*, m. p. 95—96°, which, when heated in a vacuum, gives *ethylchloroketen*, CEtCl:C:O. The latter condenses at −80° to yellow oily drops which in a few minutes, become transformed into a white solid mass. Attempts to obtain the unpolymerised keten at −180° were unsuccessful. In ethereal solutions at −80°, it can only be preserved for a short time. The keten vapours dissolve in ether with a yellow colour, but, after a few seconds, the solution becomes colourless and, on removal of ether, the keten remains as a glassy, somewhat viscous mass, which is no longer completely soluble in the solvent. The keten polymeride is soluble in carbon disulphide, and melts indefinitely at 84—86°. When heated, it decomposes completely, evolving hydrogen chloride and probably chlorobutyryl chloride.

Ethylchloroketen unites with aniline to form chlorobutyranilide.

H. W.

Conversion of Triphenylmethyl into Triphenylacetic Acid. ALEXANDER I. GORSKI (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1454—1460).—In consequence of the varying behaviour of heated and non-heated ethereal solutions of magnesium triphenylmethyl chloride towards aromatic aldehydes, Schmidlin (A., 1906, i, 392; 1907, i, 26, 601; 1908, i, 239; this vol., i, 50) assumes the existence of two isomeric organo-magnesium compounds of ω-chlorotriphenylmethane: a normal, stable β-compound, which gives β-benzopinacolin with benzaldehyde, and an unstable quinonoid α-compound, which gives *p*-benzoyltriphenylmethane.

Tschitschibabin (A., 1907, i, 1022) is, however, of the opinion that only one such organo-magnesium compound exists.

Since the experimental results given by Schmidlin in support of his assumption were not obtained under the conditions in which the conversion of the α- into the β-compound actually occurs, the author has investigated the reaction further. By passing dry carbon dioxide into a heated mixture of a benzene solution of triphenylmethyl and the etherate of magnesium iodide, he has succeeded in obtaining good yields of triphenylacetic acid and triphenylmethane; decomposition of the products by means of water failed to give any appreciable amount of triphenylmethyl peroxide. This result is regarded as evidence in favour of Tschitschibabin's view that Schmidlin's α-compound is really a mixture of an ethereal solution of triphenylmethyl with the etherate of magnesium chloride.

T. H. P.

α-*p*-Nitrophenyl-β-hydroxythionaphthen. HERMANN APITZSCH (*Ber.*, 1913, **46**, 3091—3103. Compare A., 1909, i, 46).—p-*Nitrobenzylthiosalicylic acid* [2-p-*nitrobenzylthiolbenzoic acid*],

$$NO_2 \cdot C_6H_4 \cdot CH_2 \cdot S \cdot C_6H_4 \cdot CO_2H,$$

practically colourless, shining prisms, m. p. 215·5° (corr.) after softening at 200°, is prepared by the addition of an alcoholic solution of *p*-nitrobenzyl chloride to an aqueous alcoholic solution of sodium thiosalicylate [*o*-thiolbenzoate] and acidification of the mixture with hydrochloric acid. It dissolves in alkali to a pure yellow solution,

which becomes dark reddish-brown on warming, and from which a definite compound could not be isolated. Small quantities of p-*nitrobenzyl* 2-p-*nitrobenzylthiolbenzoate*,

$$NO_2\cdot C_6H_4\cdot CH_2\cdot S\cdot C_6H_4\cdot CO\cdot O\cdot CH_2\cdot C_6H_4\cdot NO_2,$$

pale yellow crystals, m. p. 194°, are obtained as by-product in the preparation of the acid. Methyl alcohol and hydrochloric acid transform the acid into its *methyl* ester, m. p. 111—112°, which is also obtained by the action of *p*-nitrobenzyl chloride on methyl thiosalicylate in methyl alcoholic solution in the presence of the calculated amount of 2*N*-potassium hydroxide. When boiled with a methyl alcoholic solution of sodium methoxide and subsequently carefully acidified with acetic acid, the methyl ester is converted into 2-*hydroxy*-1-p-*nitrophenylthionaphthen*, $C_6H_4{<}\genfrac{}{}{0pt}{}{C(OH)}{S}{>}C\cdot C_6H_4\cdot NO_2$, which exists in a yellow ketonic form, a red enolic form, and as an orange-red mixture. The forms readily pass into one another, so that definite directions for the productions of a definite modification cannot readily be given. The red form, however, which decomposes at 195° after previous softening, is obtained when this crude product is crystallised from aqueous alcohol. From ethyl acetate, chloroform, or glacial acetic acid solution, the yellow keto-form frequently separates in well defined, rhombohedric crystals, usually mixed with the red needles. The mixed form is obtained from solutions of the crude product in benzene, toluene, or xylene in the form of thin, orange-red needles, which are stable and do not become yellow on drying.

In the following experiments the red modification was used. When treated with an equivalent quantity of sodium methoxide in absolute alcoholic solution, the *sodium* salt, $C_{14}H_8O_3NSNa$, blue needles, is obtained. Benzyl chloride in the presence of alkali in aqueous alcoholic or absolute alcoholic solution yields two *benzyl* derivatives, greenish-yellow needles, m. p. 143·5° after softening at 142°, and almost colourless, irregularly formed needles, m. p. 144—145° (corr.), which can be separated by crystallisation from alcohol. A mixture of the two forms melts at 120°. Treatment with ethyl bromide leads to the formation of only one *ethyl* derivative, yellow needles, m. p. 109·5°.

2-*Hydroxy*-1-p-*aminophenylthionaphthen*,

$$C_6H_4{<}\genfrac{}{}{0pt}{}{C(OH)}{S}{>}C\cdot C_6H_4\cdot NH_2,$$

is obtained by the reduction of an alkaline, aqueous alcoholic solution of the nitro-compound by sodium hyposulphite. The substance is purified with difficulty, since it is readily decomposed when warmed in indifferent solvents. It forms white needles, m. p. 130° (corr.), which are sensitive to the action of light and air. The *picrate*, brown needles, begins to decompose at 165°. The salts with mineral acids are generally sparingly soluble and decompose readily. The *oxalate* is converted by nitric acid into a diazonium salt, which couples with R-salt in alkaline solution.

o-Benzylthiolbenzoic acid, needles, m. p. 189°, is formed from benzyl chloride, thiosalicylic acid, and potassium carbonate in boiling aqueous alcoholic solution.

Methyl 2-o-nitrobenzylthiolbenzoate, m. p. 122·5° (corr.), and *methyl 2-m-nitrobenzylthiolbenzoate*, rhombohedric plates, m. p. 88—89° (corr.), are obtained from methyl thiosalicylate, 2*N*-potassium hydroxide, and the requisite nitrobenzyl chloride. They resemble the non-nitrated benzylthiosalicylic acid, in that they do not yield a condensation product when boiled with aqueous alcoholic alkali. H. W.

Vinylphthalimide. MARCEL BACHSTEZ (*Ber.*, 1913, **46**, 3087—3089).—Since phthalylglycyl chloride decomposes when heated into carbon monoxide and chloromethylphthalimide (Gabriel, A., 1908, i, 181), whilst α-phthalimino*iso*butyryl chloride decomposes according to the scheme:

$$C_8H_4O_2{:}N{\cdot}CMe_2{\cdot}COCl \longrightarrow CO + HCl + C_8H_4O_2{:}N{\cdot}CMe{:}CH_2$$

(Gabriel, A., 1911, i, 982), the author has examined the action of heat on α-phthalylalanyl chloride (A., 1908, i, 182), and has thereby obtained small quantities of *vinylphthalimide*,

$$C_8H_4O_2{:}N{\cdot}CH{:}CH_2,$$

rhombic plates, m. p. 86°. Attempts to improve the yield by the addition of traces of zinc chloride or aluminium chloride were unsuccessful. The substance unites with bromine to form *phthalimino-αβ-dibromoethane*, needles, m. p. 123—124°, which rapidly decomposes when preserved in the presence of moisture.

A further attempt was made to prepare vinylphthalimide by the abstraction of hydrobromic acid from β-bromoethylphthalimide (compare Johnson and Jones, A., 1911, i, 455) by the action of sodium phenoxide in alcoholic solution. Phenoxyethylphthalimide, m. p. 129—130° (Schmidt, A., 1890, 372), was thereby obtained.

Small quantities of vinylphthalimide were obtained by the action of phosphoric oxide on β-hydroxyethylphthalimide (compare Gabriel, A., 1905, i, 265). H. W.

Toad Venom. HEINRICH WIELAND and FRIEDRICH JOS. WEIL (*Ber.*, 1913, **46**, 3315—3327).—Bufotalin, the poisonous principle of the toad first isolated in an amorphous condition by Faust (A., 1902, i, 446), has now been obtained in the crystalline state. It has the composition $C_{16}H_{24}O_4$, is faintly dextrorotatory and neutral in character. Alkali converts it into the unsaturated bufotalic acid, proving bufotalin to be a lactone. The other two oxygen atoms are present as alcoholic hydroxyl groups. Concentrated hydrogen chloride in the cold eliminates two molecules of water, forming a pale yellow, crystalline compound, $C_{16}H_{20}O_2$, bufotalien. It takes up two atoms of hydrogen in presence of palladium black.

Acetyl chloride in pyridine or warming with acetic anhydride converts bufotalin into a doubly acetylated ether, one hydroxyl group in each molecule being acetylated and the two molecules united through oxygen. Treatment of this diacetyl ether with concentrated hydrochloric acid forms a yellow, strongly unsaturated compound, $C_{18}H_{22}O_3$. The same compound is obtained on heating bufotalein with acetic anhydride, which effects direct acetylation on the carbon. Acetic anhydride is added directly to the C:C complex from which acetic acid is subsequently eliminated.

During the conversion of diacetylbufotalin ether into acetyl bufotalin, the bridge oxygen is first eliminated as water. The single molecules, $-C(OAc):CH-$, undergo rearrangement to a saturated diketone, $-CO\cdot CHAc-$, which loses water to form the doubly unsaturated monoketone, $-CH:CH\cdot CH:CAc-$. The analogy between bufotalin, $C_{15}H_{22}(OH)_3\cdot CO_2H$, and cholic acid, $C_{22}H_{36}(OH)_3\cdot CO_2H$, is emphasised. The unsaturated derivatives of both groups give Liebermann's characteristic cholestol reaction with acetic anhydride and sulphuric acid.

Bufotalin is not identical with bufagin, $C_{18}H_{24}O_4$, obtained from the tropical toad by Abel and Macht (A., 1912, ii, 1193).

Bufotalin has m. p. 148° (decomp.), $[\alpha]_D^{20} + 5{\cdot}4°$; it dissolves in concentrated sulphuric acid with an orange-red coloration which becomes deep red on standing and shows a green fluorescence.

Bufotalien forms pale yellow platelets, m. p. 219°. *Acetylbufotalien* separates in lustrous, yellow platelets grouped in rosettes, m. p. 184° (decomp.). *Diacetylbufotalin ether* forms colourless, lustrous platelets, m. p. 254° to a red liquid. E. F. A.

Action of Chloroacetic Acid on Phenolcarboxylic Acids and Nitrophenols. RICHARD MEYER and CASIMIR DUCZMAL (*Ber.*, 1913, **46**, 3366—3379).—Although the reaction of chloroacetic acid with alcohols and phenols producing ethers according to the equation $R\cdot OH + CH_2Cl\cdot CO_2H = HCl + OR\cdot CH_2\cdot CO_2H$ is a fairly general one, it is usually understood that this reaction fails with salicylic acid. The authors find that the reaction can be effected with salicylic acid, although less readily than with most other substances, and, indeed, mere mention of this fact has already appeared (Bogisch, *Diss.*, Stuttgart, 1889), although it has not found its place in the usual literature. The behaviour of the isomeric hydroxybenzoic acids and of the nitrophenols towards chloroacetic acid is also investigated.

The most satisfactory procedure for the reaction with salicylic acid is to dissolve equimolecular quantities of this substance and chloroacetic acid in a concentrated solution of a termolecular quantity of sodium hydroxide. The sodium salt of *o*-carboxyphenoxyacetic acid separates, and the reaction can be completed by heating for some hours on a water-bath. Any salicylic acid in the liberated acid product can be removed by extraction with ether. The yield of *o*-carboxyphenoxyacetic acid, $CO_2H\cdot C_6H_4\cdot O\cdot CH_2\cdot CO_2H$, m. p. 190—192°, calculated on the salicylic acid consumed amounts to approximately 80%.

m-Hydroxybenzoic acid, dissolved in sodium hydroxide solution of 35% strength, when gradually treated with chloroacetic acid gave rise to *m*-carboxyphenoxyacetic acid, m. p. 206—207°.

When equimolecular quantities of ethyl chloroacetate and sodium *m*-hydroxybenzoate are heated together in a sealed tube at 170° for thirty hours, *ethyl* m-*hydroxybenzoyloxyacetate* is obtained as a viscous oil, which can be hydrolysed by sodium hydroxide solution at 3° to m-*hydroxybenzoyloxyacetic acid*,

$$CO_2H\cdot CH_2\cdot O\cdot CO\cdot C_6H_4\cdot OH,$$

prisms, m. p. 138—140°. On warming with sodium hydroxide solution it is hydrolysed to *m*-hydroxybenzoic acid.

When treated in boiling sodium hydroxide solution (35%) with an equimolecular quantity of chloroacetic acid, *p*-hydroxybenzoic acid is converted into *p*-carboxyphenoxyacetic acid, m. p. 278°.

The action of ethyl chloroacetate on sodium *p*-hydroxybenzoate is similar to the meta-compound and requires similar conditions; the product is an oily *ethyl* ester, which on hydrolysis with cooled sodium hydroxide solution yields p-*hydroxybenzoyloxyacetic acid*,

$$CO_2H\cdot CH_2\cdot O\cdot CO\cdot C_6H_4\cdot OH,$$

silky needles, m. p. 174—175°.

o-Cresotic acid when treated in sodium hydroxide solution with chloroacetic acid produces 3-*carboxy*-o-*tolyloxyacetic acid*, needles, m. p. 203—204°. In a similar manner, *m*-cresotic acid gives rise to 4-*carboxy*-m-*tolyloxyacetic acid*, nodular aggregates, m. p. 164—165°, whilst the *p*-cresotic acid yields 3-*carboxy*-p-*tolyloxyacetic acid*, leaflets, m. p. 185°.

1 : 2- and 2 : 3-Hydroxynaphthoic acids were likewise applied to this synthetic reaction, sufficient sodium hydroxide being used to just neutralise the acid reagents. The former acid gave rise to 2-*carboxy*-1-*naphthoxyacetic acid*, silky needles, m. p. 206—207°, whilst the 2 : 3-isomeride produced 3-*carboxy*-2-*naphthoxyacetic acid*, leaflets, m. p. 224—225°.

Chloroacetic acid acts quite normally on the sodium salt of 2 : 4-dinitrophenol, but as the product is rather unstable, excess of alkali must be avoided; the resulting 2 : 4-dinitrophenoxyacetic acid had m. p. 147—148°.

No success attended attempts to obtain a condensation product of chloroacetic acid with picric acid, even when the latter was applied as the silver salt; as free picric acid and silver chloride were produced, it is probable that the primary product underwent immediate decomposition.

In all the above cases especial attention was given to the yields of the products, and although the interaction of *o*- and *p*-nitrophenols with chloroacetic acid had already been investigated, experiments were performed to determine the yields; *m*-nitrophenol was found to behave similarly to the others, producing 3-*nitrophenoxyacetic acid*, needles, m. p. 154—155°.

None of the above substances gives a quantitative result; it is found that the ortho-compounds give by far the poorest yields, and the difficulty of reaction observed with salicylic acid is evidently to be attributed to its ortho-configuration. With the meta- and para-compounds the yields are much better, the para-compounds being the more satisfactory. D. F. T.

The Condensation Product of Methyl 2 : 3-Hydroxynaphthoate with Benzaldehyde. LEO ROSLAV (*Monatsh.*, 1913, **34**, 1503—1518. Compare Friedl, A., 1910, i, 741; also the three following abstracts).—As Friedl has already shown, the chlorine atom of methyl 1-α-chlorobenzyl-2-naphthol-3-carboxylate, the product obtained when hydrogen chloride is passed into a cold mixture of the above

substances, is highly reactive. Many reactions are now described in which this property is exemplified.

On condensation in presence of sodium in benzene, the compound yielded *methyl αβ-diphenylethane-αβ-bis-2-naphthol-3-carboxylate*,

$$C_2H_2Ph_2[C_{10}H_5(OH)\cdot CO_2Me]_2,$$

in microscopic prisms, m. p. 227°, which gave violet-red solutions in sulphuric acid. When boiled with *p*-cresol in benzene, it formed *methyl* 1-α-p-*tolyloxybenzyl-2-naphthol-3-carboxylate*,

$$C_6H_4Me\cdot O\cdot CHPh\cdot C_{10}H_5(OH)\cdot CO_2Me,$$

in microscopic leaflets, m. p. 192—193°, whilst thymol yielded *methyl* 1-*α-thymoxybenzyl-2-naphthol-3-carboxylate*, in yellow, microscopic, rhombic leaflets, m. p. 187—188°.

The chlorine atom in the benzyl group was also replaced by bases, and the following compounds were obtained: from *p*-aminoazobenzene, the *α-benzeneazoanilino*-derivative, slender, orange-yellow needles, m. p. 221°; from carbamide, the *α carbamido*-derivative, only one amino-group reacting, small, faintly yellow prisms, m. p. 194—195°; from benzylamine, the *α-benzylamino*-derivative, long, rectangular plates, m. p. 105—106°, *hydrochloride*, m. p. 172° (decomp.); from piperidine, the *α-piperidino*-derivative, greenish-yellow, m. p. 145—146°, unstable *hydrochloride*, m. p. 174—175°; from phenylhydrazine, the *α-phenylhydrazino*-derivative, lemon-yellow, hard rosettes, m. p. 188°; from ethyl sodiomalonate, the mixed *ester*,

$$CH(CO_2Et)_2\cdot CHPh\cdot C_{10}H_5(OH)\cdot CO_2Me,$$

long, yellow prisms, m. p. 130—131°.

It was expected that with pyridine the substance might react in its ketonic form and yield an *o*-quinone, but a *pyridinium chloride*, $C_5H_5NCl\cdot CHPh\cdot C_{10}H_5(OH)\cdot CO_2Me$, was precipitated as a yellow powder, decomp. 162—163°, when the base was added to a solution of the compound in benzene. The aqueous solution, especially with silver oxide, soon deposited methyl 1-α-hydroxy-benzyl-2-naphthol-3-carboxylate (Friedl, *loc. cit.*), and potassium hydroxide gave, in addition, the above ethane derivative. Quinoline behaved similarly, but no pure product could be isolated.

Colour reactions with ferric and stannic chlorides, sulphuric and perchloric acids are described. J. C. W.

Condensation of *p*-Tolualdehyde with Methyl 2:3-Hydroxynaphthoate. Marius Rebek (*Monatsh.*, 1913, **34**, 1519—1546).—Methyl 2:3-hydroxynaphthoate, which, with the ethyl ester, has been crystallographically examined by von Lang, condenses just as readily with *p*-tolualdehyde under the influence of hydrogen chloride or bromide as it does with benzaldehyde. *Methyl* 1-*α-chloro*-p-*methylbenzyl-2-naphthol-3-carboxylate*, $C_6H_4Me\cdot CHCl\cdot C_{10}H_5(OH)\cdot CO_2Me$, forms pale yellow, microscopic tablets, m. p. 143—145°, which give various colour reactions with sulphuric and perchloric acids and stannic and ferric chlorides. The *α-bromo*-derivative forms yellow, glittering, flat leaflets, m. p. 157—159°. In the case of hydrogen bromide, a good yield of the condensation product was obtained when molecular quantities of the reacting substances were diluted with ether. From such a solution, hydrogen chloride gave no crystals for some days,

when, finally, a condensation product of the α-chloro-derivative with more ester, namely, *methyl* p-*xylylidenebis-2-naphthol-3-carboxylate* (p-*tolyl-di-2-hydroxy-3-carbomethoxynaphthylmethane*),

$$C_6H_4Me\cdot CH[C_{10}H_5(OH)\cdot CO_2Me]_2,$$

was obtained in well-defined prisms, m. p. 218—222°, which crystallised with $\frac{1}{2}$ mol. of chloroform.

On adding water to a cold acetone solution of the α-bromo-derivative, *methyl* 1-*α-hydroxy*-p-*methylbenzyl-2-naphthol-3-carboxylate*,

$$C_6H_4Me\cdot CH(OH)\cdot C_{10}H_5(OH)\cdot CO_2Me,$$

crystallises in yellow, rhombic leaflets, m. p. 155—158°. This compound tends to condense to an ether, especially in presence of alcohol or hydrochloric acid, or on melting. When the α-chloro-derivative was boiled with moderately strong hydrochloric acid, the same compound, *methyl αα'-oxidobis*-1-p-*methylbenzyl-2-naphthol-3-carboxylate*,

$$O[CH(C_6H_4Me)\cdot C_{10}H_5(OH)\cdot CO_2Me]_2,$$

was obtained in yellow, micro-leaflets, m. p. 216·5—219°. The speed of the action with water was roughly determined at ordinary temperatures.

When warmed with acetic anhydride and sodium acetate, the yellow halogen compounds became colourless, and an amorphous, acetylated derivative, which could not be crystallised, was obtained. Methyl alcohol condensed with the compounds to form *methyl* 1-*α-methoxy*-p-*methylbenzyl-2-naphthol-3-carboxylate*,

$$C_6H_4Me\cdot CH(OMe)\cdot C_{10}H_5(OH)\cdot CO_2Me,$$

in microscopic prisms, m. p. 178—180·5°. The α-halogen atom in the xylyl group was also replaced by a number of alcohol- and basic radicles, and the following corresponding condensation products obtained: *α-ethoxy*-derivative, stout, microscopic prisms, m. p. 95·5—97·5°; *α-propoxy*-derivative, yellow, microscopic prisms, m. p. 105·5—108·5°; *α-phenoxy*-derivative, faintly yellow prisms, m. p. 175—176°; p-*tolyloxy*-derivative, rectangular plates or leaflets, m. p. 165·5—167°; *α-thymoxy*-derivative, stout, microscopic needles, m. p. 188—189°; *α-anilino*-derivative, pale yellow, m. p. 210—211·5°; *α-phenylhydrazino*-derivative, lemon-yellow needles, decomp. 140°; *α-piperidino*-derivative, silky needles, m. p. 172—173·5°; p-*benzeneazoanilino*-derivative, orange, short prisms, m. p. 210—210·5°, reddened by hydrochloric acid vapours.

Methyl α-chloro-1-*p*-methylbenzyl-2-naphthol-3-carboxylate was hydrolysed by adding hydriodic acid to a warm solution in acetic anhydride. p-*Methylbenzyl-2-naphthol-3-carboxylic acid*,

$$C_6H_4Me\cdot CH_2\cdot C_{10}H_5(OH)\cdot CO_2H,$$

formed intensely yellow crystals, m. p. 249—250° (decomp.), and gave a white *silver* salt, decomp. 210°, from which the *methyl* ester, m. p. 137—138°, was prepared. The latter was also present in the product from the above hydrolysis.

Characteristic colour reactions are exhibited by all these compounds.

J. C. W.

Condensation of Anisaldehyde with Methyl 2 : 3-Hydroxynaphthoate. FRITZ WEISHUT (*Monatsh.*, 1913, **34**, 1547—1565).—Studies analogous to the foregoing were carried out with anisaldehyde.

Methyl 1-*a-chloro*-p-*methoxybenzyl*-2-*naphthol*-3-*carboxylate*,

$OMe\cdot C_6H_4\cdot CHCl\cdot C_{10}H_5(OH)\cdot CO_2Me$,

formed yellow prisms, m. p. 171—173°, decomp. 185°, and gave a series of remarkable colour reactions with strong acids, due to the presence of a carbonium valence. Silver sulphate rendered a warm benzene solution violet-red; the colour disappeared on cooling and returned on warming. The *bromo*-analogue had m. p. 162—164°. An attempt to prepare this compound by condensation in methyl alcohol solution gave as a by-product, *methyl anisylidenebis*-2-*naphthol*-3-*carboxylate*, $OMe\cdot C_6H_4\cdot CH[C_{10}H_5(OH)\cdot CO_2Me]_2$, in pale yellow, microscopic crystals, m. p. 213—215°.

Cold water precipitated from an acetone solution of the halogen derivatives, *methyl* 1-*a-hydroxy*-p-*methoxybenzyl*-2-*naphthol*-3-*carboxylate*, which formed pale yellow leaflets, m. p. 129—130°. The speed of the reaction with water was measured in the case of the α-chlorobenzyl-, α-chloro- and α-bromo-anisyl compounds of this series, and the influence of the methoxy-group and the halogen atom were determined. The methoxy-group renders the lability of the halogen atom of the order of an ionic reaction, whilst the bromo-compounds are more reactive than the chloro-. Boiling water gave rise to *methyl* αα'-*oxidobis*-1-p-*methoxybenzyl*-2-*naphthol*-3-*carboxylate*,

$O[CH(C_6H_4\cdot OMe)\cdot C_{10}H_5(OH)\cdot CO_2Me]_2$,

in yellow prisms, m. p. (without crystal solvent) 202—204°.

Methyl alcohol yielded *methyl* 1-*a*-p-*dimethoxybenzyl*-2-*naphthol*-3-*carboxylate*, $OMe\cdot C_6H_4\cdot CH(OMe)\cdot C_{10}H_5(OH)\cdot CO_2Me$, in pale yellow, glittering tablets, m. p. 176—177°. Ammonia in benzene formed *methyl iminobis*-1-p-*methoxybenzyl*-2-*naphthol*-3-*carboxylate*,

$NH[CH(C_6H_4\cdot OMe)\cdot C_{10}H_5(OH)\cdot CO_2Me]_2$,

as a yellow substance, m. p. 145—148°. With carbamide in boiling acetone, *methyl carbamido*-s-*bis*-1-p-*methoxybenzyl*-2-*naphthol*-3-*carboxylate*, $CO[NH\cdot CH(C_6H_4\cdot OMe)\cdot C_{10}H_5(OH)\cdot CO_2Me]_2$, was obtained as a microcrystalline powder, m. p. 187—189°.

The following α-substituted condensation products were also prepared: α-*anilino*-, faint greenish-yellow, microcrystalline powder, m. p. 191—192°; α-p-*benzeneazoanilino*-, small, orange needles, m. p. 194—195°; α-*benzylamino*-, faintly yellow crystals, m. p. 107—108°; α-*piperidino*-, pale yellow powder, m. p. 166—167°. The basic substituents, in general, give rise to compounds which react in the enolic form, giving intense colours with ferric chloride, but not with strong acids.

The α-hydroxyl and α-anilino-groups were replaced by the methoxy-group, merely on boiling the substances concerned with methyl alcohol. Similarly, hydrogen chloride reconverted the ether or the methoxy-compound into the α-chloro-derivative. J. C. W.

Condensation of Methyl 2 : 3-Hydroxynaphthoate with *p*- and *m*-Nitrobenzaldehydes. JOSEF SEIB (*Monatsh.*, 1913, **34**, 1567—1591).—The influence of the nitro-group on the lability of the halogen atom in compounds analogous to the foregoing has been studied. A rough determination of the speed of the decomposition by cold water showed that the compounds were not half as reactive as

the unsubstituted ones, that the *m*-nitro-derivatives were more active than the para-isomerides and that, as before, bromine in the α-position is more labile than chlorine.

Methyl 1-*α-chloro*-p-*nitrobenzyl*-2-*naphthol*-3-*carboxylate*,

$$NO_2\cdot C_6H_4\cdot CHCl\cdot C_{10}H_5(OH)\cdot CO_2Me,$$

formed pale yellow, glistening prisms, m. p. 227—228·5°. On boiling with water it yielded the *α-hydroxy*-derivative in lemon-yellow prisms, m. p. 188—190°, which gave the *α-acetoxy*-compound, short prisms, m. p. 185—187·5°, on boiling with acetic anhydride. The *α-methoxy*-compound, formed slender, very pale yellow prisms, m. p. 149—150°; the *α-ethoxy*-derivative, long, yellow, rectangular tablets, m. p. 116—117°; the *α-phenoxy*-derivative, white needles, m. p. (with 1½ mols. C_6H_6) 181—181·5°; the *α*-p-*tolyloxy*-derivative, pale yellow needles, m. p. 180—180·5°; the *α-thymoxy*-derivative, yellow, microscopic prisms, m. p. 208—209°; the *α-anilino*-derivative, glistening, lemon-yellow tablets, with $\frac{2}{3}C_6H_6$, m. p. 197·5—198°, without crystal solvent, pure yellow, m. p. 199—201°, colourless *hydrochloride*, m. p. 168—171°; the *α*-p-*azobenzeneanilino*-derivative, long, velvety, dark yellow needles, m. p. 154—156°; the *α-benzylamino*-derivative, long, slender, white needles, m. p. 152—153°; the *α-piperidino*-derivative, yellow, rhombic leaflets, m. p. 176·5—177°. In their colour reactions, as before, the compounds with bases exhibit enolic properties, whereas the ketonic form is more pronounced in the remaining compounds.

Pyridine did not cause the total displacement of chlorine, but yielded the *α-pyridinium chloride*,

$$NO_2\cdot C_6H_4\cdot CH(C_5NH_5Cl)\cdot C_{10}H_5(OH)\cdot CO_2Me,$$

in pale yellow, prismatic tablets, m. p. 110°, which were completely hydrolysed in aqueous solution, especially in presence of silver oxide, to pyridine and the α-hydroxy-compound.

Methyl 1-*α-bromo*-p-*nitrobenzyl*-2-*naphthol*-3-*carboxylate* was obtained in yellow crystals, m. p. 207—208°. Hydriodic acid, however, yielded no crystalline product.

Methyl 1-*α-chloro*-m-*nitrobenzyl*-2-*naphthol*-3-*carboxylate* had m. p. 187—189°, and the *bromo*-analogue formed thin, pale yellow leaflets, with $1C_6H_6$, m. p. 177—178°. *o*-Nitrobenzaldehyde, on the contrary, yielded no definite condensation product with methyl 2:3-hydroxy-naphthoate. J. C. W.

Hydroxy-and Dihydroxy-diphenylcarboxylic Acids. MATHÄUS MURDROVČIĆ (*Monatsh.*, 1913, **34**, 1417—1441).—3:3′-Dihydroxy-diphenyl-4:4′-dicarboxylic acid, 3-hydroxydiphenyl-4:4′-dicarboxylic acid, and several of their derivatives have been prepared.

Dianisidine was diazotised and converted into the nitrile and this was saponified, with difficulty, by boiling for seventy to eighty hours with alcoholic potassium hydroxide. The crude 3:3′-*dimethoxydiphenyl*-4:4′-*dicarboxylic acid*, being only sparingly soluble, was converted into the methyl ester and recovered from this by hydrolysis, as a white, microcrystalline powder, m. p. 270—271·5°. The *potassium* salt, $C_{16}H_{21}O_6K_2,2H_2O$, forms long needles from dilute solutions in spirit, and the *silver* salt is a brown, crystalline powder. The *methyl* ester forms white leaflets, m. p. 170—171°. On heating either the ester or

the acid with hydriodic or hydrobromic acid, 3 : 3'-*dihydroxydiphenyl-4 : 4'-dicarboxylic acid* was obtained as a white, amorphous, sparingly soluble powder, m. p. 318° (decomp.). It gives a colourless solution in sulphuric acid, a deep violet coloration with alcoholic ferric chloride, and apparently forms anhydrides under the influence of thionyl chloride. The *methyl* ester forms slender, colourless needles, m. p. 213—215°, and is readily converted into *methyl* 3 : 3'-*diacetoxydiphenyl-4 : 4'-dicarboxylate*, which crystallises from alcohol in leaflets, m. p. 140—142°.

The methoxy-acid, in contrast to the hydroxy-acid, reacted smoothly with thionyl chloride, forming the *acid chloride*, $C_{16}H_{12}O_4Cl_2$, from a benzene solution of which, ammonia precipitated the *amide*. This forms large needles, $C_{16}H_{16}O_4N_2$,EtOH, from dilute alcohol, m. p. 254—260° (260—261° alcohol-free). On condensing the acid chloride with benzene in presence of aluminium chloride, 3 : 3'-*dihydroxy*-4 : 4'-*dibenzoyldiphenyl*, $C_{26}H_{18}O_4$, was obtained. The ketone was purified by solution in alkali, reprecipitation by carbon dioxide, heating with hydriodic acid, and crystallisation from alcohol. It forms yellow needles, m. p. 215·5—217·5°, gives a deep yellowish-green, fluorescent solution in sulphuric acid and a reddish-brown coloration with ferric chloride. It was converted by methyl sulphate into 3 : 3'-*dimethoxy-4 : 4'-dibenzoyldiphenyl*, which forms colourless, flat needles, m. p. 156—158°.

As starting material for the preparation of the monohydroxy-compounds, technical ethoxybenzidine was chosen. This was converted into a black, spongy nitrile, which was then hydrolysed as before. Owing to the ready solubility of the acid, however, the crude product could not easily be purified. It was therefore hydrolysed by heating in phenol solution with hydriodic acid, and the crude 3-*hydroxydiphenyl*-4 : 4'-*dicarboxylic acid* was esterified and recovered by hydrolysis. It forms a white, microcrystalline powder, m. p. 324—325°, crystallises with $1H_2O$ from diluted methyl alcohol, and gives a violet ferric chloride reaction. The *potassium* salt, $C_{14}H_8O_5K_2,H_2O$, and the light brown *silver* salt were prepared. The *methyl* ester forms long, white, glistening needles or leaflets, m. p. 168°, and does not condense with benzaldehyde. *Methyl* 3-*acetoxydiphenyl*-4 : 4'-*dicarboxylate* crystallises in very soluble, flat needles, m. p. 119°.

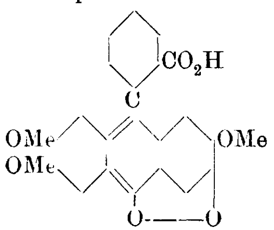
The isomeric mono-esters were prepared according to Wegscheider's directions for hydroxyterephthalic acid (A., 1900, i, 658). Partial hydrolysis of the dimethyl ester with potassium hydroxide yielded 4'-*methyl* 4-*hydrogen* 3-*hydroxydiphenyl*-4 : 4'-*dicarboxylate*, which could be separated from the dicarboxylic acid by benzene, in which the latter is insoluble. It has m. p. 240—241·5° (decomp.), gives a deep violet coloration with ferric chloride, and forms a *potassium* salt. 4-*Methyl* 4'-*hydrogen* 3-*hydroxydiphenyl*-4 : 4'-*dicarboxylate* was obtained in small yield by heating the acid potassium salt with methyl iodide in a sealed tube. It crystallises from benzene in needles, m. p. 215—216°, which give no coloration with ferric chloride.

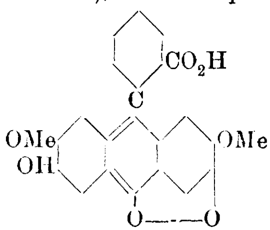
Schmidt and Schall (A., 1906, i, 23) described 4-hydroxydiphenic acid as a yellow compound. The author also obtained a yellow product,

but on attempting to condense it with benzaldehyde it crystallised as a colourless compound, m. p. 246·5°, the impurity remaining dissolved.

J. C. W.

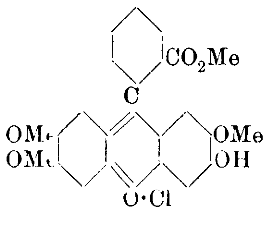
The Ethers and Esters of Hydroxyquinolphthalein. FRIEDRICH KEHRMANN and RICHARD BERG (*Ber.*, 1913, **46**, 3020—3028).—When hydroxyquinolphthalein in solution in sufficient aqueous sodium hydroxide to form the normal salt is warmed with one and two-third times its weight of methyl iodide, the solution on acidification with acetic acid deposits the *trimethyl ether* (formula I), which frequently

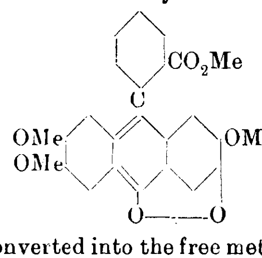
(I.) 

(II.) 

separates from a mixture of benzene and methyl alcohol in a feebly coloured, presumably lactonoid form; this on recrystallisation from methyl alcohol passes into the quinonoid form, orange-yellow, microscopic leaflets, m. p. 257°; the solution in alkali is yellow with a green fluorescence. The mother liquor from which the trimethyl ether has separated contains the sodium salt of the *dimethyl ether* (formula II), and this substance is deposited as the *hydrochloride* on the addition of concentrated hydrochloric acid; the free ether is liberated from its hydrochloride by the action of sodium acetate solution. This dimethyl ether, m. p. 270—271°, crystallises from methyl alcohol in reddish-brown prisms containing 1MeOH; it dissolves in sodium hydrogen carbonate solution, giving the *sodium* carboxylic salt as a yellowish-red solution with a green fluorescence; addition of sodium hydroxide solution causes the formation of the *disodium* salt, with an increase of the fluorescence; *silver* salt, insoluble reddish-brown precipitate.

On saturating a concentrated methyl-alcoholic solution of the trimethyl ether with hydrogen chloride and keeping for several weeks, needles of the *chloride* (formula III) are obtained. By treatment

(III.) 

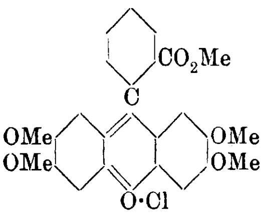
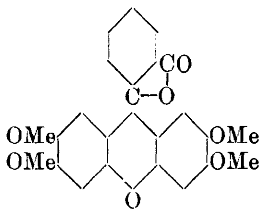
(IV.) 

with warm sodium acetate solution, this is converted into the free methyl *ester* of the trimethyl ether (formula IV), which crystallises from a mixture of benzene and methyl alcohol in orange-yellow, iridescent leaflets, m. p. 271—272°.

A similar esterification of the above-mentioned dimethyl ether gives rise to an analogous ester *chloride*, yellow needles, which on decomposition by sodium acetate solution passes into the free *ester* of the dimethyl ether, red crystals, m. p. 248°.

The action of methyl sulphate on a solution of the ester of the trimethyl ether in nitrobenzene solution gave rise to the methyl sulphate salt of the methyl ester of the tetramethyl ether. From this "mixed" sulphate the more ordinary salts were easily obtainable, and their solubility is found to be comparable with those of the corresponding potassium salts; formula V is the *chloride.*

The chloride, *bromide*, and *iodide* are very soluble, the *nitrate, chlorate, dichromate*, and *persulphate* are moderately soluble, whilst the *perchlorate* and *platinichloride* are sparingly soluble in water. If an aqueous solution of the nitrate is treated in the cold with an excess of

(V.)  (VI.) 

fairly concentrated sodium hydroxide solution, a precipitate is produced, which subsequently redissolves as the *sodium* salt of the tetramethyl ether carboxylic acid; on the addition of acetic acid and warming, the tetramethyl ether lactone (formula VI), colourless prisms, m. p. 202°, is obtained. D. F. T.

Resorcinolbenzein and Fluorescein. FRIEDRICH KEHRMANN (*Ber.*, 1913, **46**, 3028—3036).—A reply to von Liebig (A., 1912, i, 376; this vol., i, 79, 865). In the case of derivatives of fluorescein with which von Liebig obtained results at variance with those of the author and his collaborators, the substances have been reinvestigated with entire confirmation of the earlier results.

It has already been stated by Fischer and Hepp (A., 1895, i, 291) that the quinonoid dimethyl ether of fluorescein crystallises in two forms, namely, orange-yellow needles and deep red prisms. The difference in the m. p.'s recorded by von Liebig and by Kehrmann and Dengler (A., 1909, i, 249) is due to this dimorphism. Indeed, if a quantity of the orange-yellow needles is heated rapidly to 180°, it melts momentarily and resolidifies to melt again at approximately 194°; under similar treatment the red prisms melt at 208°.

The substance, m. p. 255°, obtained by von Liebig by the action of ammonia solution on the ether-insoluble residue (correctly regarded as trimethylfluorescein chloride) from the reaction product of methyl sulphate and disodium fluorescein, is not a dimethyl ether of fluorescein, but contains almost 2% of nitrogen and probably represents a carbinylimide or a carboxylimide. D. F. T.

Synthesis of Depsides, Moss Acids, and Tannins. EMIL FISCHER (*Ber.*, 1913, **46**, 3253—3289).—A lecture before the German

Natural Science Congress (compare A., 1908, i, 892; 1909, i, 161, 309; Fischer and Freudenberg, A., 1910, i, 265; 1911, i, 874; 1912, i, 471, 887; Fischer and Hoesch, A., 1912, i, 859, etc.). The following facts are new. Evernic acid is dissolved by an ethereal solution of diazomethane after a time, and converted into the crystalline neutral ester, which is identified as methyl trimethyl-lecanoric acid. The constitution of evernic acid is thus established. Pentasalicyloglucose and the corresponding derivative of caffeic acid have been prepared, also pentacinnamoyl derivatives of α- and β-glucose, galactose, and mannose. *Penta-acetyl mannose* has m. p. 114—116°, $[\alpha]_D^{20}$ $-24.8°$.

E. F. A.

Humic Acids. IV. Investigations of Tacke and Süchting EUGEN GULLY (*Bied. Zentr.*, 1913, **42**, 655—659; from *Mitt. K. Bayr. Moorkulturanst.*, 1912, Heft. 5).—A reply to Tacke and Süchting (A., 1912, i, 473), in which the non-existence of humic acids is maintained. Further experiments showed that peat has no action on calcium oxalate; and that bases absorbed by *Sphagna* can be extracted by water free from carbon dioxide. The various results obtained with peat, such as the liberation of iodine from its salts, the inversion of sucrose, and the production of hydrogen from peat and iron are not considered sufficient evidence that humic acids exist.

N. H. J. M.

The Autoxidation of Organic Compounds. I. Autoxidation of Aromatic Aldehydes. HERMANN STAUDINGER [with E. HENE and J. PRODROM (*Ber.*, 1913, **46**, 3530—3535).—It has been previously shown (A., 1911, i, 877) that diphenylketen reacts more readily with methoxy- or dimethylamino-substituted aromatic compounds than with the unsubstituted substances, and similar observations have been made during experiments on the action of oxalyl chloride on carbonyl compounds (A., 1909, i, 905). The authors have therefore been led to the determination of the rate of autoxidation of benzaldehyde and a number of its p-substituted derivatives.

Weighed quantities of benzaldehyde, p-methoxybenzaldehyde, p-hydroxybenzaldehyde, and p-dimethylaminobenzaldehyde were heated with an excess of oxygen in closed flasks at 131° and the amount of oxygen absorbed was estimated. In a second series of experiments, a regular stream of oxygen was bubbled through the aldehyde, the course of the reaction being followed by estimation of the acid formed. At 131°, however, dimethylaminobenzoic acid readily evolved carbon dioxide; a temperature of 80° was found suitable. The results show that p-dimethylaminobenzaldehyde is much less autoxidisable than anisaldehyde, which, however, is less affected than benzaldehyde. This is inexplicable on Engler and Weissberg's hypothesis that the primary product during autoxidation is formed by the addition of a molecule of oxygen to the unsaturated carbonyl group; it is, however, to be expected if Baeyer and Villiger's supposition is adopted that the addition of the oxygen molecule is accompanied by dissociation of the hydrogen atom, $Ph\cdot C\Big\langle{}^{O}_{H} + O\cdot O \longrightarrow Ph\cdot C\Big\langle{}^{O}_{O\cdot O\cdot H}$ (A., 1900, i, 437).

If Staudinger's views as to the asymmetric nature of the intermediate compound are accepted, the hydrogen atom would be more firmly attached to the strongly unsaturated carbonyl group of *p*-dimethylaminobenzaldehyde than to the relatively saturated carbonyl group of benzaldehyde, and therefore less capable of addition to the oxygen molecule. From this point of view, *o*-methoxybenzaldehyde should be the least readily, and *m*-methoxybenzaldehyde the most readily, autoxidisable of the three methoxybenzaldehydes, and this is shown to be actually the case.

Anti-auxochrome groups weaken the unsaturated character of the carbonyl group, and should therefore increase the mobility of the hydrogen atom and the tendency of the substance to autoxidation. *p*-Nitrobenzaldehyde, which should thus be readily autoxidised, absorbs little oxygen, since it is speedily resinified. The problem was, however, investigated by the introduction of acyl groups into amino- and hydroxy-groups. Acetoxybenzaldehyde, in contrast with hydroxy- and methoxy-benzaldehyde, was found to be almost as readily autoxidised as benzaldehyde. H. W.

The Autoxidation of Organic Compounds. II. Relationships between Autoxidation and Benzoin Formation. HERMANN STAUDINGER [with E. HENE] (*Ber.*, 1913, **46**, 3535—3538).—If the possibility of formation of intermediate products be disregarded, the formation of benzoin derivatives from aldehydes is comparable with the autoxidation of the latter substances; in the one case, addition of the aldehyde to the carbonyl group occurs, in the other to the oxygen molecule (compare preceding abstract). A benzoin will only be readily produced, therefore, from an aldehyde which contains a relatively unsaturated carbonyl group and a relatively mobile hydrogen atom; thus, dimethylaminobenzaldehyde does not yield a benzoin, since, although the carbonyl group is strongly unsaturated, the hydrogen atom lacks mobility. Favourable conditions for benzoin formation are found in benzaldehyde, anisaldehyde, and *p*-chlorobenzaldehyde (compare Hantzsch and Glover, A., 1907, i, 538). From this point of view, mixed benzoin derivatives should be obtainable from a pair of aldehydes if the one possesses a sufficiently mobile hydrogen atom, the other a sufficiently unsaturated carbonyl group; the condensation products of *p*-dimethylaminobenzaldehyde and *p*-chlorobenzaldehyde with benzaldehyde are described.

p-*Dimethylaminobenzoin*, $NMe_2\cdot C_6H_4\cdot CH(OH)\cdot COPh$, m. p. 163—164°, is obtained in 86% yield when a solution of benzaldehyde and *p*-dimethylaminobenzaldehyde in alcohol is boiled with an aqueous solution of potassium cyanide. The constitution of this substance is deduced from the fact that it condenses with dimethylaniline in the presence of phosphoryl chloride to yield *benzoyltetramethyldiaminodiphenylmethane*, $COPh\cdot CH(C_6H_4\cdot NMe_2)_2$, pale yellow needles, m. p. 162—164°, which are readily oxidised to a blue dye. Oxidation with Fehling's solution converts *p*-dimethylaminobenzoin into p-*dimethylaminobenzil*, yellowish-green crystals, m. p. 115—116°.

Under similar conditions, *p*-dimethylaminobenzaldehyde condenses

with *p*-chlorobenzaldehyde to yield p-*chloro*-p′-*dimethylaminobenzoin*, m. p. 127—128°.

Benzaldehyde and anisaldehyde, as also chlorobenzaldehyde and anisaldehyde, appear to yield mixed benzoins. A uniform product could not be isolated. Probably a mixture of benzoins is formed in each case which cannot be separated.

Attempts to prepare benzoins from aromatic and aliphatic aldehydes were unsuccessful. H. W.

The Existence of Mandelaldehyde in Aqueous Solution. W. LLOYD EVANS and CHARLES RAYMOND PARKINSON (*J. Amer. Chem. Soc.*, 1913, **35**, 1770—1774. Compare this vol., i, 173).—It is already known that, whereas lactaldehyde is incapable of existence in water at 100° (Nef, A., 1905, i, 3), it is sufficiently stable in water at the ordinary temperature to be studied experimentally (Wohl and Lange, A., 1908, i, 943). Nef has shown that mandelaldehyde also cannot exist in water at 100°, and the present investigation demonstrates that it cannot exist even in the presence of cold aqueous alcohol or of dilute sulphuric acid.

Dibromoacetophenone was converted successively into phenylglyoxal acetal, $CHBz(OEt)_2$, and mandelaldehyde acetal, $CH(OEt)_2\cdot CHPh\cdot OH$. The last-named substance was found to undergo hydrolysis, yielding benzoylcarbinol, $CH_2Bz\cdot OH$, when suspended in *N*/20-sulphuric acid at 0°, when suspended in water at 0°, or even when exposed to the moisture of the atmosphere. D. F. T.

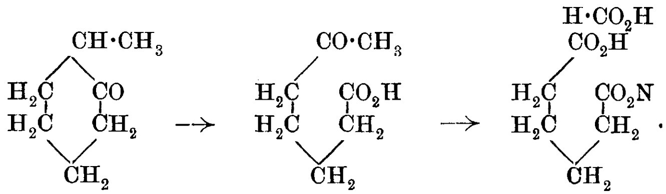
6-Aminopiperonal. AUGUSTE RILLIET and L. KREITMANN (*Compt. rend.*, 1913, **157**, 782—784).—Various unsuccessful attempts have been made to prepare the above substance by reduction of 6-nitropiperonal (compare Haber, A., 1891, 704; Friedländer and Schreiber, A., 1895, i, 524). The authors have succeeded by first protecting the aldehyde group.

6-Nitropiperonal condenses readily with various amines to give the corresponding piperonylidene derivatives, of which the following have been prepared: 6-*nitropiperonylidene*-p-*toluidine*, yellow needles, m. p. 121·5°; 6-*nitropiperonylidene*-p-*anisidine*, golden-yellow plates, m. p. 125·5°, and 6-*nitropiperonylidene*-o-*toluidine*, yellow needles, m. p. 128°. All of these are readily reduced in boiling alcoholic solution by sodium sulphide to the corresponding *amino*-compounds, having respectively m. p.'s 134·5°, 162°, and 106°. The hydrolysis of the two latter compounds has not given the desired results, being only brought about with difficulty, but 6-aminopiperonylidene-*p*-toluidine is readily hydrolysed by prolonged boiling with dilute aqueous alkali, giving 6-*aminopiperonal*, brilliant yellow prisms, m. p. 107°, dissolving in acids to a bright red solution. From it the following derivatives have been prepared: the *mercurichloride*, white needles, decomposing at 135°; a *platinichloride*, a red, amorphous powder, decomposing suddenly on heating; 6-*benzoylaminopiperonal*, pale yellow needles, m. p. 187·5°; 6-*acetylaminopiperonal*, long, white needles, m. p. 161°, yielding a *phenylhydrazone*, white needles, m. p. 205°, and 6-*aminopiperonalphenylhydrazone*, m. p. 222° (decomp.). W. G.

Chemical Action of Light. XXVII. Autoxidation. V. GIACOMO CIAMICIAN and PAUL SILBER (*Ber.*, 1913, **46**, 3077—3084; *Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 339—348).—The action of oxygen and light on acetone, *cyclo*hexanone, the three methyl*cyclo*hexanones, and methylheptenone has been studied. Except in the cases of acetone and methylheptenone (A., 1910, i, 496), the products obtained are due to the combined effect of autoxidation and hydrolysis (compare A., 1908, i, 277).

Acetone yields formaldehyde and acetic acid, whilst *cyclo*hexanone gives hexoic and adipic acids.

1-Methyl*cyclo*hexan-2-one yields *n*-heptoic acid (œnanthoic acid), adipic acid, and acetylvaleric acid, together with traces of aldehyde, the main reaction proceeding in accordance with the scheme:



δ-Acetylvaleric acid has m. p. 31—33°, whilst the semicarbazone melts at 147°. Wallach gives the m. p.'s about 50° and 144—146° respectively (A., 1904, i, 425).

1-Methyl*cyclo*hexan-3-one is less affected than the 1 : 2-derivative, and gives a heptoic acid, b. p. 215—216°, which must have the constitution $CH_2Me\cdot CH_2\cdot CHMe\cdot CH_2\cdot CO_2H$, a dibasic acid, m. p. 97°, identical with the corresponding compound from 1 : 4-methyl*cyclo*hexanone, and hence having the formula

$$CO_2H\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot CO_2H,$$

and a lactone which could not be prepared in the pure state.

1-Methyl*cyclo*hexan-4-one gives γ-methylhexoic acid, the above-mentioned dicarboxylic acid and the lactone corresponding with the hydroxy-acid. The latter could not be obtained in a pure condition.

Methylheptenone yields carbon dioxide, acetone, formic acid, acetic acid, and lævulic acid, together with a ketoglycol consisting mainly of the compound $OH\cdot CMe_2\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3$, possibly mixed with the hydroxydiketone, $OH\cdot CMe_2\cdot CO\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3$. Crystalline derivatives could not be obtained, but the identity of the product follows from its conversion by boiling dilute sulphuric acid into β-methylheptane-γζ-dione, $CHMe_2\cdot CO\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3$, and identification of the semicarbazone and dioxime of the latter with the similar compounds obtained by the oxidation of methylheptenone with potassium permanganate (compare Harries, A., 1902, i, 345). The autoxidation of methylheptenone in light proceeds mainly, therefore, according to the scheme: $CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3 \longrightarrow$

$$OH\cdot CMe_2\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3 \longrightarrow$$
$$OH\cdot CMe_2\cdot CO\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3 \longrightarrow$$
$$CH_3\cdot CO\cdot CH_3 + CO_2H\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3,$$

the acetic and formic acids, as probably also the carbon dioxide, being formed by a partial further oxidation of the acetone. H. W.

Alkylation of 3- and 4-Methyl*cyclo*hexan-3- and 4-ones by means of Sodamide. ALBIN HALLER (*Compt. rend.*, 1913, **157**, 737—743).—Methyl*cyclo*hexan-3- and 4-one not only undergo methylation and allylation under the influence of sodamide, but also ethylation. During the latter reaction condensation of the product on itself is much more pronounced than with the methyl and allyl derivatives. Further, a comparative study of the alkylation of the three methyl*cyclo*hexanones shows that this condensation is much more pronounced the more remote the methyl group is from the ketonic group, and attains its maximum with *cyclo*hexanone itself.

Starting with 1-methyl*cyclo*hexan-3-one, ethyl iodide yields, in ethereal solution in the presence of sodamide, 1-methyl-4-ethyl*cyclo*hexan-3-one (compare A., 1905, i, 214, and Wallach, this vol., i, 482) and 1-*methyl*-2 : 4-*diethyl*cyclo*hexan*-3-*one*, b. p. 216—219°/760 mm., D_4^{17} 0·9061, n_D^{17} 1·4577, together with about 22% of the condensation product. Subsequent successive ethylation of this diethyl derivative furnishes:

1-*Methyl*-2 : 2 : 4-*triethyl*cyclo*hexan*-3-*one*, b. p. 242—244°/770 mm., D_4^{23} 0·9077, n_D^{23} 1·4609.

1-*Methyl*-2 : 2 : 4 : 4-*tetraethyl*cyclo*hexan*-3-*one*, b. p. 266—270°/770 mm., D_4^{20} 0·9358, n_D^{20} 1·4697, having an odour resembling menthone.

1-Methyl*cyclo*hexan-4-ol, b. p. 173—173·5°/760 mm., D_4^{20} 0·9170, n_D 1·4573, obtained by the hydrogenation of *p*-cresol, on oxidation with chromic acid yields 1-methyl*cyclo*hexan-4-one, b. p. 170°/760 mm., D_4^{20} 0·9132, n_D^{20} 1·4458. This ketone on successive methylation under the prescribed conditions with methyl iodide yields:

1 : 3-Dimethyl*cyclo*hexan-4-one (compare Wallach, *loc. cit.*).

1 : 3 : 5-*Trimethyl*cyclo*hexan*-2-*one*, b. p. 184—185°/748 mm., D_4^{20} 0·8992, n_D^{20} 1·4458.

1 : 1 : 3 : 5-*Tetramethyl*cyclo*hexan*-2-*one*, b. p. 190—191°/753 mm., D_4^{20} 0·8903, n_D^{20} 1·4459.

1 : 1 : 3 : 3 : 5-*Pentamethyl*cyclo*hexan*-2-*one*, b. p. 196—198°, D_4^{20} 0·8828, n_D^{20} 1·4461.

Successive introduction of a methyl group produces a regular rise in the boiling point of 6° to 7°, and a steady diminution in the density, whilst the refractive index remains practically constant.

The pentamethyl ketone on hydrogenation with sodium in absolute alcohol yields 1 : 1 : 3 : 3 : 5-*pentamethyl*cyclo*hexan*-2-*ol*, b. p. 203°/760 mm., D_4^{20} 0·8929, n_D^{20} 1·4581, a viscous liquid having an odour resembling that of eugenol.

Progressive ethylation of 1-methyl*cyclo*hexan-4-one similarly yields:

1-*Methyl*-3-*ethyl*cyclo*hexan*-4-*one*, b. p. 196—198°/761 mm., D_4^{20} 0·8996, n_D^{20} 1·4494, having an odour of menthone.

1-*Methyl*-3 : 5-*diethyl*cyclo*hexan*-4-*one*, b. p. 216—218°/765 mm., D_4^{20} 0·9023, n_D^{20} 1·4562, its odour being identical with that of menthone.

1-*Methyl*-3 : 3 : 5-*triethyl*cyclo*hexan*-4-*one*, b. p. 237—240°/758 mm., D_4^{20} 0·9047, n_D^{20} 1·4615.

1-*Methyl*-3 : 3 : 5 : 5-*tetraethyl*cyclo*hexan*-4-*one*, b. p. 258—262°/760 mm., D_4^{20} 0·9301, n_D^{20} 1·4675 : a viscous liquid with an odour of turpentine. W. G.

5-Acetylamino-2-hydroxyacetophenone and its Derivatives. FRANZ KUNCKELL (*Ber. Deut. pharm. Ges.*, 1913, **23**, 472—490. Compare A., 1900, i, 663; 1911, i, 990; 1912, i, 268).—2-Hydroxy-5-acetylaminoacetophenone, $NHAc\cdot C_6H_3(OH)\cdot COMe$ (compare Kunckell and Hammerschmidt, this vol., i, 1204), is prepared by the gradual addition of aluminium chloride in bright sunlight to a solution of phenacetin in anhydrous carbon disulphide and acetyl bromide (Schmidt, *Diss.*, 1900) or acetyl chloride (Dirks, *Diss.*, 1906). It forms monoclinic crystals, m. p. 165°. Concentrated hydrochloric acid converts it into 5-*amino*-2-*hydroxyacetophenone*, yellowish-green needles, m. p. 105°, the *hydrochloride*, white leaflets, m. p. 155° (decomp.), and *sulphate*, m. p. 150°, of which are also described. The *phenylhydrazone* of 2-hydroxy-5-acetylaminoacetophenone forms small, yellow needles, m. p. 107°, whilst the *oxime*, white needles, has m. p. 160°; the nitro-derivative, $C_{10}H_{10}O_5N_2$, yellow needles, m. p. 170°, is obtained by the gradual addition of concentrated nitric acid to a well-cooled solution of the substance in glacial acetic acid.

When treated with a solution of sodium ethoxide in absolute alcohol, 2-hydroxy-5-acetylaminoacetophenone yields the corresponding *sodium* derivative, lemon-yellow leaflets, m. p. 225° (decomp.), which, when heated with ethyl iodide and ethyl alcohol, is converted into 5-*acetylamino*-2-*ethoxyacetophenone*, white needles, m. p. 155° (*phenylhydrazone*, brown needles, m. p. 180°; *mononitro*-derivative, yellowish-red needles, m. p. 125°). Attempts to prepare the substance directly by the action of acetyl chloride and aluminium chloride on phenacetin were unsuccessful, the ethyl group being invariably eliminated. Boiling hydrochloric acid converts it into 5-*amino*-2-*ethoxyacetophenone hydrochloride*, m. p. 215°.

ω-*Chloro*-2-*hydroxy*-5-*acetylaminoacetophenone*,

$$CH_2Cl\cdot CO\cdot C_6H_3(OH)\cdot NHAc,$$

yellow needles, m. p. 190°, is prepared by the gradual addition of aluminium chloride in sunlight to a solution of phenacetin and chloroacetyl chloride in carbon disulphide. The free *base*, yellowish-green needles, has m. p. 135°; *hydrochloride*, white leaflets, m. p. 210° (decomp.). The *oxime* of 2-hydroxy-5-acetylamino-ω-chloroacetophenone has m. p. 195°.

ω-*Chloromononitro*-2-*hydroxy*-5-*acetylaminoacetophenone*, yellow needles, m. p. 160°, is obtained by the gradual addition of concentrated nitric acid to a well cooled solution of ω-chloro-2-hydroxy-5-acetylaminoacetophenone in glacial acetic acid. The *oxime* has m. p. 230° (decomp.). The free *base* forms red needles, m. p. 145° (decomp); the *hydrochloride* of the latter decomposes, without melting, at 210°.

ω-*Chloro*-2-*hydroxy*-5-*benzoylaminoacetophenone*,

$$CH_2Cl\cdot CO\cdot C_6H_3(OH)\cdot NHBz,$$

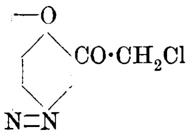
m. p. 203°, is prepared by the action of benzyl chloride on an alcoholic solution of ω-chloro-5-amino-2-hydroxyacetophenone. The corresponding *benzoate* has m. p. 166—167°; the *oxime*, m. p. 197°. The *mononitro*-derivative, yellow needles, m. p. 190° (decomp.), is obtained by nitrating the benzoyl derivative in glacial acetic acid solution.

ω-Chloro-5-amino-2-hydroxyacetophenone couples with a diazotised

solution of aniline, yielding a *diazoamino*-compound,

$$CH_2Cl\cdot CO\cdot C_6H_3(OH)\cdot NH\cdot N_2Ph,$$

unstable, golden-yellow crystals, m. p. 127°. Attempts to diazotise the base led to the isolation of a *compound* (annexed formula), which explodes without melting at 140°. This substance is decomposed by boiling water, but a pure substance could not be isolated from the product.



The *phenylurethanes* of ω-chloro-2-hydroxy-5-acetylaminoacetophenone and of ω-chloro-5-amino-2-hydroxyacetophenone have m. p.'s 139° and 204° respectively.

The action of phenylhydrazine at a temperature not exceeding 120° on ω-chloro-2-hydroxy-5-acetylaminoacetophenone leads to the formation of the *substance*, $NHAc\cdot C_6H_3(OH)\cdot C(:N\cdot NHPh)\cdot CH:N\cdot NHPh$, needles, m. p. 223°. If the reaction is carried out at a higher temperature and with a relatively smaller quantity of phenylhydrazine, a *substance*, m. p. 247°, is obtained, which has not been completely investigated owing to lack of material. Phenylhydrazine reacts with ω-chloro-5-amino-2-hydroxyacetophenone in a similar manner, yielding the *hydrochloride* of the osazone,

$$HCl,NH_2\cdot C_6H_3(OH)\cdot C(:N\cdot NHPh)\cdot CH:N\cdot NHPh;$$

the pure *osazone*, m. p. 205°, is unstable. H. W.

ε-Aminoketones. KARL A. BÖTTCHER (*Ber.*, 1913, **46**, 3158—3167).—The salts of several benzene-substituted ε-aminoketones have been prepared. Like the simple phenyl ε-aminoamyl ketone in contrast to methyl ε-aminoamyl ketone (Gabriel, A., 1909, i, 492), the new bases do not lose water to form heptacyclic imines, but unlike those simple amines, they yield no definite products under the influence of reducing agents, but are usually unaffected.

Benzoyl-leucine was converted into the chloride, and this condensed with toluene in presence of aluminium chloride. The new benzoyl derivative could not be purified, but was hydrolysed by means of fuming hydrochloric acid in a sealed tube and converted into *tolyl ε-aminoamyl ketone hydrochloride*, $C_{13}H_{20}ONCl$. This salt crystallises in rhombohedra, m. p. 163°, and forms a *platinichloride*, orange-yellow, crystalline powder, m. p. 211°, an *aurichloride*, sulphur-yellow rhombohedra, m. p. 114—116°, and a *picrate*, yellow, jagged crystals, m. p. 148°. The yield of the base was only 18%, but was raised to 41·5% by employing the phthalyl derivative in the condensation. For this purpose, benzoyl-leucine was hydrolysed with fuming hydrochloric acid, the resulting ε-aminohexoic acid was heated with phthalic anhydride, and then converted into ε-phthaliminohexoyl chloride by means of phosphorus pentachloride. On condensation with toluene, the *phthalimino*-derivative, $C_8H_4O_2:N\cdot[CH_2]_5\cdot CO\cdot C_7H_7$, was obtained in well-defined prisms, m. p. 134°. The phthalamino-acid was then prepared by boiling the imide with potassium hydroxide and precipitating with acid, and was finally hydrolysed in a sealed tube. Free *tolyl ε-aminoamyl ketone*, $NH_2\cdot[CH_2]_5\cdot CO\cdot C_7H_7$, was obtained as a colourless oil, b. p. 185—189°/15 mm., m. p. 39—40°, with a basic odour and

strongly alkaline reaction. The *benzenesulphonamide*,

$$C_7H_7\cdot CO\cdot[CH_2]_5\cdot NH\cdot SO_2Ph,$$

formed long, rectangular tablets, m. p. 135—136°. Like the sulphonyl derivative of heptylamine (Marckwald, A., 1900, i, 149) and like ε-*benzoylamylbenzenesulphonamide* [*benzenesulphonyl-ε-aminohexophenone*], $COPh\cdot[CH_2]_5\cdot NH\cdot SO_2Ph$, which was prepared in rhombic tablets, m. p. 84—85°, from ε-benzoylamylamine [ε-aminohexophenone], it did not dissolve in alkalis, but was changed into oily drops on boiling with 33% potassium hydroxide.

ε-Phthaliminohexoyl chloride was also condensed with anisole. The *phthalimino*-derivative, $C_8H_4O_2\colon N\cdot[CH_2]_5\cdot CO\cdot C_7H_7O$, was obtained in leaflets, m. p. 104°, and converted into the *hydrochloride* of ε-p-*methoxybenzoylamylamine* (ε-*anisoylamylamine*) [p-*anisyl* ε-*aminoamyl ketone*], $OMe\cdot C_6H_4\cdot CO\cdot[CH_2]_5\cdot NH_2,HCl$, which crystallised in thin leaflets, m. p. 166°, and formed a *platinichloride*, sparingly soluble, pale orange, hexagonal leaflets, m. p. 212°; an *aurichloride*, long, orange-yellow rhombohedra, m. p. 118°, and a *picrate*, yellow leaflets, m. p. 135°. The oily base yielded a *phenylthiocarbamide*,

$$C_{13}H_{17}O_2\cdot NH\cdot CS\cdot NHPh,$$

small tablets, m. p. 123°, and a *benzenesulphonamide*, prisms, m. p. 142°.

The following derivatives of ε-*o*-xyloylamylamine [*o*-xylyl ε-aminoamyl ketone] were also prepared: the *phthalimino*-derivative,

$$C_8H_4O_2\colon N\cdot C_{14}H_{19}O,$$

in long needles, m. p. 92°; the *hydrochloride*,

$$C_6H_3Me_2\cdot CO\cdot[CH_2]_5\cdot NH_2,HCl,$$

long leaflets, m. p. 122°; *platinichloride*, pale orange leaflets, m. p. 214°; *aurichloride*, thin, lemon-yellow leaflets, m. p. 129°; *picrate*, jagged leaflets, m. p. 142°. The corresponding derivatives of *m*-xylyl ε-aminoamyl ketone are as follows: *phthalimino*-compound, lanceolate crystals, m. p. 71°; *hydrochloride*, hygroscopic needles, m. p. 88—90°; *platinichloride*, very slender, pale orange needles, m. p. 208°; *aurichloride*, yellow, rectangular, thick tablets, m. p. 99°; *picrate*, small, rectangular, yellow tablets, m. p. 136°. The following derivatives of *p*-xylyl ε-aminoamyl ketone were also prepared: *phthalimide*, needles, m. p. 82°; *hydrochloride*, hexahedra, m. p. 86—87°; *platinichloride*, orange-yellow needles, m. p. 206°; *aurichloride*, thin, yellow leaflets, m. p. 125°; *picrate*, branched needles, m. p. 122°.

Derivatives of ε-3:4-dimethoxybenzoylamylamine [veratryl ε-aminoamyl ketone] are also described: *phthalimide*, tufted needles, m. p. 147°; *hydrochloride*, $(OMe)_2C_6H_3\cdot CO\cdot[CH_2]_5\cdot NH_2,HCl$, small, slender needles, m. p. 106°; *platinichloride*, orange-yellow, slender, branched needles, m. p. 205°; *aurichloride*, ochreous needles, m. p. 165°. The following derivatives of 2:4-dimethoxyphenyl ε-aminoamyl ketone were also prepared: *phthalimide*, long needles, m. p. 117°; *hydrochloride*, tufted leaflets, m. p. 151—152°; *picrate*, tufted prisms, m. p. 167°; *platinichloride*, orange-yellow, flat needles, m. p. 220°; *aurichlorides*, $C_8H_9O_2\cdot CO\cdot[CH_2]_5\cdot NH_2,HCl,2AuCl_3$, from an aqueous solution, yellow leaflets, m. p. 96°, or

$$C_8H_9O_2\cdot CO\cdot[CH_2]_5\cdot NH_2,HCl,AuCl_3,H_2O,$$

from warm 50% acetic acid, orange-yellow prisms, m. p. 96°. Finally,

the following derivatives of 2 : 5-dimethoxyphenyl ε-aminoamyl ketone are described: *phthalimide*, lanceolate crystals, m. p. 108—109°, which was largely resinified on hydrolysis; *hydrochloride*, yellowish-green, long needles, m. p. 109°; *picrate*, yellow rhombohedra, m. p. 151°; the platini- and auri-chlorides are unstable. J. C. W.

Action of Heat on Ketoximes. ARTHUR KÖTZ and O. WUNSTORF (*J. pr. Chem.*, 1913, [ii], **88**, 519—530. Compare Angeli and Alessandri, this vol., i, 983).—When heated in the absence of air, ketoximes, which do not distil or sublime without change, undergo decomposition in one of two ways: (1) into ketones, nitrogen, and ammonia: $3CR_2\text{:}N\cdot OH \longrightarrow 3COR_2 + N_2 + NH_3$; (2) into nitriles and aldehydes or alcohols:

$$OH\cdot N\text{:}CPh\cdot CH_2Ph \longrightarrow CNPh + CH_2Ph\cdot OH$$

$$OH\cdot N\text{:}CPh\cdot CHPh\cdot OH \longrightarrow CNPh + C_6H_5\cdot CHO + H_2O.$$

Acetoxime and *cyclo*hexanoneoxime distil without change under ordinary pressure; at 210—216°, acetoxime decomposes into ammonia, methane, and a mixture of bases, not identified.

When heated in an atmosphere of carbon dioxide, benzophenoneoxime yields benzophenone, nitrogen, and ammonia. Under diminished pressure, acetophenoneoxime may be distilled unchanged, but at ordinary pressures is resolved into acetophenone and ammonia.

Deoxybenzoin decomposes explosively at 270°, yielding benzonitrile, lophine, and benzyl alcohol. At 240°, α-benzoinoxime yields lophine, benzaldehyde, and benzonitrile, whilst oximinocamphor gives rise to camphoric anhydride and αε-dimethyl-Δ^{α}-heptenonitrile (Tiemann, A., 1901, i, 18).

4-Oximino-1-methyl*cyclo*hexan-3-one (Takens, *Diss.*, Göttingen, 1910), m. p. 158—159° or 171°, accordingly as it is slowly or rapidly heated, undergoes complete decomposition when heated in an atmosphere of carbon dioxide above its m. p. F. B.

Polychromic Salts of Oximino-ketones. ISRAEL LIFSCHITZ (*Ber.*, 1913, **46**, 3233—3250).—Additional information as to the constitution of chromoisomerides is given by the study of the electrical conductivity of polychromic salt solutions. Oximinodimethyldihydroresorcinol, $CMe_2{<}{\begin{matrix}CH_2\cdot CO\\CH_2\cdot CO\end{matrix}}{>}C\text{:}N\cdot OH$, has been studied as a more simple oximinoketone than violuric acid which contains nitrogen in the ring. The name dimethylviolanic acid is suggested for it. In addition to red and blue, it forms deep green alkali salts indicating that neither the third CO group nor the ring nitrogen in violuric acid are the cause of polychromism. The ring structure is, however, of importance, since oximinoacetylacetone, $(CH_3\cdot CO)_2C\text{:}N\cdot OH$, only forms orange to red salts and polychromic forms of the same salt do not exist. Moreover, these coloured salts are unstable. Ring structure alone does not cause polychromism, as neither fluorenoneoxime, benzophenoneoxime, benziloxime, nor oximinodibenzoylmethane exhibit the phenomenon.

When the cornflower-blue plates of sodium dimethylviolanate are

dissolved in methyl alcohol, the solution, likewise cornflower-blue, changes more or less quickly to bluish-green and then to a deep green, when the crystalline green chromoisomeride may be obtained from the solution. At the intermediate stage, it is possible to prepare crystalline, bluish-green or greenish-blue mixed salts. All these solutions contain unimolecular partly dissociated salt, as proved by ebullioscopic measurements.

The green solution is characterised by a new second absorption band in the visible part of the spectrum, and belongs to a new series of chromoisomeric oximino-salts.

The change is rapid only in dilute solutions which are sufficiently dissociated, as it is retarded by additions which check the dissociation. The conductivity of the green isomeride is 2—3% less than that of the blue form.

The two forms differ chemically, the green form being very readily decomposed. In the case of oximinoacetylacetone the cæsium salt decomposes immediately, the rubidium salt can be kept for a time, and the potassium salt is relatively stable. The rate of decomposition, like the depth of colour, increases with the atomic weight of the metal.

Conductivity measurements indicate that dimethylviolanic acid contains yellow oxime ions, and has the structure

$$CMe_2{<}{\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CO\end{matrix}}{>}C{:}N\cdot OH,$$

whereas the blue sodium salt is derived from a blue acid having a higher dissociation constant, and probably the nitrosoenol structure, $CMe_2{<}{\begin{matrix}CH_2\cdot C(OH)\\ CH_2\text{——}CO\end{matrix}}{>}C\cdot NO$. This result is in agreement with the optical behaviour.

The behaviour of the blue potassium salt and the red lithium salt of diphenylvioluric acid in methyl alcohol and in acetone indicates that the red lithium salt in acetone contains an internal alkali complex salt, whereas in the violet-red solution in methyl alcohol this complex has decomposed. Probably the yellowish-red and violet salts are not mixed salts, but their isomerism is not due to differences in partial valency. The copper-red magnesium dimethylviolanate forms a violet-red solution in water, and a red solution of very low conductivity in organic solvents.

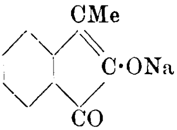
The green sodium dimethylviolanate is considered to have the structure $CMe_2{<}{\begin{matrix}CH_2\text{———}CO\\ CH_2\cdot C(ONa)\end{matrix}}{>}C\cdot NO$.

Dimethylviolanic acid is prepared as described by Haas (T., 1906, **89**, 189). The *methyl* ester forms a yellow, crystalline crust, m. p. 92°. The *magnesium* salt forms lustrous, bright copper-red platelets; the *copper* salt separates in brown platelets with a bronze lustre; the *silver* salt, $2H_2O$, forms a dark green, microcrystalline powder.

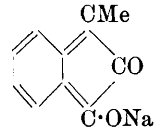
Phenylviolanic acid, $CHPh{<}{\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CO\end{matrix}}{>}C{:}N\cdot OH$, is a pale yellowish-green, crystalline powder, m. p. 175°. When warmed with water a chocolate-brown, lustrous powder is obtained.

The alkali salts of oximinoacetylacetone are described. E. F. A.

3-Methyl-1 : 2-diketohydrindene, an Analogue of Isatin. JULIUS VON BRAUN and G. KIRSCHBAUM (*Ber.*, 1913, **46**, 3041—3050).—3-*Methyl*-1 : 2-*diketohydrindene* is readily obtained by the action of cold formaldehyde and hydrochloric acid on oximino-3-methylhydrindone (compare Perkin, Roberts, and Robinson, T., 1912, **101**, 232). It strongly resembles isatin, having a deep reddish-yellow colour, giving the same indophenine reaction, and dissolving in alkali with a very intense bluish-violet colour, which is much more stable than the corresponding coloration from isatin. Of the two possible formulæ (I. and II.) for the sodium salt, the authors are led to prefer (II), since the great change in colour from red to bluish-violet is better explained (especially in view of the fact that the salts of 2-methyldiketohydrindene, which must have a structure similar to that of formula I, are red), whilst, also, the free diketone gives no coloration with ferric chloride, and does not combine with bromine, that is, it has no tendency towards enolisation of the usual type.

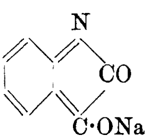


(I.)



(II.)

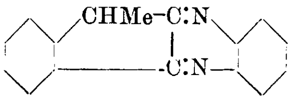
With benzoyl chloride, the sodium salt of 1 : 2-diketo-3-methylhydrindene yields 1 : 2-*diketo*-3-*benzoyl*-3-*methylhydrindene*, which is readily explained by 1 : 4-addition. In this light, the authors are led to propose the annexed formula for the bluish-violet salts of isatin prepared by Heller (A., 1907, i, 442), and find confirmation, therefore, in the fact, that all derivatives of isatin, in which, the carbonyl group adjacent to the NH group is substituted and which themselves are red or brown, yield blue solutions with alkali, whilst derivatives in which the β-carbonyl group is substituted yield yellow or brown solutions with alkali.



3-*Methyl*-α-*hydrindone*, b. p. 118—119°/11 mm., is obtained as a pale yellow oil which could not be caused to solidfy by the action of aluminium chloride on a solution of β-phenylbutyryl chloride in light petroleum. The oily *phenylhydrazone*, *semicarbazone*, m. p. 230—231°, *oxime*, m. p. 141·5°, *benzylidene* derivative, m. p. 88—89°, and *salicylidene* derivative, yellow needles, m. p. 172°, were analysed. The regulated action of amyl nitrite and hydrochloric acid on an alcoholic solution of 3-methyl-α-hydrindone leads to the formation of the somewhat unstable oximinomethylhydrindone,

$$C_6H_4<\genfrac{}{}{0pt}{}{CHMe}{CO}>C:N\cdot OH,$$

almost colourless crystals, m. p. 130°, which readily yields a *benzoyl* derivative, m. p. 125°. Cold concentrated hydrochloric acid and formaldehyde convert the oximino-derivative into 1 : 2-diketo-3-methylhydrindene, which is obtained as a viscous red oil which could not be distilled without decomposition and did not solidify. It yields a *disemicarbazone*, m. p. 267° (decomp.), and condenses with *o*-phenylenediamine in warm methyl-alcoholic solution to a *quinoxaline* derivative (annexed formula), m. p. 202°. It dissolves instantly in



aqueous alkali with the formation of an intensely bluish-violet solution, which, in comparison with the similar solutions obtained from isatin or 1 : 2-diketohydrindene, is remarkably stable; after four hours the colour commences to disappear, whilst after five hours the solution is dirty brown. Addition of acid then precipitates an *acid* which softens at 133°, and has m. p. 143° (decomp.). This substance could not be obtained pure, but probably has the composition

$$C_6H_4Et\cdot CO\cdot CO_2H.$$

The rupture of the ring occurs more easily after benzoylation. When benzoyl chloride is added to an alkaline solution of the ketone, the *benzoyl* derivative, $C_{17}H_{12}O_3,H_2O$, m. p. 195° (decomp.), is precipitated, and the alkaline filtrate yields on acidification benzoic acid and a *diketo-acid*, $C_{17}H_{14}O_4$, m. p. 203°, which gives a *diphenylhydrazone*, $C_{29}H_{26}O_2N_4$, m. p. 238°, reaction occurring according to the scheme:

$$C_6H_4<\begin{matrix}CMe\text{——}\\C(ONa)\end{matrix}>CO \longrightarrow C_6H_4<\begin{matrix}CMeBz\\CO\text{———}\end{matrix}>CO \longrightarrow C_6H_4<\begin{matrix}CHMeBz\\CO\cdot CO_2H\end{matrix}.$$

Methylhydrindone differs remarkably from hydrindone in its behaviour towards Grignard's reagents. Whereas the latter reacts vigorously with methyl magnesium iodide, yielding 1-*hydroxy*-1-*methylhydrindene*, $C_6H_4<\begin{matrix}CH_2\text{———}\\CMe(OH)\end{matrix}>CH_2$, b. p. 118°/14 mm., D_4^{20} 1·068, which can be distilled under ordinary pressure without notable elimination of water, the tertiary alcohol primarily formed from 3-methylhydrindone by a similar process loses the elements of water almost completely at 90°, and forms 1 : 3-*dimethylindene*,

$$C_6H_4<\begin{matrix}CHMe\\\text{--}CMe\end{matrix}>CH,$$

b. p. 212—214°/ordinary pressure, 86—88°/11 mm., D_4^{20} 0·9553, n_D^{20} 1·53444, which, unlike methylindene, is practically stable to air. It forms a *picrate*, yellow needles, m. p. 94—95°. H. W.

1 : 2-Diketo-3-methylhydrindene. A Correction. JULIUS VON BRAUN (*Ber.*, 1913, **46**, 3250. Compare preceding abstract).—The author has inadvertently overlooked the fact that the views advanced by him on the constitution of salts of isatin have been previously advocated by Ruhemann, T., 1909, **95**, 984). H. W.

Diacetyldi-imino-α-naphthol and its Transformations. IV. OSWALD MILLER (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1480—1488. Compare this vol., i, 877).—Neither Meerson (A., 1888, 713) nor Kehrmann (A., 1895, i, 151) succeeded in obtaining diacetyldi-imino-α-naphthol by the action of acetic anhydride and sodium acetate on di-imino-α-naphthol hydrochloride. The latter, as the author has already pointed out (A., 1911, i, 308), crystallises with $2H_2O$, which partly decomposes the diacetyl compound at the moment of its formation; the inaccuracy of Meerson's view that acetic anhydride plays a part in this decomposition, is evident from the fact that diacetyldi-imino-α-naphthol may be crystallised from this solvent, as from any other free from hydroxyl ions, without undergoing any decomposition.

Diacetyldi-imino-α-naphthol, $C_{14}H_{12}O_3N_2$, obtained by the action of

acetic anhydride and sodium acetate on anhydrous di-imino-α-naphthol hydrochloride, forms yellow prisms, m. p. 187°, and dissolves in fuming nitric acid or acetic acid with production in almost theoretical yields of acetylamino-1 : 4-naphthaquinone. The latter (1 mol.) combines with diacetyldi-iminonaphthol (1 mol.) to give the compound, $C_{14}H_{12}O_3N_2,C_{12}H_9O_3N$, m. p. 178° (decomp.), described by Meerson (*loc. cit.*). Decomposition of diacetyldi-iminonaphthol by heating in aqueous alcoholic solution results in the formation of four parts of 2-acetylamino-1 : 4-naphthaquinone and 1 part of 4-acetylamino-1 : 2-naphthaquinone.

The action of a glacial acetic acid solution of aniline on a solution of diacetyldi-iminonaphthol in 95% alcohol yields a mixture of the ordinary dianilide with a new anilide, *2-acetylamino-4-phenylimino-1 : 4-naphthaquinone*, $C_{18}H_{14}O_2N_2$, which crystallises in yellowish-red needles, or in red plates with marked metallic lustre, m. p. 185°; by boiling acetic acid it is decomposed quantitatively into aniline and acetylamino-1 : 4-naphthaquinone. Its *platinichloride*,

$$(C_{18}H_{14}O_2N_2,HCl)_2,PtCl_4,$$

which forms yellowish-brown plates, is accompanied by that of 2-amino-4-phenylimino-1 : 4-naphthaquinone, m. p. 121° (compare Miller and Smirnov, A., 1911, i, 121). Thus, this new anilide, like the derivatives of naphthaquinones already investigated, shows a marked tendency to react in two directions.

The above method of obtaining the new anilide leads also to the formation of three compounds of this anilide with the dianilide: (1) $2C_{18}H_{14}O_2N_2,C_{22}H_{16}ON_2$, which forms reddish-yellow plates, m. p. 170—171°; (2) $1{\cdot}66C_{18}H_{14}O_2N_2,C_{22}H_{16}ON_2$, which forms red plates, m. p. 147—148°; (3) red needles and plates, m. p. 160°. The melting points of these compounds rise on melting and re-solidification.

T. H. P.

The Three Isomeric Di-α-naphthoylbenzenes. CHRISTIAN SEER and OTTO DISCHENDORFER (*Monatsh.*, 1913, **34**, 1493—1502).—The *p*- and *m*-di-α-naphthoylbenzenes have been prepared by condensing terephthalyl chloride and *iso*phthalyl chloride respectively, with naphthalene in cold carbon disulphide solution, by means of aluminium chloride. Since phthalyl chloride reacts in the unsymmetrical form, and α-naphthoyl-*o*-benzoyl chloride will not react in the cold, such a condensation could not be carried out for the ortho-isomeride. The latter was obtained, however, from α-naphthoyl-*o*-benzoic acid by Guyot and Vallette's method (A., 1911, i, 652).

The yield of crude, light brown p-*di-α-naphthoylbenzene*,

$$C_6H_4(CO{\cdot}C_{10}H_7)_2,$$

was very high, but the compound was obtained crystalline with great difficulty, by distilling the crude product, dissolving the oily distillate, b. p. 315—330°/11—20 mm., in boiling glacial acetic acid, and filtering from resinous matter as soon as crystals appeared. It forms, colourless, glistening leaflets, m. p. 233—234°, and gives a blood-red solution in sulphuric acid. m-*Di-α-naphthoylbenzene* was also obtained in good yield in colourless, glistening leaflets from dilute pyridine, m. p. 191°.

α-Naphthoyl-*o*-benzoic acid was reduced by zinc and 80% acetic acid,

when the *lactone* of *phenyl-α-naphthylcarbinol-o-carboxylic acid*,

$$C_{10}H_7\cdot CH<\underset{C_6H_4}{\overset{-O-}{}}>CO,$$

crystallised on cooling. It was purified by extraction with boiling dilute hydrochloric acid, and formed faintly yellow spikelets from alcohol, m. p. 135—136°. The lactone was treated with magnesium α-naphthyl bromide, and the white, flocculent magnesium compound was decomposed with dilute hydrochloric acid, when 2 : 5-*di-α-naphthyl-3 : 4-benzofuran*, $C_6H_4<\begin{matrix}C(C_{10}H_7)\\C(C_{10}H_7)\end{matrix}>O$, was obtained in bright yellow, glistening needles, m. p. 166°, which give deep yellow solutions with brilliant green fluorescence. On oxidation with sodium dichromate and acetic acid, a quantitative yield of o-*di-α-naphthoylbenzene* was obtained. This isomeride is freely soluble, forms colourless needles, m. p. 130—131°, and condenses with hydrazine hydrate to 1 : 4-*di-α-naphthylphthalazine*, $C_6H_4<\begin{matrix}C(C_{10}H_7):N\\C(C_{10}H_7):N\end{matrix}$, which crystallises in rhombic plates, m. p. 176°.

Attempts to prepare condensation products by heating these isomeric diketones with aluminium chloride were without success.

J. C. W.

Preparation of Bromoaminoanthraquinones. BADISCHE ANILIN- & SODA FABRIK (D.R.-P. 263395, 265727. Compare this vol., i, 1071).—The preparation of 3-bromo-2-aminoanthraquinone from 1-bromo-2-aminoanthraquinone-3-sulphonic acid by elimination of the sulphonic group (with sulphuric acid) and migration of the bromine atom has been previously described; and it is now found that this reaction is a general one when a bromine atom, amino- and sulphonyl group are all present in the same benzene nucleus.

3 : 7-Dibromo-2 : 6-diaminoanthraquinone is prepared by heating sodium 1 : 5-dibromo-2 : 6-diamino-3 : 7-disulphonate with 20 parts of sulphuric acid (60° Bé.) at 180—190°; it does not react with aniline.

3 : 6-*Dibromo*-2 : 7-*diaminoanthraquinone* is obtained in a similar manner from 1 : 8-dibromo-2 : 7-diaminoanthraquinone-3 : 6-disulphonic acid, and does not react with aniline or *p*-toluidine.

4-*Bromo*-1-*aminoanthraquinone*-2-*sulphonic acid* is obtained by sulphonating, and subsequently brominating (in aqueous solution), 1-aminoanthraquinone; when it is boiled with concentrated sulphuric acid it gives rise to 2-bromo-1-aminoanthraquinone (*loc. cit.*).

The second patent states that if the heating in the reactions described previously is carried out for a few moments only in the presence of mercury (or its salts) that the sulphonic group is eliminated, but the migration of the bromine atom does not occur; thus, when sodium 1-bromo-2-aminoanthraquinone-3-sulphonate (10 parts) is heated with 100 parts of sulphuric acid (66° Bé.) and mercury sulphate (0·5 part) at 180° during three minutes, it gives rise to 1-bromo-2-aminoanthraquinone, which readily furnishes 2-*amino*-1-p-*toluidinoanthraquinone* with *p*-toluidine, whilst 4-bromo-1-aminoanthraquinone-2-sulphonic acid gives rise to 4-bromo-1-aminoanthraquinone.

F. M. G. M.

Bromohydroxynaphthaquinones. V. OSWALD MILLER (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1467—1479).—The author finds that the dibromide, m. p. 149·5—151·5°, described by Diehl and Merz (*Ber.*, 1881, **14**, 1912) does not exist, and establishes the identity of the bromohydroxynaphthaquinones prepared from: (1) the dibromide, m. p. 218° (compare Miller, A., 1885, 667); (2) 2-hydroxy-α-naphthaquinone (compare Diehl and Merz, A., 1878, 888); (3) α-naphthaquinoneanilide (compare Balzer, A., 1882, 204), and (4) bromo-β-naphthaquinone (compare Zincke, A., 1887, 53). In the last of these methods, which is aerobic, only one-third of the oxygen absorbed reacts according to the equation $C_{10}H_{15}O_2Br + O = C_{10}H_5O_3Br$, the remaining two-thirds acting on a second molecule of the bromonaphthaquinone to form secondary products.

3-*Bromo*-2-*hydroxy*-1 : 4-*naphthaquinone*, $C_6H_4<\begin{matrix}CO\cdot C(OH) \\ CO\cdot CBr\end{matrix}>$, crystallises in monoclinic prisms or hemihedral forms, m. p. 198·5° (corr. 202°). The canary-yellow colour of the powdered compounds persists on heating to 170°, at which temperature a number of orange-yellow spots make their appearance. These spots gradually increase in magnitude as the temperature is raised, until at 190° the whole mass exhibits the orange-yellow colour, the powder becoming converted at the same time into small prisms. On cooling, these prisms become somewhat paler and undergo disintegration. The golden-yellow liquid obtained on fusion solidifies only at about 170°, but subsequently melts as before at 198·5°. The identity of the products yielded by the different methods of preparation was ascertained by investigation of (1) the solubility in 95% alcohol; (2) the potassium salt, which is anhydrous; (3) the barium salt ($+4H_2O$), and (4) the aniline salt, m. p. 166·5° (decomp.). The homogeneity of the compound was established by heating it at various temperatures for ten hours, the non-volatilised residues in all cases melting at 198·5°.

The yields of phthalic acid obtained by oxidising various naphthaquinone derivatives by means of potassium permanganate in sulphuric acid solution are: α-naphthaquinone, 95·2%; 2-hydroxy-α-naphthaquinone, 93·4%; bromohydroxynaphthaquinone from Miller's dibromide, m. p. 218°, 96·4%; bromohydroxynaphthaquinone from 2-hydroxy-α-naphthaquinone, 97·3%. These results are regarded as a confirmation of the ordinary structural formula for naphthalene.

T. H. P.

Purpurogallin. I. MAXIMILIAN NIERENSTEIN and C. W. SPIERS (*Ber.*, 1913, **46**, 3151—3157).—The authors have oxidised pyrogallol by several processes, and have shown that the purpurogallin obtained is identical in all cases. This substance has the formula $C_{11}H_8O_5$, contains four free hydroxyl groups (estimated by Zerevitinov's method, A., 1908, i, 593, in a modified apparatus) and a carbonyl group, and yields naphthalene on distillation with zinc dust. The oxidation was effected by the following means: with sodium nitrite and acetic acid (Perkin and Steven, T., 1903, **83**, 197), which is the best method, and yields 10—16% of the substance; with silver nitrate or acid permanganate (Girard, 1869); with chromic acid or *p*-benzoquinone

(Wichelhaus, A., 1872, 172, who called the compound, in the latter case, pyrogalloquinone, and obtained quinol as a by-product); by passing a current of air through a solution of pyrogallol and gum arabic (Struve, A., 1872, 703); with horse-radish peroxydase; with potassium ferricyanide (Hooker, A., 1888, 292), and by electrolysis (Perkin and Perkin, T., 1904, **85**, 243).

Purpurogallin was obtained in deep-red needles from glacial acetic acid. It always melted at 274—275° in a sulphuric acid bath, but in a paraffin bath, or in very long capillary tubes, it sublimed without melting.

Tetra-acetylpurpurogallin was easily prepared in orange-yellow needles, m. p. 179—180° (Herzig, A., 1910, i, 677, described a colourless product). The molecular-weight determinations with certain solvents gave abnormal results, which could be explained in the case of acetic acid by partial hydrolysis to *monoacetylpurpurogallin*, which formed brownish-red needles, m. p. 169—170°; these could be separated mechanically. The tetra-acetyl derivative was completely hydrolysed by 50% acetic acid, and readily formed a *phenylhydrazone*, $C_{11}H_4O_4(COMe)_4$:N·NHPh, in brick-red needles, m. p. 254—258°.

The authors are studying the formation of hydroxy-*o*-benzoquinone, which Wichelhaus, Perkin and Steven, and Perkin (T., 1913, **104**, 661) have assumed to represent an intermediate stage in the oxidation of pyrogallol. J. C. W.

Preparation of Nitrogenous Condensation Products of the Anthraquinone Series. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 265725).—When aminoanthraquinones are heated at 200—220° with naphthols in the presence of zinc chloride they furnish condensation products which are formed from 1 molecule of the aminoanthraquinone and 2 molecules of the naphthol, with elimination of 3 molecules of water. The following *compounds* are described: (1) from 1-aminoanthraquinone with β-naphthol, a red, crystalline powder; (2) from 2-aminoanthraquinone with β-naphthol, a yellowish red, crystalline powder; (3) from 1-aminoanthraquinone with α-naphthol, a dark violet powder, and (4) from 4-chloro-1-aminoanthraquinone with β-naphthol, a red, crystalline powder. F. M. G. M.

Retene. III. Condensation of Retenequinone with Ketonic Compounds. ALFRED HEIDUSCHKA and CH. KHUDADAD (*Arch. Pharm.*, 1913, **251**, 401—437. Compare A., 1912, i, 107).—Retenequinone, which resembles benzil and phenanthraquinone in its behaviour towards organomagnesium haloids (Heiduschka and Grimm, *loc. cit.*), has been examined as to its behaviour during condensation with various types of ketones, to ascertain whether its analogy to benzil and phenanthraquinone is also evident in such reactions. In the presence of aqueous or, better, alcoholic potassium hydroxide, retenequinone (1 mol.) condenses with only 1 mol. of an aliphatic ketone, CH_2R·COMe (where R may be hydrogen and no negative group, other than the carbonyl, is present) to form, unlike benzil and phenanthraquinone, only one product. Four formulæ are possible for the substance, but the two containing >C:CR· are excluded because the condensation product is rapidly attacked by Baeyer's reagent, whereby the presence

of the group $>C:CH\cdot$ is indicated. The condensation product, therefore, may have the constitution: $C_{16}H_{16}<\begin{matrix}C:CH\cdot CO\cdot CH_2R \\ | \\ CO\end{matrix}$ or

$$C_{16}C_{16}<\begin{matrix}C{=\!=\!=}CH \\ | \\ C(OH)\cdot CHR\end{matrix}>CO;$$

the first, however, is excluded because the substance, except where R is hydrogen, does not condense with benzaldehyde in alkaline solution, thereby showing that a methyl or methylene group adjacent to a carbonyl group is not present.

Anhydroacetoneretenequinone, $C_{16}H_{16}<\begin{matrix}C{=\!=\!=}CH \\ | \\ C(OH)\cdot CH_2\end{matrix}>CO$, m. p. 206·5°, colourless needles, does not react with phenylhydrazine or with phenylcarbimide in the cold, condenses with benzaldehyde in the presence of alcoholic potassium hydroxide to form a *substance*, $C_{28}H_{24}O_2$, m. p. 203—204° (decomp.), pale yellow needles, and is reduced by zinc dust and acetic acid to a *substance*, $C_{21}H_{20}O$, m. p. 201°, colourless needles. *Methylanhydroacetoneretenequinone*,

$$C_{16}H_{16}<\begin{matrix}C{=\!=\!=}CH \\ | \\ C(OH)\cdot CHMe\end{matrix}>CO,$$

m. p. 205°, colourless needles, obtained together with a small quantity of an isomeride from methyl ethyl ketone, forms a *dibromide*, $C_{22}H_{22}O_2Br_2$, m. p. about 195° (decomp.), and is reduced to a *substance*, probably $C_{16}H_{16}<\begin{matrix}C{-}CH_2 \\ \| \\ C\cdot CHMe\end{matrix}>CO$, m. p. 153—155°, by zinc dust and acetic acid, or by boiling hydriodic acid, D 1·96, and to a *substance*, $C_{22}H_{24}O$, m. p. 192—193° (decomp.), by zinc and alcoholic hydrochloric acid. Retenequinone and methyl propyl ketone yield *ethylanhydroacetoneretenequinone*, $C_{23}H_{24}O_2$, m. p. 186—187°, colourless needles. Retenequinone condenses with methyl hexyl ketone and with methyl hexenyl ketone to form corresponding *substances*, $C_{26}H_{30}O_2$, m. p. 181—182°, and $C_{26}H_{28}O_2$, m. p. 213—214°, both colourless needles, and with mesityl oxide (only in the presence of alcoholic potassium hydroxide) to form iso*propylideneanhydroacetoneretenequinone*, $C_{24}H_{24}O_2$, m. p. 219°.

Retenequinone and benzyl methyl ketone in the presence of aqueous potassium hydroxide yield two *substances*, one, probably

$$C_{16}H_{16}<\begin{matrix}C:CPh\cdot COMe \\ | \\ C:CPh\cdot COMe\end{matrix},$$

m. p. 200—202° (decomp.), faintly red crystals, the other, $C_{45}H_{40}O_2$, m. p. 214—215°, deep red crystals; the residue from the mother liquor, by boiling with glacial acetic acid, yields a *substance*, $C_{29}H_{26}O_3$, m. p. 210—212°, colourless needles, which is *phenylanhydroacetoneretenequinone acetate*, since it is also obtained by heating phenylacetoneretenequinone with glacial acetic acid. *Phenylacetoneretenequinone*, probably $C_{16}H_{16}<\begin{matrix}C(OH)\cdot CHPh\cdot COMe \\ | \\ CO\end{matrix}$, m. p. 190—192° (decomp.), yellow crystals, is obtained from retenequinone and benzyl methyl ketone in the presence of alcoholic potassium hydroxide.

Retenequinone and ethyl acetonedicarboxylate in the presence of

alcoholic potassium hydroxide condense to form a *substance*, $C_{27}H_{28}O_6$, m. p. 185—187° (decomp.), yellow needles or leaflets, which receives the constitution $C_{16}H_{16}<\begin{matrix}C\text{=====}C(CO_2Et)\\ C(OH)\cdot CH(CO_2Et)\end{matrix}>CO$.

Retenequinone and ethyl benzoylacetate, by treatment with acetic anhydride and a little concentrated sulphuric acid at 45—50° yield a *substance*, $C_{40}H_{36}O_6$, m. p. 235°, faintly yellow needles, which is probably $C_{16}H_{16}<\begin{matrix}C:CBz\cdot CO_2Et\\ C:CBz\cdot CO_2Et\end{matrix}$. C. S.

Action of Zinc on a Mixture of Fenchone and Allyl Iodide. MICHAEL ZAJCEV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1578—1580).—The action of zinc on a mixture of fenchone and allyl iodide in presence of ether yields *allylfenchyl*, $C_{13}H_{22}O$, b. p. 107—109°, D_0^0 0·9747, D_{20}^{20} 0·96144, D_4^{20} 0·9597, $[\alpha]_D$ +12·44°, n_D 1·49143. Attempts to prepare the corresponding *chloride*, $C_{13}H_{21}Cl$, by saturating allylfenchyl with dry hydrogen chloride in the cold, yielded an impure product, b. p. 122—124°. The investigation is being continued. T. H. P.

Synthesis of 3-Ethylpulegol. MICHAEL ZAJCEV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1571—1577).—The preparation of 3-methylpulegol by the action of magnesium and methyl bromide on pulegone was unsuccessfully attempted by Grignard (A., 1901, i, 679) and by Rupe and Emmerich (A., 1908, i, 556), and this compound has only recently been prepared (compare Rupe, Schobel and Abegg, A., 1912, i, 573). The corresponding ethyl compound is, however, readily obtainable.

3-*Ethylpulegol*, $CHMe<\begin{matrix}CH_2\cdot CEt(OH)\\ CH_2\text{——}CH_2\end{matrix}>C:CMe_2$, has b. p. 105—110°/9 mm., D_0^0 0·9379, D_{20}^{20} 0·9239, D_4^{20} 0·9223, $[\alpha]_D^{20}$ +43·22°, and exhibits normal cryoscopic behaviour in benzene. When oxidised by means of permanganate, it yields (1) the *trihydric alcohol*,

$$CHMe<\begin{matrix}CH_2\cdot CEt(OH)\\ CH_2\text{——}CH_2\end{matrix}>C(OH)\cdot CMe_2\cdot OH,$$

which is a viscous, cinnamon-coloured liquid; (2) β-methyladipic acid; (3) formic acid, and other products. T. H. P.

Chemistry of Caoutchouc. VII. Theory of Vulcanisation. V. DAVID SPENCE and J. YOUNG (*Kolloid. Zeitsch.*, 1913, **13**, 265—271. Compare A., 1912, i, 706).—Further experiments have shown that there is no lower limiting temperature, as previously suggested, below which vulcanisation does not take place. By extending the period of observation it has been found that vulcanisation occurs at 50°, and from experiments made at intervals of 5° between 50° and 75°, the velocity of the vulcanisation process increases on the average in the ratio of 2·84 : 1 for a rise of temperature of 10°. The value of the temperature-coefficient lends support to the view that the vulcanisation process is a chemical change.

From comparative experiments on the speed of the vulcanisation

of caoutchouc, gutta-percha, and balata at 135°, it appears that the rate of the change is practically the same in all three cases. In each case, also, the vulcanisation reaches a limit when the quantity of sulphur, non-extractable with acetone, amounts to 32%. This proportion of sulphur corresponds with the formula $(C_{10}H_{16}S_2)_n$, and it is supposed that this compound is formed from each of the three substances.

The difference between caoutchouc, gutta-percha, and balata is considered to have its origin in differences in the colloidal condition of the hydrocarbon, the close similarity in the behaviour on vulcanisation being entirely opposed to the view that the differences are chemical in nature. H. M. D.

Formation of the Anthocyan Pigments of Plants. VI. FREDERICK KEEBLE, E. FRANKLAND ARMSTRONG, and W. NEILSON JONES (*Proc. Roy. Soc.*, 1913, *B*, **87**, 113—131. Compare A., 1912, ii, 673; this vol., i, 325, 803).—The pale yellow sap colour of the petals of the wallflower is a mixture of hydroxyflavone glucosides (compare A. G. Perkin, T., 1896, 1566; Perkin and Pilgrim, T., 1898, 267). The mixture is hydrolysed by heating with acids and more slowly by emulsin. The hydrolysed pigment if reduced and subsequently oxidised yields a red pigment. A red pigment is obtained from most flowers containing similar soluble yellow pigments, suggesting that red mutations should be of possible occurrence in such species.

Oxidation by oxydase of the hydrolysed products of glucosides in presence of amino-acids yields pigments. Arbutin, for example, yields a red pigment probably produced by the interaction of quinhydrone with ammonia. It is suggested that many of the pigments and odorous substances formed during the ripening of fruits arise as results of reactions of this type.

A competition for oxydase ensues when a mixture of phenols is treated with a plant oxydase.

Quinol monomethyl ether gives no colour reaction with oxydase, but when a little benzidine solution is added, a deep and persistent carmine colour is obtained. The benzidine acts catalytically, playing the part of an organic peroxide, and bringing about the oxidation of a substance which resists the action of oxydase and hydrogen peroxide. It is suggested that the higher members of a flower colour series owe their origin to the presence of specific substances which, acting as receivers of oxygen, reduce the pigments characteristic of the lower members of the colour series, accept oxygen therefrom, and become oxidised to pigments of specific colour. E. F. A.

Anthocyanins. I. Pigment of Cornflowers. RICHARD WILLSTÄTTER and ARTHUR E. EVEREST (*Annalen*, 1913, **401**, 189—232).—Since Morot in 1849, and Frémy and Cloëz in 1854, isolated in an impure state the blue pigment of the cornflower, very little work has been recorded, probably on account of the instability of the anthocyanin. An important observation by Molisch (*Bot. Zeit.*, 1905, **63**, 145), that in the flowers and red leaves of many plants the anthocyanin occurs, not merely in solution in the cell juice, but also in the crystal-

line or amorphous state, revived interest in the subject, and observations, many of which are erroneous, have been recorded by Grafe, by Glan, by Griffiths (A., 1904, i, 179), and by Combes (A., 1911, ii, 1125).

Anthocyanins are the blue, violet, and red pigments which are extracted from flowers, fruits, and many leaves by water or aqueous alcohol, and are insoluble in ether; they are roughly classified by their colour reactions in acid and in alkaline solution and with lead acetate. For the sake of completeness, it may be recalled that red and blue flowers also contain yellow pigments, anthoxanthins, which are soluble in water or dilute alcohol, and are quite different from the chemically indifferent carotins. The blue pigment of the cornflower is unstable and very difficult to isolate, and has not yet been obtained crystalline. The various shades of colour in different parts of the flower are due to various derivatives of one substance. Thus the blue pigment is the potassium salt of an acid (cyanin), the violet pigment is the free acid, and the red pigments are oxonium salts of cyanin and plant-acids. In addition, a colourless substance can be isolated from the flowers, which is an isomeride of cyanin and is acid and forms colourless alkali salts.

All anthocyanins are present in flowers as glucosides and not, as previously stated by Grafe, partly in combination with dextrose and partly not. They all exhibit a characteristic reaction, the anthocyanidin reaction; an anthocyanin dissolved in *N*- or 2*N*-sulphuric acid is quite unaffected by shaking with amyl alcohol, but after hydrolysis on the water-bath, the coloured fission product (anthocyanidin) is quantitatively extracted by the alcohol, forming a reddish-violet solution, which is changed to bluish-violet by washing, or more rapidly by sodium acetate. (In this connexion, Erdmann's test for new, or comparatively new, red wine is discussed.)

In order to isolate the colouring matter, dried cornflower meal, mixed with six parts of sand to facilitate filtration, is rapidly extracted with water or 20% alcohol, preferably in the presence of sodium nitrate or chloride to retard the change of the anthocyanin to the colourless modification. The deep blue solution is treated with alcohol and the potassium cyanin, after repeated fractional precipitation with water and alcohol, is obtained mixed with at least twice the weight of carbohydrates, albumins, and pentosans. In its further purification, the blue pigment is treated with alcohol and hydrochloric acid, whereby the pentosans (one of which is probably xylan) are precipitated, and the pigment is converted in *cyanin chloride*, $C_{28}H_{33}O_{17}Cl,3H_2O$, m. p. 203—204° (corr.) (anhydrous), dark blue, rhombic leaflets with golden reflex. The chloride is extremely hygroscopic, and forms stable red solutions in acids; its aqueous solution rapidly becomes colourless, but recovers its red colour by the addition of an acid. A solution of the chloride becomes violet in the presence of calcium carbonate, and changes from red through violet to cornflower blue by treatment with sodium carbonate.

By hydrolysis with boiling 20% hydrochloric acid for three to three and a half-minutes, cyanin chloride yields dextrose (2 mols.) and *cyanidin chloride*, $C_{16}H_{13}O_7Cl$, long, brownish-red, metallic needles,

which decomposes by slow heating, but has m. p. 220° (decomp.) when placed directly in a bath at this temperature. Like cyanin chloride, cyanidin chloride is converted by aqueous sodium carbonate, firstly, into a violet solution of the acid, cyanidin, and then into a blue solution of sodium cyanidin. Moreover, cyanidin chloride in dilute alcohol at 85° is slowly converted into an *isomeride*, colourless crystals, which is reconverted into red cyanidin salts by boiling dilute mineral acids; by prolonged keeping of its aqueous alcoholic or ethereal solution, the colourless isomeride changes to another *substance*, colourless needles, from which the red cyanidin salts cannot be regenerated.

Little can be stated at present with regard to the constitutions of cyanin and cyanidin. The fact, that the two substances form very stable salts with hydrochloric acid, indicates that cyanin and cyanidin are related to benzopyronium (Decker and Fellenberg, A., 1909, i, 116) rather than to the flavones. C. S.

Hydrogenation of a Secondary Alcohol derived from Furfuraldehyde in the Presence of Nickel. ROGER DOURIS (*Compt. rend.*, 1913, **157**, 722—724).—During the catalytic hydrogenation of certain secondary α-ethylenic alcohols, dehydration occurs, followed by hydrogenation of the ethylenic hydrocarbon produced. The author is extending this study to heterocyclic alcohols derived from furfuraldehyde. Furfuraldehyde itself gives α-methylfuran, α-methyltetrahydrofuran, methyl propyl ketone, and pentan-β-ol (compare Padoa and Ponti, A., 1907, i, 146). Furylethylcarbinol on hydrogenation in the presence of reduced nickel at 175° yields propyltetrahydrofuran, dipropyl ketone, *ethyltetrahydrofurylcarbinol*, $C_4H_7O \cdot CHEt \cdot OH$, a colourless, syrupy liquid, b. p. 87—90°/15 mm., D_4^0 1·0051, D_4^{20} 0·9869, and a small quantity of a liquid, b. p. 110—120°/15 mm., which contains a glycol.

Whilst furylethylcarbinol, unlike its propyl and *iso*amyl homologues, will not yield an acetic ester, yet its tetrahydro-derivative readily yields an *ester*, a colourless liquid, b. p. 90—91°/12 mm., D_4^0 1·0334, D_4^{16} 1·0149. W. G.

Action of Fermenting Yeast on Furfuraldehyde. Formation of Furyltrimethylene Glycol. II. CARL J. LINTNER and H. J. VON LIEBIG (*Zeitsch. physiol. Chem.*, 1913, **88**, 109—121. Compare A., 1911, ii, 816).—Furfuraldehyde in presence of yeast which is actively fermenting sucrose is converted into *furyltrimethylene glycol* [*$\alpha\gamma$-dihydroxy-α-furylpropane*], $C_4H_3O \cdot CH(OH) \cdot CH_2 \cdot CH_2 \cdot OH$. This crystallises in very tiny needles, m. p. 50·5°, $[\alpha]_D$ $-10·5°$; with concentrated sulphuric acid it gives a gentian-blue coloration.

The *diacetate* forms a pale yellow oil with an aromatic odour, b. p. 246—248°/720 mm.; the *dibenzoyl* derivative is likewise a pale yellow oil. Both compounds have a normal molecular weight and give a blue coloration with sulphuric acid.

The *di*-p-*nitrobenzoate* forms an almost colourless, crystalline powder, m. p. 150—151°. The *diphenylurethane*, which is a colourless, light powder, has m. p. 195°.

It is assumed that the acetaldehyde formed as the first product of the fermentation of dextrose undergoes an aldol condensation with furfuraldehyde and that this aldol is immediately reduced to the glycol by the yeast. E. F. A.

Thioflavones [2-Phenyl-1 : 4-benzothiopyrones]. SIEGFRIED RUHEMANN (*Ber.*, 1913, **46**, 3384—3395).—The sodium salts of the thiophenols, like the ordinary phenols (this vol., i, 891), can undergo condensation with ethyl phenylpropiolate with formation of the ethyl esters of the corresponding β-arylthiolcinnamic acids. The free acids on heating lose carbon dioxide with formation of arylthiolstyrenes, and by successive treatment with phosphorus pentachloride and aluminium chloride they are almost quantitatively converted into thioflavones (2-phenyl-1 : 4-benzothiopyrones). The last-named substances are more resistant than the flavones towards alkali, but by prolonged boiling with concentrated potassium hydroxide solution two concurrent decompositions are effected, one yielding (with thioflavone itself) benzoic acid and *o*-thiolacetophenone, and the other acetophenone and *o*-thiolbenzoic acid.

The corresponding 1 : 4-benzothiopyrone, $C_6H_4<\begin{matrix}CO\cdot CH\\ \|\\ S—CH\end{matrix}$, could not be produced in a similar manner on account of the impossibility of hydrolysing ethyl phenylthiofumarate (obtainable from the sodium compound of the thiophenol and ethyl chlorofumarate) without complete decomposition.

Ethyl β-o-*tolylthiolcinnamate*, $C_6H_4Me\cdot S\cdot CPh{:}CH\cdot CO_2Et$, a viscous, yellow oil, b. p. 230°/12 mm., which slowly crystallises, is obtainable by the gradual addition of ethyl phenylpropiolate to a hot solution of sodium in excess of *o*-tolyl mercaptan diluted with toluene; β-o-*tolylthiolcinnamic acid*, produced by hydrolysis with alcoholic potassium hydroxide, forms colourless needles, m. p. 160—161° (decomp.), and on heating passes into o-*tolylthiolstyrene*, $C_6H_4Me\cdot S\cdot CPh{:}CH_2$, a yellow oil, b. p. 183—184°/12 mm., with loss of carbon dioxide. When powdered aluminium chloride is gradually introduced into a mixture of phosphorus pentachloride and β-*o*-tolylthiolcinnamic acid in benzene, intramolecular condensation to 2-*phenyl*-8-*methyl*-1 : 4-*benzothiopyrone* (8-*methylthioflavone*), $C_6H_3Me<\begin{matrix}CO\cdot CH\\ \|\\ S—CPh\end{matrix}$, pale yellow needles, m. p. 124—125°, is effected.

p-Tolyl mercaptan, obtained by reduction of *p*-toluenesulphonyl chloride, condenses in a similar manner to the ortho-isomeride, with ethyl phenylpropiolate, producing the *ethyl* ester, yellowish prisms, m. p. 77—78°, b. p. 240—242°/12 mm., of β-p-*tolylthiolcinnamic acid*, colourless needles, m. p. 167° (decomp.). By successive treatment with phosphorus pentachloride and aluminium chloride the acid is converted into 2-*phenyl*-6-*methyl*-1 : 4-*benzothiopyrone* (6-*methylthioflavone*), colourless needles, m. p. 153—154°.

Thiol-*p*-xylene, b. p. 211—212°, obtained from the corresponding sulphinic acid, which was prepared by the diazo-reaction, condensed with ethyl phenylpropiolate, giving the viscous, yellow *ethyl* ester,

b. p. 242°/12 mm., of *β-p-xylylthiolcinnamic acid*, colourless prisms, m. p. 186—187° (decomp.). Treatment with phosphoric and aluminium chlorides converts this into *2-phenyl-5 : 8-dimethyl-1 : 4-benzothiopyrone* (*5 : 8-dimethylthioflavone*), $C_6H_2Me_2<\begin{matrix}CO\cdot CH \\ S—CPh\end{matrix}$, colourless needles, m. p. 133—134°.

Thiol-*m*-xylene, b. p. 212—214°, in a similar manner, condenses with ethyl phenylpropiolate, giving the *ethyl* ester, yellow prisms, m. p. 91—92°, b. p. 242—244°/12 mm., of *β-m-xylylthiolcinnamic acid*, yellow prisms, m. p. 184° (decomp.). This acid, when heated, loses carbon dioxide with formation of *3 : 4-dimethylphenylthiolstyrene*, a yellow oil, b. p. 197—198°/14 mm., and under the usual treatment with phosphoric and aluminium chlorides gives rise to *2-phenyl-6 : 8-dimethyl-1 : 4-benzothiopyrone* (*6 : 8-dimethylthioflavone*), yellow needles, m. p. 152—153°.

o-Anisyl mercaptan, in the form of its sodium compound, reacts with ethyl phenylpropiolate in the general manner, giving the *ethyl* ester, colourless needles, m. p. 67—68°, b. p. 246—248°/12 mm., of *β-o-anisylthiolcinnamic acid*, colourless needles, m. p. 148° (decomp.). The acid is readily converted into *8-methoxy-2-phenyl-1 : 4-benzothiopyrone* (*8-methoxythioflavone*), $OMe\cdot C_6H_3<\begin{matrix}CO\cdot CH \\ S—CPh\end{matrix}$, colourless needles, m. p. 129—130°. This compound, like the oxygen analogue (*loc. cit.*), can be demethylated by hydriodic acid, producing *8-hydroxy-2-phenyl-1 : 4-benzothiopyrone*, yellow prisms, m. p. 292° (decomp.).

The sodium compound of *p*-anisylmercaptan with ethyl phenylpropiolate produces the *ethyl* ester, b. p. 255—256°/14 mm., of *β-p-anisylthiolcinnamic acid*, colourless prisms, m. p. 217—218° (decomp.). This was transformed in the usual manner into *6-methoxy-2-phenyl-1 : 4-benzothiopyrone* (*6-methoxythioflavone*), colourless needles, m. p. 155—156°.

The behaviour of the benzothiopyrone compounds with alkali, towards which they are very stable, was especially investigated with 2-phenyl-1 : 4-benzothiopyrone (that is, thioflavone itself). It is completely changed by boiling with concentrated alcoholic sodium hydroxide for five to six hours; acetophenone, *o*-thiolacetophenone, as an oil oxidisable to dithiodiacetophenone $(C_6H_4Ac)_2S_2$, needles, m. p. 167—168° (compare Farbwerke Meister, Lucius, & Brüning, A., 1908, i, 987), benzoic acid, *o*-thiolbenzoic acid, and dithiodisalicylic acid could be recognised among the reaction products. D. F. T.

Aconitine Alkaloids. Pyraconitine. HEINRICH SCHULZE and A. LIEBNER (*Arch. Pharm.*, 1913, **251**, 453—467. Compare Schulze and Bierling, this vol., i, 287).—Pyraconitine, $C_{32}H_{43(\text{or }41)}O_9N$ (Dunstan and Carr give $C_{31}H_{41}O_{10}N$; T., 1894, **65**, 176), prepared by heating aconitine at 192°, has m. p. 171°, $[\alpha]_D^{20}$ $-112\cdot2°$, in 95% alcohol ($c = 8\cdot6918$), and crystallises from ether in colourless needles containing $1\frac{1}{2}Et_2O$, and from alcohol in crystals containing $2\frac{1}{2}EtOH$. Dunstan and Read's pyrojapaconitin (T., 1900, **77**, 60), obtained by heating japaconitine at 192°, is identical with pyraconitine. The following

salts, prepared in all cases from both pyraconitine and "pyrojapaconitine," are described: hydrochloride, m. p. 167° (decomp.); aurichloride, m. p. 157—158° (decomp.); hydrobromide, m. p. 240—242° (decomp.) (hydrated) or 243—244° (decomp.) (anhydrous), $[\alpha]_D^{20} - 105.87°$ in water ($c = 4.5339$); hydriodide, m. p. 157—158° (decomp.) (hydrated), and perchlorate, m. p. about 190°. The preceding constants differ from those recorded by Dunstan and Carr (*loc. cit.*). C. S.

*isoapo*Caffeine. HEINRICH BILTZ [with PAUL KREBS and KARL STRUFE] (*Ber.*, 1913, **46**, 3407—3410).—The substance *isoapo*caffeine, which is obtained together with *apo*caffeine in the oxidation of caffeine and 1 : 3 : 7-trimethyluric acid (Biltz and Krebs, A., 1910, i, 523), is 3 : 7-dimethylcaffolide; this has been demonstrated by a course of degradation detailed in this paper. The formation of *isoapo*caffeine from caffeine or trimethyluric acid must evidently be a fairly complex process which is partly synthetic; it is suggested that in addition to the direct oxidation to *apo*caffeine, some dimethylalloxan and methylcarbamide are produced, the latter substances then condensing to *isoapo*caffeine and *apo*caffeine. In support of this view it is mentioned that only when the oxidation is so moderated as to proceed slowly is any *isoapo*caffeine formed.

When an aqueous solution of *isoapo*caffeine is evaporated to a syrup, iso*caffuric acid*, $\begin{matrix}\text{NMe·CO}\\ |\\ \text{CO--NH}\end{matrix}\!\!>\!\text{C(OH)·CO·NHMe}$, is obtained, which gradually crystallises in prisms, m. p. 191° (decomp.).

When heated on a water-bath with hydriodic acid (D 1·96), *isoapo*caffeine undergoes reduction to 3-*methylhydantoin*-5-*carboxymethylamide*, $\begin{matrix}\text{NMe·CO}\\ |\\ \text{CO--NH}\end{matrix}\!\!>\!\text{CH·CO·NHMe}$, prisms, m. p. 240°. This substance is hydrolysed by barium hydroxide solution with formation of methylamine and 3-*methylhydantoin*-5-*carboxylic acid*, $\begin{matrix}\text{NMe·CO}\\ |\\ \text{CO--NH}\end{matrix}\!\!>\!\text{CH·CO}_2\text{H}$, tablets, m. p. 130 (decomp.); the latter, on gradually heating to 190°, eliminates carbon dioxide with production of 3-methylhydantoin, $\begin{matrix}\text{NMe·CO}\\ |\\ \text{C}\end{matrix}\!\!>\!\text{CH}_2$.

*isoapo*Caffeine consequently has the structure $\begin{matrix}\text{NMe·CO}\\ |\\ \text{CO--NH}\end{matrix}\!\!>\!\text{C}\!<\!\begin{matrix}\text{O—CO}\\ |\\ \text{CO·NMe}\end{matrix}$.

D. F. T.

Some New Salts of Quinine, Euquinine, Aristoquinine, Saloquinine, and Quinaphenine. DECIO ANGELONI (*Boll. chim. farm.*, 1913, **52**, 675—685).—A basic *salicylate* of *quinaphenine*, $C_{20}H_{23}O_2N_2$·CO·NH·C_6H_4·OEt,OH·C_6H_4·CO_2H, has m. p. 125—126°, and is obtained by adding an ethereal solution of the acid to an ethereal solution of an equimolecular quantity of the base. When 2 mols. of acid are taken and the base is poured into the acid, a *salt*, m. p. 112°, is obtained, which is, however, a mixture of the normal and basic salts.

When an ethereal solution of euquinine (1 mol.) is added to an ethereal solution of novaspirin ($\frac{1}{2}$ mol.), the normal *salt*, m. p. 95°, is obtained. By working in alcoholic solution, the basic *salt* may be prepared; it has m. p. 178°.

Novaspirin and aristoquinine yield the normal *salt*, m. p. 89—90°, in which the aristoquinine behaves as a tetracidic base. Novaspirin and saloquinine in ethereal solution yield the normal *salt*, m. p. 116°. Novaspirin and quinaphenine also yield the normal *salt*, m. p. 118—120°.

Diaspirin and quinine in ethereal solution yield the basic *salt*, which crystallises in needles, m. p. 125°. By taking an excess of acid, the normal *salt* may also be prepared. Diaspirin and quinaphenine in ethereal solution yield the normal *salt*, m. p. 116°.

Diplosal and quinine in ethereal solution yield the basic *salt*, m. p. 105°, which crystallises in needles. Diplosal and quinaphenine in ethereal solution also form the basic *salt*, m. p. 86°.

The compositions of the salts obtained were established by nitrogen estimations. Information is also given as to the solubilities of the bases and acids employed in ether. R. V. S.

The Apparent Colloidal Character and the Molecular Weight of Colchicine. SIMON ZEISEL and K. VON STOCKERT (*Monatsh.*, 1913, **34**, 1327—1338).—In aqueous solution, colchicine has many of the physical and physiological properties of a colloid. Diffusion experiments with a 20% solution show, however, that it is a crystalloid. The amyloid of the diffusion thimble has a great adsorptive power for the alkaloid, and until this is satisfied, the diffusion does not reach a normal value. Cryoscopic and ebullioscopic determinations of the molecular weight of colchicine, colchiceine, and trimethylcolchicinic acid in various solvents have also been made. In acetic acid or boiling ethylene dibromide, the results for colchicine agreed with the formula $C_{22}H_{25}O_6N$. In cold ethylene dibromide and especially in water, which is most unusual, bi- or even ter-molecular values were obtained. Colchiceine gave high values in freezing ethylene dibromide, and trimethylcolchicinic acid in boiling acetic acid. J. C. W.

Bromine Derivatives of Colchicine. SIMON ZEISEL and K. VON STOCKERT (*Monatsh.*, 1913, **34**, 1339—1347).—When an excess of hydrobromic acid is added to a dilute solution of colchicine, sulphur-yellow *dibromocolchicine*, $C_{22}H_{23}O_6NBr_2$, is precipitated, m. p. 146—150° (open tube), 125° (sealed capillary). One molecular proportion of the acid precipitates the *monobromide*, which crystallises in various forms from methyl alcohol, but with constant properties,

$$C_{22}H_{24}O_6NBr,MeOH,$$

m. p. 151·5° (corr., open tube), 133—135° (sealed tube). It is somewhat soluble in water, and the addition of excess of hydrobromic acid to the aqueous mother liquors causes the precipitation of the above dibromide. In methyl alcohol solution, colchicine gives with excess of bromine in the cold, a *tribromide*, $C_{18}H_{10}(OMe)_4O_2NBr_3$, m. p. 131° (open), 118—122° (sealed). The behaviour of these derivatives

towards alkali hydroxides, in open vessels or in sealed tubes, shows that two bromine atoms are firmly combined, whilst the third is fairly labile. *Tribromocolchiceine*, $C_{21}H_{20}O_6NBr_3,H_2O$, and *tribromotrimethylcolchicinic acid*, $C_{19}H_{18}O_5NBr_3$, were also prepared. J. C. W.

Synthesis of Hygrine. I. KURT HESS (*Ber.*, 1913, **46**, 3113—3125).—Hygrine should have either the constitution I or II.

$$\text{(I)}\ CH_2{<}\begin{matrix}CH_2\cdot NMe\\ \vert\\ CH_2\cdot CH\cdot COEt\end{matrix} \qquad \text{(II)}\ CH_2{<}\begin{matrix}CH_2\cdot NMe\\ \vert\\ CH_2\cdot CH\cdot CH_2\cdot COMe\end{matrix}.$$

Willstätter (A., 1900, i, 405) suggested that the second formula was probable, assuming, therefore, that hygrine and tropinone are somewhat similarly constituted, but the fact that the oxidation product, hygric acid (Liebermann and Cybulski, A., 1895, i, 310; Willstätter, *loc. cit.*, and A., 1903, i, 362), is not an acetic acid derivative akin to tropic acid supports formula I. The author has attempted to synthesise the above isomerides, and has so far succeeded in preparing the corresponding hydroxy-compounds:

$$\text{(III)}\ CH_2{<}\begin{matrix}CH_2\cdot NMe\\ \vert\\ CH_2\cdot CH\cdot CHEt\cdot OH\end{matrix} \qquad \text{(IV)}\ CH_2{<}\begin{matrix}CH_2\cdot NMe\\ \vert\\ CH_2\cdot CH\cdot CH_2\cdot CHMe\cdot OH\end{matrix}$$

The former compound was obtained by treating magnesium pyrryl bromide with propionyl chloride, reducing the 2-propionylpyrrole so obtained by sodium and alcohol, and methylating the product. The other compound was prepared by the addition of propylene oxide to magnesium pyrryl bromide, reduction of the *iso*propyl alcohol derivative by means of hydrogen in presence of spongy platinum, and methylation of the pyrrolidyl-2-*iso*propyl alcohol.

a-2-Pyrrylpropan-β-ol, $C_4H_4N\cdot CH_2\cdot CHMe\cdot OH$, is a colourless, odourless, viscous oil, b. p. 94—96°/0·25 mm., which changes into a thick, red syrup in the air, and is soluble in water. No picrate nor oxidation product could be isolated, but it yielded 2-propylpyrrole (Dennstedt and Zimmermann, A., 1893, i, 226) on reduction with red phosphorus and hydriodic acid. It was accompanied by an isomeride, probably, $CH{<}\begin{matrix}CH\cdot NH\\ \vert\\ CH{:}C\cdot CHMe\cdot CH_2\cdot OH\end{matrix}$, which had b. p. 99—107°/0·25 mm.

For the methylation, it was found necessary to prepare the potassium compound and then to add methyl iodide. *a-1-Methylpyrrylpropan-β-ol*, $C_8H_{13}ON$, is a pleasant smelling oil, b. p. 116—117°/18 mm. The reduction of pyrrylpropan-β-ol with hydrogen in presence of platinum was successful when the necessity of excluding all traces of oxygen was realised. For this purpose an apparatus is described which consists essentially of a cylinder and bulb connected by a tap, the cylinder being also fitted with an inlet tube and a ground-on cap. The suspension of platinum in glacial acetic acid was saturated with hydrogen in the bulb, the solution of the alcohol was then washed with hydrogen in the cylinder, and finally the two liquids were shaken together under a slightly increased pressure. The platinum was not added all at once, but fresh portions were occasionally saturated with hydrogen in the cylinder and then allowed to flow into the bulb. The process required a few days. In

this way the formation of pyrrole dyes by catalytic oxidation was entirely prevented, and only a small quantity of platinum was required. A quantitative reduction of pyrrole itself, without the occurrence of a coloured solution, was also effected (compare Willstätter and Hatt, A., 1912, i, 545). *a-2-Pyrrolidylpropan-β-ol*, $C_4H_8N\cdot CH_2\cdot CHMe\cdot OH$, is a viscous oil, b. p. 115—120°/15 mm., with the usual properties of a base and an unsaturated compound. On methylation with methyl iodide and potassium hydroxide, a moderate yield of *a-1-methylpyrrolidylpropan-β-ol* (IV) was obtained as an oil, b. p. 98—103°/16 mm.

2-Pyrrylpropane-βγ-diol (future communication) was also reduced as above, yielding *a-2-pyrrolidylpropane-βγ-diol*

$$C_4H_8N\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH,$$

b. p. 145—150°/18 mm., which formed a very hygroscopic potassium salt.

The reduction of the isomeric alcohols was first studied in the case of 2-acetylpyrrole. Sodium was added to the boiling alcoholic solution of the substance and *a-2-pyrrolidylethan-a-ol* (*pyrrolidyl-2-methylcarbinol*), $C_4H_8N\cdot CHMe\cdot OH$, was extracted from the product as a colourless oil, b. p. 187—192°/759 mm. It smells like acetamide and absorbs moisture and carbon dioxide with avidity. *a-2-Pyrrolidylpropan-a-ol* (*pyrrolidyl-2-ethylcarbinol*), $C_4H_8N\cdot CHEt\cdot OH$, was prepared in this way from 2-propionylpyrrole. It is a well-defined, crystalline base, m. p. 50°, b. p. 95—98°/17 mm., 195—200°/756 mm., with a narcotic odour, is hygroscopic, and gives the Liebermann reaction. *a-1-Methylpyrrolidylpropan-a-ol* (*1-methylpyrrolidyl-2-ethylcarbinol*) (III.) is also a very hygroscopic base, m. p. 45°, b. p. 92—95°/17 mm., 190—195°/757 mm. J. C. W.

Origin of the Cyclic Bases of Coal-tar. LOUIS C. MAILLARD (*Compt. rend.*, 1913, **157**, 850—852).—The humic substances obtained by the condensation of sugars with different amino-acids (compare A., 1912, i, 169) readily yield cyclic bases when heated. The author applies this to the formation of coal from the constituents of cellulose and proteins and to its distillation, yielding coal-tar containing pyridine and other cyclic bases. W. G.

Allylpyrroles. KURT HESS (*Ber.*, 1913, **46**, 3125—3129).—When magnesium pyrryl bromide is treated with allyl bromide, a mixture of approximately equal quantities of 2-allyl- and 2 : 5-diallyl-pyrroles is obtained. The formation of the latter compound is explained by assuming that some magnesium pyrryl bromide reacts with 2-allylpyrrole, forming pyrrole and 5-magnesium-2-allylpyrryl bromide, which then unites with more allyl bromide. This view is supported by the fact that carbon dioxide converts the reaction product of 2-allylpyrrole and magnesium pyrryl bromide into 2-allylpyrryl-5-carboxylic acid, acid, from which it follows that allylpyrrole is more acidic than pyrrole.

The reaction between allyl bromide and magnesium pyrryl bromide

was vigorous but was not moderated by cooling. After steam distillation and extraction with ether, 2-*allylpyrrole*,

$$CH\begin{matrix}\diagup CH\cdot NH \\ \diagdown CH:C\cdot CH_2\cdot CH:CH_2\end{matrix},$$

was obtained as a colourless, mobile liquid, b. p. 82—83°/24 mm., D_4^{24} 0·9376. It has an unpleasant odour, rapidly becomes yellow in the air, finally forming a red, amorphous mass, and is extremely sensitive towards reagents. 2 : 5-Diallylpyrrole, $C_4H_3N(CH_2\cdot CH:CH_2)_2$, is a similar liquid, b. p. 110—115°/17 mm., D_4^{24} 0·9321. The addition of allylpyrrole to magnesium pyrryl bromide caused a change in colour from grey to dark green. After treatment with dry carbon dioxide, 2-*allylpyrrylcarboxylic acid*, $CH\begin{matrix}\diagup C(CO_2H)\cdot NH \\ \diagdown CH{=\!=\!=}C\cdot CH_2\cdot CH:CH_2\end{matrix}$, was obtained in indefinite crystals, m. p. 117—118°. It is unstable, and partly decomposes into violet-pink dyes even when boiled with light petroleum. J. C. W.

Equilibrium in the System Cobalt Chloride and Pyridine. J. NEWTON PEARCE and T. E. MOORE (*Amer. Chem. J.*, 1913, **50**, 218—231).—In order to investigate the formation of compounds of cobalt chloride with pyridine of crystallisation, a study has been made of this system by the solubility method at temperatures between −50·3° and 100°. The results show the existence of three distinct crystalline compounds, $CoCl_2,2C_5H_5N$; $CoCl_2,4C_5H_5N$, and $CoCl_2,6C_5H_5N$. The first two of these have been isolated previously by Reitzenstein (A., 1895, i, 121). The compound $CoCl_2,2C_5H_5N$ has m. p. 195—200°, but the m. p.'s of the other two compounds cannot be ascertained, as they rapidly lose pyridine when heated under the ordinary pressure.

The compound $CoCl_2,6C_5H_5N$ exists as the solid phase between −50·3° and 15°, $CoCl_2,4C_5H_5N$ between 15° and 70°, $CoCl_2,2C_5H_5N$ between 70° and 90°, whilst between 90° and the b. p. of the saturated solution $CoCl_2$ is the stable, solid phase.

The usual methods of estimating cobalt are not satisfactory in presence of pyridine, and the following method was therefore devised. The weighed sample of solution was heated at 120° until all the pyridine had been removed. It was then dissolved in 50% alcohol, and an excess of oxalic acid was added to the solution. The precipitated cobalt oxalate was washed with 50% alcohol, dried at 100°, and dissolved in sulphuric acid (1 : 3). The solution was diluted to 300 c.c., heated nearly to boiling, and titrated with potassium permanganate. This method was found to be very accurate. E. G.

Cyclic Imines. VIII. Ring Opening in Substituted Indoles and Quinolines. JULIUS VON BRAUN, ALFRED GRABOWSKI, and MARGARETE RAWICZ (*Ber.*, 1913, **46**, 3169—3182).—A number of cyclic imines (substituted quinoline and indole derivatives) have been converted into compounds of the phenylpropane series primarily to determine with what yield the chlorinated amides could be obtained on treating the *N*-benzoyl compounds of the imines with phosphorus pentachloride, and to study the hydrolysis of these amides to the

chlorinated bases. It appears that the substituted anilides are formed even more readily than the unsubstituted compounds previously described, and they are readily purified from unchanged imine. They are hydrolysed with difficulty as the temperatures necessary to ensure hydrolysis and at which decomposition begins lie very near together.

6-*Chlorotetrahydroquinoline*, $C_6H_3Cl<\begin{matrix}CH_2\cdot CH_2\\ NH-CH_2\end{matrix}$, obtained by reduction of 6-chloroquinoline and isolated by means of the benzoyl compound, has b. p. 160°/11 mm., m. p. 43°. The *hydrochloride* crystallises in lustrous needles, m. p. 190°; the *platinichloride* is yellow, m. p. 185°. The *benzoyl* derivative has m. p. 84°. The *picrate*, m. p. 151°, and the *nitroso*-compound, m. p. 65°, are also described.

On heating the benzoyl derivative with phosphorus pentachloride at 140°, *benzo*-p-*γ-dichloro*-o-*propylanilide*,

$$CH_2Cl\cdot CH_2\cdot CH_2\cdot C_6H_3Cl\cdot NH\cdot COPh,$$

is obtained in a mass of snow-white crystals, m. p. 108°. On prolonged heating with concentrated hydrochloric acid at 125°, p-*γ-dichloro*-o-*propylaniline hydrochloride* is obtained, m. p. 170°. The free base, $C_3H_6Cl\cdot C_6H_3Cl\cdot NH_2$, is a slightly coloured, almost odourless oil. The yellow *platinichloride*, has m. p. 181—182°, and the *picrate* has m. p. 143°.

On diazotisation and treatment with cuprous chloride, 2 : 5-*γ-trichloropropylbenzene*, $C_6H_3Cl_2\cdot C_3H_6Cl$, is obtained as a colourless oil of agreeable odour, b. p. 152°/16 mm.

7-*Nitrotetrahydroquinoline*, $NO_2\cdot C_6H_3<\begin{matrix}CH_2\cdot CH_2\\ NH\cdot CH_2\end{matrix}$, prepared by nitrating tetrahydroquinoline in concentrated sulphuric acid, forms a yellowish-red, crystalline mass, m. p. 90°. The *hydrochloride* separates in colourless needles, m. p. 203°; the colourless *benzoyl* derivative has m. p. 141°, whereas the *nitroso*-compound has m. p. 118—120°.

On opening the ring with phosphorus pentachloride, *benzo-γ-chloro-5-nitro-2-propylanilide*, $C_3H_6Cl\cdot C_6H_3(NO_2)\cdot NHBz$, is obtained in well formed, colourless needles, which are converted on hydrolysis at 120° into *γ-chloro-5-nitro-2-propylaniline*, a red compound, m. p. 76°. The *hydrochloride* has m. p. 217°, the *platinichloride* forming a yellow, crystalline precipitate.

Heating with dimethylamine converts the benzonitroanilide into *benzo-γ-dimethylamino-5-nitro-2-propylanilide*,

$$NMe_2\cdot C_3H_6\cdot C_6H_3(NO_2)\cdot NHBz,$$

crystallising in well formed, colourless needles, m. p. 157°. The *hydrochloride* and *picrate* are oily.

γ-Dimethylamino-5-nitro-2-propylaniline, obtained on hydrolysis, separates in yellow crystals, m. p. 65—66°. The *dihydrochloride* has m. p. 191°, and the *dipicrate*, m. p. 146°.

6-*Chloro*-7-*nitrotetrahydroquinoline* forms red crystals, m. p. 84°. The *hydrochloride*, m. p. 184°, becomes red in presence of moisture. The yellow *nitroso*-derivative has m. p. 124°, and the *benzoyl* derivative has m. p. 126°.

Dichlorobenzo-4-*γ-dichloro*-5-*nitro*-2-*propylanilide* is colourless, m. p. 173—174°. Hydrolysed at 120—125° it forms 4-*γ-dichloro*-5-*nitro*-2-

propylaniline : this is yellow, m. p. 90°, and forms a colourless *hydrochloride*, m. p. 150—151°, which becomes bright yellow when wet.

7-*Benzoylaminotetrahydroquinoline*, m. p. 189°, forms a *platinichloride*, m. p. 280—282°.

7-*Aminotetrahydroquinoline*, obtained either on hydrolysis of the above or by reducing the corresponding nitro-compound, forms a colourless oil, b. p. 195°/15 mm., m. p. 60°. The *hydrochloride*, m. p. 240°, and the *dibenzoyl* derivative, m. p. 233°, are described. The 2 : 3-*dibenzoylamino-γ-chloropropylbenzene*,

$$C_3H_6Cl\cdot C_6H_3(NHBz)_2,$$

obtained from this has m. p. 198—200°, forming a colourless powder.

The *acetyl* derivative, $NHAc\cdot C_6H_3 < \begin{matrix} CH_2-CH_2 \\ NMe\cdot CH_2 \end{matrix}$, of 7-aminokairoline, m. p. 114°, when treated with cyanogen bromide forms 1-*cyano*-7-*acetylaminotetrahydroquinoline*, m. p. 152°, which is hydrolysed to 7-*aminotetrahydroquinoline*, m. p. 60°.

6-*Nitrodihydroscatole*, $NO_2\cdot C_6H_3 < \begin{matrix} CHMe \\ -NH- \end{matrix} > CH_2$, from dihydroscatole, has m. p. 75°; the *hydrochloride* has m. p. 192°, the yellow *nitroso*-compound has m. p. 100°, and the *benzoyl* derivative, which crystallises in lustrous platelets, has m. p. 148°. *Benzo-5-nitro-2-β-chloroisopropylanilide*, $NHBz\cdot C_6H_3(NO_2)\cdot CHMe\cdot CH_2Cl$, crystallises in colourless, matted needles, m. p. 110°. Hydrolysis at 125° converts it into *nitrodihydroscatole hydrochloride*, m. p. 192°.

6-*Nitrodihydromethylindole*, $NO_2\cdot C_6H_3 < \begin{matrix} CH_2 \\ NH \end{matrix} > CHMe$, has m. p. 50°, and forms a *benzoyl* compound, m. p. 137°, a *hydrochloride*, m. p. 200° after sintering previously, and a nitroso-compound, m. p. 103—104°. *Benzo-5-nitro-2-β-chloropropylanilide*,

$$PhCO\cdot NH\cdot C_6H_3(NO_2)\cdot CH_2\cdot CHMeCl,$$

is colourless, m. p. 150°, and is converted on hydrolysis into 5-*nitro*-2-*β-chloropropylaniline*, a yellowish-red, crystalline mass, m. p. 84°. Treatment with dimethylamine converts it into 2-*β-benzo-5-nitro*-2-*dimethylaminopropylanilide*, $NO_2\cdot C_6H_3(NHBz)\cdot CH_2\cdot CHMe\cdot NMe_2$, crystallising in colourless needles, m. p. 122°. The analogous *piperidino*-compound, $NO_2\cdot C_6H_3(NHBz)\cdot CH_2\cdot CHMe\cdot NC_5H_{10}$, has m. p. 117°. E. F. A.

Action of Phosphoric Oxide on Benzylideneacetoneoxime. H. BURSTIN (*Monatsh.*, 1913, **34**, 1443—1448).—Goldschmidt (A., 1895, i, 392) by warming benzylideneacetoneoxime with phosphoric oxide could only isolate *iso*quinoline, whereas 2-methylquinoline or 1-methyl*iso*quinoline would represent a normal course for the condensation. The author has obtained a similar product, b. p. 240—250°, which gave a platinichloride, and corresponded with a mixture of the homologous quinolines. By the formation of quinophthalone (Jacobsen and Reimer, A., 1883, i, 812) and quinoline-2-carboxylic acid (Koenigs, A., 1899, i, 390), the presence of 2-methylquinoline was proved, whilst the formation of *iso*quinoline-red (Vongerichten and Homann, this vol., i, 99) indicated the presence of a mixture of 2-methylquinone and *iso*quinoline. J. C. W.

Condensation of Phenyl*iso*oxazolone with Ethyl Mesoxalate. ANDRÉ MEYER (*Bull. Soc. chim.*, 1913, [iv], **13**, 903—909).—By the condensation of these two products it was expected that coloured substances of the general formula $\begin{matrix} N{:}CPh \\ | \\ O{-}CO \end{matrix}\!\!>\!C{:}C(CO{\cdot}R){\cdot}CO_2R'$ would be produced, but instead it was found that two molecules of phenyl*iso*oxazolone took part in the reaction with the formation of compounds of the type $\begin{matrix} N{:}CPh \\ | \\ O{-}CO \end{matrix}\!\!>\!CH{\cdot}C(CO_2R)_2{\cdot}CH\!<\!\!\begin{matrix} CPh{:}N \\ | \\ CO{-}O \end{matrix}$, or their enolic forms.

*Ethyl mesoxalate bisphenyl*isooxazolone [*Bis-3-phenyl*isooxazolone*-4-malonate*], m. p. 187° (decomp.), forms large octahedra by slow evaporation of its solutions or small, prismatic crystals from acetic acid or boiling alcohol; it is soluble in alkalis and can be titrated, 1 mol. requiring 2 mols. of alkali to produce neutrality in presence of phenolphthalein. The sodium *salt* is crystalline and hygroscopic; those of the heavy metals are colourless and amorphous; ferric chloride gives a violet precipitate.

The sodium salt with ethyl iodide furnishes the *diethyl ether*, m. p. 200—201°, crystallising in silky, slender needles. The *diacetyl* derivative, m. p. 165—166°, forms small, prismatic crystals, and the *dibenzoyl* derivative, m. p. 194°, colourless leaflets or stellate groups of prismatic needles. Cryoscopic determinations of the molecular weight of the latter gave abnormal results. With benzenediazonium chloride, ethyl bis-3-phenyl*iso*oxazolone-4-malonate gave benzeneazophenyl*iso*oxazolone. T. A. H.

The Constitution of Dinitrothiodiphenylamine [Dinitrophenthiazine]. FRIEDRICH KEHRMANN and FERD. RINGER (*Ber.*, 1913, **46**, 3014—3020. Compare Möhlau, Beyschlag, and Köhres, A., 1912, i, 212).—The authors believe that the dinitrophenthiazine obtained by Möhlau and his collaborators (*loc. cit.*) by the condensation of picryl chloride with *o*-benzoylaminophenyl mercaptan and subsequent treatment with sodium hydroxide solution is actually identical with and not an isomeride of the 3 : 5-dinitrophenthiazine described by Kehrmann and Schild (A., 1900, i, 61). In spite of the presence of the benzoyl radicle, the picryl chloride must therefore have made the amino-group and not the mercaptan group its main point of attack. In the action of picryl chloride on free aminophenyl mercaptan as well as on its benzoyl derivative, however, by-products are obtained which probably represent the isomerides of the main products and have the picryl radicle attached at the sulphur atom.

The compound, golden-yellow prisms, m. p. 169°, which is the main product of the interaction of picryl chloride and *o*-benzoylaminophenyl mercaptan, is therefore considered to have the structure

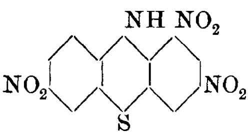
$$SH{\cdot}C_6H_4{\cdot}NBz{\cdot}C_6H_2(NO_2)_3,$$

that is, *benzo-2 : 4 : 6-trinitro-2′-thioldiphenylamide*, whilst the substance, orange-yellow, leafy crystals, m. p. 142°, which results in smaller quantity, is probably the true trinitrophenyl *o*-benzoylaminophenyl sulphide. If the former substance, m. p. 169°, dissolved in alcohol is

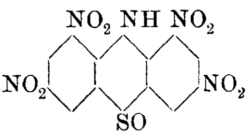
treated with dilute sodium hydroxide solution and left at the ordinary temperature, there slowly separates 3 : 5-*dinitro-6-benzoylphenthiazine*, $C_6H_4<{NBz \atop S}>C_6H_2(NO_2)_2$, straw-yellow leaflets, m. p. 209°, which on hydrolysis by alcoholic sodium hydroxide undergoes conversion into 3 : 5-dinitrophenthiazine, m. p. 188—190°, identical with the product of Kehrmann and Steinberg (A., 1911, i, 1034); the m. p. 218°, observed by Möhlau and his collaborators, must be due either to the occurrence of dimorphism or to the presence of impurities.

The substance described by Möhlau as 2 : 4-diaminophenazthionium ferrichloride (*loc. cit.*) is in reality the ferrichloride of 3 : 5-diaminophenazthionium, the experimental conditions deciding whether the ferrichloride or merely the chloride (Kehrmann and Schild, *loc. cit.*) shall separate.

When a suspension of 3 : 5-dinitrophenthiazine in cold acetic acid is gradually treated with powdered sodium nitrite (compare this vol., i, 1231), the substance passes into solution and there separates 3 : 5 : 9-*trinitrophenthiazine* (annexed formula), brownish-red, lustrous prisms, m. p. 214°. This substance by reduction in alcoholic solution by stannous chloride and hydrochloric acid, followed by oxidation of the separated, colourless *zincochloride* with ferric chloride, passes into 3 : 5 : 9-*trinitrophenazthionium chloride*, long needles with a metallic green lustre; *nitrate*, sparingly soluble; *platinichloride*, violet-black, crystalline powder.



The identity of the dinitrophenthiazine resulting from the methods of the two above-mentioned groups of investigators was further confirmed by energetic nitration, when 3 : 5 : 7 : 9-tetranitrodiphenylaminesulphoxide (annexed formula) was obtained in each case as well as in the nitration of 3 : 9-dinitro- and of 3 : 5 : 9-trinitro-phenthiazine.



A closer examination of the reaction product from *o*-aminophenyl mercaptan and picryl chloride reveals the presence of a small quantity of a *substance*, straw-yellow tablets, in addition to the 2 : 4 : 6-trinitro-2′-thioldiphenylamine which was described earlier. It is believed that the former is possibly trinitrophenyl aminophenyl sulphide. D. F. T.

Preparation of *N*-Alkyl-*p*-phenylenediaminesulphonic Acids CHEMISCHE FABRIKEN VORM. WEILER-TER MEER (D.R.-P. 264927).—*N*-Alkyl-*p*-phenylenediaminesulphonic acids are obtained by the action of neutral alkali sulphites on *p*-nitroso-compounds of secondary or tertiary amines of general formula $NO\cdot R\cdot NR_1R_2$, where R is phenyl or a homologue of the same, R_1 hydrogen, alkyl or alkylaryl, and R_2 alkyl or alkylaryl.

p-*Phenylene-as-dimethyldiaminesulphonic acid*, $C_8H_{12}O_3N_2S$ (in which the sulphonic group is probably ortho- to the primary amino-group), is obtained when an aqueous solution of *p*-nitrosodimethylaniline (10 parts) is slowly treated at the ordinary temperature with a solution

of sodium sulphite (30 parts), and when the nitroso-compound has completely dissolved the mixture boiled with concentrated hydrochloric acid (90 parts); the acid is extremely soluble in water, but can be purified and finally isolated by means of its crystalline *benzylidene* derivative.

p-*Phenylene*-as-*diethyldiaminesulphonic acid* (prepared from nitrosodiethylaniline) is more readily isolated in crystalline form, whilst p-*phenylene*-as-*benzylethyldiaminesulphonic acid* furnishes a sparingly soluble *sodium* salt.

o-*Tolylene*-2-*ethyldiaminesulphonic acid* is obtained in a similar manner from *p*-nitrosoethyl-*o*-toluidine, and is isolated through its *benzylidene* derivative. F. M. G. M.

Leuco-bases and Colouring Matters Derived from Diphenylethylene. VI. The First Stage in the Oxidation of the *cyclo*Hexylidene Leuco-base, $C_6H_{10}:C[C_6H_4\cdot NMe_2]_2$. Tetrahydromalachite-green. PAUL LEMOULT (*Compt. rend.*, 1913, **157**, 597—599. Compare A., 1912, i, 791).—Tetramethyldiaminodiphenyl-*cyclo*hexylidenemethane (formula I), when acted on by lead peroxide, gives a bluish-coloured substance, which spontaneously decomposes in aqueous solution, giving the compound (formula III) having two atoms of hydrogen less than the initial leuco-base (compare *loc. cit.*):

$$\text{(I.)}\ CH_2{<}{CH_2\cdot CH_2 \atop CH_2\cdot CH_2}{>}C:C(C_6H_4\cdot NMe_2)_2$$

$$\text{(II.)}\ C_6H_9\cdot C(OH)(C_6H_4\cdot NMe_2)_2 \qquad \text{(III.)}\ C_6H_8:C(C_6H_4\cdot NMe_2)_2.$$

The author has now succeeded in isolating the unstable substance (formula II) by precipitating it from acid solution with ammonia, drying it in a vacuum over sulphuric acid, followed by crystallisation from benzene. Heated slowly, it has m. p. 130—135°, heated rapidly, m. p. 160°, whilst the instantaneous m. p. is 145°. If the liquid is allowed to cool and re-melted it has m. p. 165°, which is in accord with elimination of water, giving substance III, m. p. 169° (*loc. cit.*). This transformation is also brought about by simple crystallisation from hot alcohol.

The oxygenated compound on solution in cold alcohol to which one drop of acetic acid has been added, gives a persistent, deep blue solution, thus differing from substances I and II, and in slightly acid solution it dyes cotton, mordanted with tannin, a tint comparable to that given by malachite-green, but appreciably bluer. The absorption spectra of these two compounds, however, show marked differences.

W. G.

Leuco-bases and Colouring Matters of Diphenylethylene. VII. Action of Magnesium Methyl and Ethyl Iodides on Michler's Ketone. PAUL LEMOULT (*Compt. rend.*, 1913, **157**, 724—726).—A repetition of Fecht's experiments on the action of magnesium methyl and ethyl iodides on Michler's ketone (compare A., 1907, i, 926). Contrary to Fecht's statements, but in agreement with the results of Freund and Mayer (compare A., 1906, i, 384), the author obtained no carbinols of the type $OH\cdot CMe(C_6H_4\cdot NMe_2)_2$, but a mixture of substances from which he separated unchanged ketone,

an ethylenic derivative of the type $CH_2:C(C_6H_4 \cdot NMe_2)_2$, and in the case of magnesium methyl iodide, small quantities of a *substance*, crystallising in yellow needles, m. p. 157—158°, having the composition $C_{18}H_{22}N_2$, but a molecular weight corresponding to twice this, together with two other basic substances, crystallising (*a*) in yellow plates, m. p. 227°, and (*b*) in yellow crystals, m. p. 274°, the constitutions of which have not yet been determined. In the case of magnesium ethyl iodide, no substances corresponding with the last three were found, but a 90% yield of the ethylenic compound, $CHMe:C(C_6H_4 \cdot NMe_2)_2$, was obtained. W. G.

Ditertiary Hydrazines. XVI. Mechanism of the Blue Colour Reaction of Diphenylamine. HEINRICH WIELAND [with CARL MÜLLER] (*Ber.*, 1913, **46**, 3296—3303).—The blue coloration formed in sulphuric acid solutions of diphenylamine by oxidising agents was considered to be an acid sulphate of diphenyl dihydrophenazonium. Kehrmann and Micewicz (A., 1912, i, 1020) have shown that it is more probably a quinonoid derivative of diphenylbenzidine, $PhN:C_6H_4:C_6H_4:NHPh \cdot O \cdot SO_3H$. This explanation is now accepted, although it is not applicable to the colour reactions obtained with diphenylhydrazine, diphenylhydroxylamine, and *p*-dianisylamine.

Diphenylamine in dilute sulphuric acid and acetic acid solution is readily oxidised to the blue dye, which is easily reduced without the formation of by-products to diphenylbenzidine. Tetramethylhydrazine gives only small quantities of diphenylbenzidine as well as amorphous products; its formation cannot, therefore, be regarded as an intermediate stage in the colour reaction.

Triphenylamine shows a similar blue coloration on oxidation, when quinonoid salts of tetraphenylbenzidine are formed. *Tetraphenylbenzidine* crystallises in pale yellow needles, m. p. 226°, to a brownish-yellow liquid.

s-*Diphenyl*-o-*phenylenediamine*, $C_6H_4(NHPh)_2$, obtained by the action of iodobenzene and copper powder on *o*-aminodiphenylamine, crystallises as colourless double pyramids, m. p. 152·5°. On attempting to combine it with *o*-dibromobenzene to diphenyldihydrophenazine, only amorphous products were obtained. E. F. A.

Ditertiary Hydrazines. XVII. Diphenylhydroxylamine and Some Colour Reactions Related to the Blue Diphenylamine Reaction. HEINRICH WIELAND and CARL MÜLLER (*Ber.*, 1913, **46**, 3304—3314).—Diphenylhydroxylamine reacts with 75% sulphuric acid to form 70% of diphenylbenzidine, together with a little diphenylamine and a green dye of high molecular complexity. The quinonoid-blue salt is formed in this instance by direct elimination of water from diphenylhydroxylamine. When the sulphuric acid is diluted with acetic acid instead of water, the anhydro-product obtained is carbazole together with considerable quantities of *p*-hydroxydiphenylamine.

Even ice-cold sulphuric acid converts diphenylhydrazine into diphenylhydroxylamine, which is converted into diphenylbenzidine

as described. Much ammonia is also formed, also traces of *o*-aminodiphenylamine and some *p*-hydroxydiphenylamine.

p-Tolylhydrazine and concentrated sulphuric acid give at first a bluish-green and green coloration due to hydroxylamine, and ammonia is also formed. Further decomposition yields a yellowish-brown, amorphous substance and much ditolylamine.

Tetraphenyl- and *p*-tetratolyl-hydrazine dissolve in sulphuric acid with a reddish-violet coloration which changes to blue. Diphenylamine and ditolylamine are also formed respectively.

On oxidation of *p*-dianisylamine with persulphate and sulphuric acid, the salt, $OMe\cdot C_6H_4\cdot N{:}C_6H_4{:}OMe\cdot O\cdot SO_3H$, is first formed, but could not be isolated. A blue sulphate of the character of an indophenol which is red in solution was obtained; it very readily yields *p*-benzoquinone on treatment with dilute acids, and is considered to be the acid sulphate of a polymerised bimolecular *anisylquinone monoimine*,

$$HO\cdot C_6H_4\cdot N(C_6H_4\cdot OMe)\cdot C_6H_3(OMe)\cdot N{:}C_6H_4O.$$

E. F. A.

The Action of Organomagnesium Compounds on Diazomethane and Ethyl Diazoacetate. II. ERNST ZERNER (*Monatsh.*, 1913, **34**, 1631—1638. Compare this vol., i, 1312).—The author makes some observations on the paper by Forster and Cardwell (T., 1913, **103**, 86) on the constitution of aliphatic diazo-compounds, and describes the preparation of benzaldehydephenylhydrazone by the action of diazomethane on magnesium phenyl bromide. The formation of this compound is assumed to follow the course:

$$CH_2{:}N\cdot N + PhMgBr \longrightarrow CH_2{:}N\cdot NPh\cdot MgBr + PhMgBr \longrightarrow$$
$$CH_2Ph\cdot NMgBr\cdot NPh\cdot MgBr \longrightarrow CH_2Ph\cdot NH\cdot NH\cdot CH_2Ph \longrightarrow$$
$$CHPh{:}N\cdot NHPh.$$

The ring formula for the fatty diazo-compound would require that at least one nitrogen atom would be involved in the addition of two molecules of the magnesium compound, which is contrary to experience.

J. C. W.

The Condensation of Ethyl Oxalate with Pyrazolones. WILHELM WISLICENUS, HEINRICH ELVERT, and PAUL KURTZ (*Ber.*, 1913, **46**, 3395—3407).—On the addition of a benzene solution of phenylmethylpyrazolone (prepared from ethyl acetoacetate) to a mixture of ethyl oxalate and potassium ethoxide dissolved in ether, there separates slowly the *potassium* derivative, yellowish-white crystals, decomp. between 138° and 145°, of *ethyl* 1-*phenyl*-3-*methyl*-5-*pyrazolone*-4-*glyoxylate*, $CO_2Et\cdot CO\cdot CH<\begin{matrix}CO-NPh\\ CMe\cdot N\end{matrix}$, yellowish-white needles, m. p. 81—82°, which can be liberated by addition to cold dilute hydrochloric acid; the ester gives a deep red coloration with ferric chloride and also with common benzene and sulphuric acid; its tendency to enolisation is further evidenced by the formation of a green *copper* derivative, m. p. 220—223°, and of an *ammonium* derivative, m. p. 120—123° (decomp.). Treatment of the ester with phenylcarbimide caused the formation of the *carbanilate* of *ethyl* 1-*phenyl*-3-*methyl*-5-*pyrazolol*-4-*gly*-

oxylate, $N\Big\langle\begin{matrix}NPh-C\cdot O\cdot CO\cdot NHPh \\ CMe-C\cdot CO\cdot CO_2Et\end{matrix}$, colourless needles, m. p. 97°, which like the corresponding additive compound from phenylcarbimide and phenylmethylpyrazolone, namely, 1-*phenyl*-3-*methyl*-5-*pyrazolyl carbanilate*, colourless needles, m. p. 92—93°, is unstable, and when heated gives an odour of phenylcarbimide.

Ethyl phenylmethylpyrazoloneglyoxylate gives a *phenylhydrazone*, almost colourless needles, m. p. 182—183°, in the formation of which a difficultly isolable *isomeride*, yellow leaflets, is also produced; p-*bromophenylhydrazone*, yellowish-white needles, m. p. 213—214°.

1-*Phenyl*-3-*methyl*-5-*pyrazolone*-4-*glyoxylic acid*, yellowish-white needles, m. p. 236—238°, is obtainable by hydrolysis of the ester. With sulphuric acid it gives on warming a green coloration changing successively to red and brown, and at 200° it is converted with loss of carbon dioxide into the already known phenylmethylpyrazolonesulphonic acid (Möllenhoff, A., 1892, 1245). Heated with aniline at 150°, the acid gives rise to the *anil* of 1-*phenyl*-3-*methyl*-5-*pyrazolone*-4-*aldehyde*, greenish-yellow needles, m. p. 151—152°. The acid reacts slowly with phenylhydrazine in alcoholic solution at the ordinary temperature, giving rise to a *phenylhydrazone*, almost colourless needles, m. p. 205—206°, which can be esterified by alcohol and hydrogen chloride to the previously mentioned phenylhydrazone of the ester. If phenylmethylpyrazoloneglyoxylic acid is heated with methyl or ethyl alcohol for an hour in a sealed tube at 160—180°, orange-yellow needles of 1-phenyl-3-methyl-4-methylene-5-pyrazolone,

$$\begin{matrix}NPh-CO \\ | \\ N{=\!=}CMe\end{matrix}\Big>C{:}CH_2,$$

separate (compare Pellizzari, A., 1889, 517), a small amount of a colourless *substance*, m. p. above 280°, which in alcoholic solution gives a violet precipitate with ferric chloride being present in the mother liquor.

1 : 3-Diphenyl-5-pyrazolone condenses with ethyl oxalate under the same conditions as the above methylpyrazolone, giving the *sodium* or *potassium* derivatives of *ethyl* 1 : 3-*diphenyl*-5-*pyrazolone*-4-*glyoxylate*, which after acidifying is obtainable in yellowish-white, prismatic needles, m. p. 108—109°. The ester, which gives similar colour reactions to the analogous 1-phenyl-3-methyl compound, is, however, not hydrolysed on boiling with alcoholic potassium hydroxide; it gives a deep green *copper* derivative, m. p. 245—246° (decomp.); the *phenylhydrazone* as first obtained from reaction in chloroform or alcohol forms colourless needles, m. p. 208—209°, but on recrystallisation from alcohol passes into yellow, prismatic needles of an isomeride, m. p. 204—205°, which is directly produced in benzene solution.

1-*p*-Tolyl-3-methylpyrazolone, prepared from *p*-tolylhydrazine and ethyl acetoacetate, undergoes condensation with ethyl oxalate under the previous conditions, yielding yellow needles of the *potassium* derivative of *ethyl* 1-p-*tolyl*-3-*methyl*-5-*pyrazolone*-4-*glyoxylate*; this ester, which forms yellow needles, m. p. 87—88°, gives a deep red coloration with alcoholic ferric chloride, and a red changing to violet with common benzene and sulphuric acid.

1-p-*Tolyl-3-methyl-5-pyrazolone-4-glyoxylic acid* forms colourless needles, m. p. 218—219°. Treatment of the ester with the calculated quantity of phenylhydrazine gives a mixture of almost colourless needles and yellow leaflets. The former, purified by recrystallisation from alcohol, have m. p. 195—196°, whilst the latter, m. p. 209—210°, are obtained pure by crystallisation from warm chloroform; these two *phenylhydrazones* are isomeric, the structures:

$$\begin{matrix}\mathrm{NPh{\cdot}CO}\\ \mid \\ \mathrm{N{=}CMe}\end{matrix}\!\!>\mathrm{CH{\cdot}C({:}N{\cdot}NHPh){\cdot}CO_2Et} \quad \text{and}$$

$$\begin{matrix}\mathrm{NPh{\cdot}CO}\\ \mid \\ \mathrm{N{=}CMe}\end{matrix}\!\!>\mathrm{C{:}C({\cdot}NH{\cdot}NHPh){\cdot}CO_2Et}$$

being suggested for the colourless and yellow forms respectively. A similar explanation is proposed for the occurrence of the other isomeric phenylhydrazones described above.

Tolylmethylpyrazoloneglyoxylic acid with phenylhydrazine in benzene solution first gives colourless needles, m. p. 201—202°, of a *phenylhydrazine* salt, which loses a molecule of water on recrystallisation from hot alcohol, producing the *phenylhydrazone*, yellow leaflets, m. p. 217°. No isomerism was observed with this phenylhydrazone or with the *diphenylhydrazone* of ethyl tolylmethylpyrazoloneglyoxylate, prisms, m. p. 137—138°. D. F. T.

Preparation of *N*-Halogenalkyl-5 : 5-dialkylbarbituric Acids. E. MERCK (D.R.-P. 265726).—*N*-Halogenalkyl-5 : 5-dialkylbarbituric acids of general formula $\mathrm{CRR_1}<\begin{matrix}\mathrm{CO{\cdot}NX}\\ \mathrm{CO{\cdot}NY}\end{matrix}>\mathrm{CO}$ (where R and R_1 are alkyl, X halogenalkyl, and Y hydrogen or halogenalkyl groups) are obtained when *N*-alkylen-5 : 5-dialkylbarbituric acids are treated with the required halogen, or when dialkylmalonyl haloids are combined with halogenated alkylcarbamides.

5 : 5-*Diethyl*-1-*allylbarbituric acid* forms colourless needles, m. p. 77°; and when treated (in cooled acetic acid solution) with bromine, gives rise to 5 : 5-*diethyl*-1-*βγ-dibromopropylbarbituric acid*,

$$\mathrm{CO}<\begin{matrix}\mathrm{CEt_2{\cdot}CO}\\ \mathrm{NH{-}CO}\end{matrix}>\mathrm{N{\cdot}CH_2{\cdot}CHBr{\cdot}CH_2Br},$$

colourless needles, m. p. 126° (corr.); the latter compound can also be prepared by heating βγ-dibromopropylcarbamide,

$$\mathrm{CH_2Br{\cdot}CHBr{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}NH_2},$$

with diethylmalonyl chloride during fifteen to twenty hours at 120°.

5 : 5-*Dibenzyl*-1 : *γ-bromopropylbarbituric acid*, small, hard prisms, m. p. 111°, is obtained in a similar manner from 5 : 5-dibenzyl-1-allylbarbituric acid.

5 : 5-*Diethyl*-1-*βγ-dichloropropylbarbituric acid* has m. p. 127°, and 5 : 5-*diethyl*-1 : *γ-bromopropylbarbituric acid*, m. p. 100°.

When 5-*phenyl*-5-*ethyl*-1-*allylbarbituric acid*, m. p. 68—69° (prepared from allylcarbamide and phenylethylmalonyl ester) is treated with bromine it gives rise to 5-*phenyl*-5-*ethyl*-1-*βγ-dibromopropylbarbituric acid*, $C_{15}H_{16}O_3N_2Br_2$, whilst 5 : 5-*diethyl-βγβ'γ'-tetrabromo*-1 : 1-*dipropylbarbituric acid*, $C_{14}H_{20}O_3N_2Br_4$, colourless prisms, m. p. 64°, is obtained by brominating 5 : 5-diethyl-1 : 1-diallylbarbituric acid

or by brominating *s*-diallylcarbamide and heating the *tetrabromodipropylcarbamide* with diethylmalonyl chloride at 120—130° for twenty-five hours in a vacuum. F. M. G. M.

Products of Decomposition of Indigo in the Vat. HERBERT EHRHARDT (*J. Soc. Dyers*, 1913, **29**, 321—322).—The loss of dye which is often experienced when indigo vats are reduced, not by pure solutions of sodium hyposulphite, but by metallic reducing agents, is traced to the formation of anthranilic acid. A vat containing 200 grams of pure 20% indigo-paste, 120 grams of lime slaked with 600 c.c. of water, 200 c.c. of sodium hydrogen sulphite solution of 57° Tw., and 30 grams of zinc was left for a few days. The sediment was then filtered and extracted with boiling water, whilst the solution was oxidised by a current of air and the precipitated indigo extracted with dilute hydrochloric acid. The combined solutions were then cooled, roughly titrated with sodium nitrite, and treated with the requisite amount of β-naphthol, when 2 grams of the azo-dye of anthranilic acid were obtained. J. C. W.

Formation of Pyrazine Compounds from Quinoxaline Derivatives. K. A. BÖTTCHER (*Ber.*, 1913, **46**, 3084—3087. Compare Gabriel and Sonn, A., 1908, i, 60).—2-*Methylquinoxaline*,

$$C_6H_4<\begin{matrix}N:CMe\\ |\\ N:CH\end{matrix},$$

b. p. 245—247°, is formed by the condensation of *o*-phenylenediamine with oximinoacetone in aqueous acetic acid solution. It solidifies in a freezing mixture of ice and salt, and is rapidly discoloured on exposure to sunlight. The *platinichloride*, unstable, yellow needles, darkens at 130°, and is not melted at 250°, whilst the *gold* salt softens at 122° and has m. p. 135° (decomp.). The *picrate* blackens below 200° and has m. p. 215°. Oxidation with alkaline permanganate converts 2-methylquinoxaline into 2-*methylpyrazine*-5 : 6-*dicarboxylic acid*,

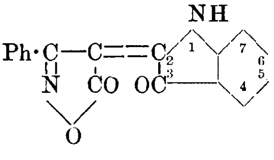
$$\begin{matrix}CMe\cdot N:C\cdot CO_2H\\ \| \qquad\quad |\\ CH-N:C\cdot CO_2H\end{matrix},$$

which, after purification through the *calcium* and *barium* salts, has m. p. 196°. The *copper* salt, $C_7H_4O_4N_2Cu,H_2O$, pale blue needles which decompose below the m. p., and the *silver* salt, $C_7H_4O_4N_2Ag_2$, were analysed.

2 : 3-Dimethylquinoxaline (compare Gabriel and Sonn, *loc. cit.*) crystallises with $2H_2O$. 2 : 3-Dimethylpyrazine-5 : 6-dicarboxylic acid, after purification by means of the barium salt, has m. p. 190°, instead of 200° as previously recorded. When treated with methyl alcohol and hydrogen chloride, it yields an oily *methyl* ester, which is also prepared by the action of methyl iodide on the silver salt. The *diamide*, needles, m. p. 227°, is obtained by the action of methyl alcoholic ammonia on the ester. H. W.

Indigoid Derivatives of Phenyl*iso*oxazolone. ANDRÉ MEYER (*Bull. Soc. chim.*, 1913, [iv], **13**, 992—1000).—The author has prepared a number of indigoid derivatives from phenyl*iso*oxazolone or its substituted derivatives as follows. Phenyl*iso*oxazole-2-indole,

prepared by heating indoxylic acid with dibromophenyl*iso*oxazolone in acetic acid in the presence of sodium acetate, crystallises from glacial acetic acid in red needles (compare Wahl, A., 1909, i, 261). In order to study the effect of substitution on the colour and properties of this indigoid dye, the author has prepared the following derivatives by the condensation of substituted isatin chlorides with phenyl*iso*oxazolone, which gives substances with the general constitution (annexed formula).



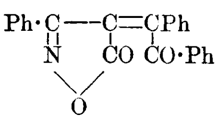
*Phenyl*iso*oxazole*-5-*bromo*-2-*indole* crystallises from acetic acid in deep, reddish-brown needles, its properties being closely allied to those of the non-halogenated indigoid dye.

*Phenyl*iso*oxazole*-5 : 7-*dibromo*-2-*indole* crystallises in red plates, its colour being brighter and its solubility in organic solvents much greater than that of the two preceding compounds.

*Phenyl*iso*oxazole*-2-*nitroindole*, scarlet-red needles, m. p. 220°, gives an eosin-red solution in concentrated sulphuric acid.

β-Naphthisatin chloride reacts similarly with phenyl*iso*oxazolone, giving *phenyl*iso*oxazole*-2-β-*naphthindole*, crystallising from ethylene bromide in brown needles.

Oxythionaphthen reacts with dibromophenyl*iso*oxazolone in acetic acid solution, yielding *phenyl*iso*oxazole*-2-*thionaphthen*, crystallising in scarlet red needles, giving a greenish coloration with sulphuric acid and a deep red precipitate from benzene solution with stannic chloride.



Phenyl*iso*oxazolone, unlike other heterocyclic compounds, such as indoxyl and oxythionaphthen, does not condense with cyclic ketones to give any well-defined products, but with benzil in alcoholic solution in the presence of piperidine the author has succeeded in preparing *phenyl*iso*oxazoledibenzil* (annexed formula), yellow needles, m. p. 208°. W. G.

3 : 6-Diaminoacridine. Relationships between Acridine Derivatives and Analogous Phenazine Compounds. EUGÈNE GRANDMOUGIN and K. SMIROUS (*Ber.*, 1913, **46**, 3425—3434).—In view of the similarity in the structure of 3 : 6-diaminoacridine (Benda, A., 1912, i, 651) and 3 : 6-diaminophenazine, the authors have undertaken a comparison of the behaviour of these two compounds and their derivatives, the present paper dealing particularly with the salt-formation and diazotisation of the first-mentioned compound. The salts of 3 : 6-diaminoacridine with one equivalent of acid are quite stable, whilst those with two or three equivalents are readily hydrolysed by water.

Addition of alkali to a concentrated solution of 3 : 6-diamino-10-methylacridinium chloride (trypaflavine of Ehrlich and Benda this vol., i, 904) precipitates the orange-yellow *imine base*,

$$NH_2\cdot C_6H_3 <\substack{-CH-\\ NMe} > C_6H_3 : NH,$$

ethereal solutions of which, when shaken with water, yield the *ammonium base*, $NH_2\cdot C_6H_3<\overset{\text{———CH}}{\text{NMe(OH)}}>C_6H_3\cdot NH_2$, the latter being converted by heating with water into the *carbinol base*,

$$NH_2\cdot C_6H_3<\begin{matrix}CH(OH)\\NMe——\end{matrix}>C_6H_3\cdot NH_2.$$

On diazotisation, 3 : 6-diaminoacridine yields a violet monodiazo-compound, which on account of its colour is considered to have a *p*-quinonoid structure: $NH{:}C_6H_3<\begin{matrix}CH\\NH\end{matrix}>C_6H_3\cdot N_2Cl$.

The diazo-compound combines with resorcinol, β-naphthol, and R-salt to form reddish-brown to reddish-violet *azo-dyes*, and is reduced by alcohol to 3-*aminoacridine*, m. p. 170°, which is orange-yellow in colour, yields yellow aqueous solution having a green fluorescence, and can be further diazotised and reduced to acridine.

On treatment with potassium iodide, the monodiazo-compound yields 3-*iodo*-6-*aminoacridine*, orange crystals, m. p. 230° (decomp.).

Diazotisation with excess of sodium nitrite in concentrated sulphuric acid solution yields a bisdiazo-compound, which, with potassium iodide, gives rise to 3 : 6-*di-iodoacridine*. This forms dark brown crystals of a metallic lustre, m. p. 270° (decomp.), and, when methylated by means of methyl sulphate in nitrobenzene solution and subsequently treated with potassium iodide, is converted into an orange-yellow, crystalline 3 : 6-*di-iodo*-10-*methylacridinium iodide*.

The *dihydrochloride* of 3 : 6-diaminoacridine, prepared by the addition of concentrated hydrochloric acid to an alcoholic solution of the monohydrochloride, crystallises in orange-yellow needles.

The *trihydrobromide*, obtained from the free base and alcoholic hydrogen bromide, forms orange crystals. The *monohydrochloride* of 3 : 6-diacetylaminoacridine forms slender, yellow crystals.

3 : 6-*Diamino*-10-*methylacridinium dihydrochloride*, prepared by the action of methyl sulphate on 3 : 6-diacetylaminoacridine in nitrobenzene solution, and subsequent hydrolysis of the resulting brownish-yellow *methosulphate* by means of hydrochloric acid, forms dark brownish-red crystals of a metallic lustre, and when warmed readily loses hydrogen chloride with the formation of the monohydrochloride.

3 : 6-*Diamino*-10-*methylacridinium bromide* forms Bordeaux-red leaflets of a metallic lustre, the *iodide*, orange needles, and the *nitrate*, reddish-brown needles.

The diazotisation of safranine has also been studied. According to Kehrmann, Havas, and Grandmougin (this vol., i, 1241), the green safranine salts formed by the combination of one molecule of the base with three equivalents of acid, consist of a mixture of the yellow *o*-quinonoid salt I and the blue *p*-quinonoid salt II:

$$\text{(I.)}\quad NH_3X\cdot C_6H_3<\!\!\!<\begin{matrix}N——\\NPhX\end{matrix}>C_6H_3\cdot NH_3X$$

$$\text{(II.)}\quad NH_3X\cdot C_6H_3<\begin{matrix}——N\\NPhX\end{matrix}>\!\!\!>C_6H_3{:}NH,HX.$$

Of these two salts only the *o*-quinonoid form should be capable of complete diazotisation.

This view has been confirmed by the behaviour of phenosafranine, which on treatment with solid sodium nitrite in concentrated sulphuric acid solution is partly converted into a bisdiazo-compound. If the solution is kept, the *p*-quinonoid salt II is slowly transformed into the *o*-quinonoid form and then undergoes complete diazotisation.

Reduction of the resulting solution by means of alcohol yields the phenylphenazonium of Kehrmann (A., 1897, i, 107). F. B.

The Degradation of Allantoin to Hydroxonic Acid, and a New Synthesis of Allantoin. HEINRICH BILTZ and ERHARD GIESLER (*Ber.*, 1913, **46**, 3410—3425).—Allantoin, prepared from uric acid by oxidation with alkaline potassium permanganate solution, was further oxidised to potassium allantoxanate; by treating this in aqueous solution with slightly less than the calculated amount of *N*-sulphuric acid, more than 90% of the theoretical quantity of allantoxaidin (from decomposition of the unisolable allantoxanic acid,

$$\begin{matrix}\mathrm{CO{\cdot}NH} \\ | \\ \mathrm{NH{-}CO}\end{matrix}\!\!>\!\mathrm{C{:}N{\cdot}CO_2H}),$$

was obtainable (compare Ponomarev, A., 1879, 226, 228, 461); the allantoxaidin, $\mathrm{CO}\!<\!\begin{matrix}\mathrm{NH{\cdot}C{:}NH} \\ | \\ \mathrm{NH{\cdot}CO}\end{matrix}$, was obtained in short prisms containing $1H_2O$, and of m. p. 282° (decomp.); its aqueous solution on heating yields biuret and formic acid, and a similar decomposition ensues on heating the substance with acetic anhydride, the product being *formylacetylbiuret*, probably $CHO{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NHAc$, leaflets, m. p. 184—185°.

The reduction of potassium allantoxanate by sodium amalgam and water (compare Ponomarev, *loc. cit.*) gave rise to the product described by Ponomarev as hydroxonic acid, $C_8H_{10}O_7N_6$, but when this was purified by means of the ester, it was found to be of the composition $C_4H_5O_4N_3$, that is, *dihydroallantoxanic acid*,

$$\begin{matrix}\mathrm{CO{\cdot}NH} \\ | \\ \mathrm{NH{-}CO}\end{matrix}\!\!>\!\mathrm{CH{\cdot}NH{\cdot}CO_2H};$$

potassium salt, rectangular prisms, rapid decomp. near 333°; *ammonium* salt, colourless needles, unfused even at 340; *silver* salt with $1H_2O$; *methyl* ester, leaflets, m. p. 275° (decomp.); *ethyl* ester, rectangular tablets, m. p. 277° (decomp.).

The above results indicate that allantoin is the amide of dihydroallantoxanic acid, but it was not found possible to convert the esters of the latter substance into allantoin, nor was it possible to obtain allantoxanic acid directly from allantoin, but the existence of the relationship could be demonstrated in the following manner.

When hydroxonic acid is boiled with acetic anhydride for eight hours, it undergoes loss of carbon dioxide with formation of 1 : 3 : 6-*triacetyl*-5-*aminohydantoin*, $\begin{matrix}\mathrm{CO{\cdot}NAc} \\ | \\ \mathrm{NAc{-}CO}\end{matrix}\!\!>\!\mathrm{CH{\cdot}NHAc}$, tablets from acetone or prisms from benzene, m. p. 184—185°; this substance when boiled with alcohol gives leaflets, m. p. 240—241°, of 1 : 6-*diacetyl*-5-*aminohydantoin*, which on evaporation with concentrated hydrochloric acid is converted into 5-*aminohydantoin hydrochloride*, m. p. 218—222°

(decomp.); the free base, of which the *platinichloride* was also prepared, could not be isolated; the action of silver oxide on the hydrochloride produced insoluble 3-*silver-5-aminohydantoin.* Allantoin itself was obtainable from the hydrochloride of the aminohydantoin by treatment with potassium cyanate in aqueous solution. D. F. T.

Ring Formation between the Nitro- and Amino-groups with Production of Triazines. FRITZ ARNDT (*Ber.*, 1913, **46**, 3522—3530).—The preparation and properties of a number of triazines are described which are obtained from *o-nitrophenylguanidine* and *o*-nitrophenylcarbamide by loss of water under the influence of sodium or potassium hydroxide. Since neither sodium carbonate, ammonia nor acids bring about this change, it seems probable that ring formation is preceded by formation of the alkali salt of the ψ-nitro-form. This is the more likely, since the originally orange-yellow solution becomes red when warmed with alkali, and then yields a yellow precipitate. After ring formation, the reverse change immediately occurs, since the product obtained does not possess the properties of an *o*-quinone.

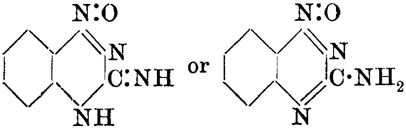
If Angeli's formula for the azoxy-group (this vol., i, 658) is adopted, the compounds obtained by the author may be regarded as containing this group in the triazine ring, and it therefore seems to be produced with remarkable ease by loss of water from an amino- and nitro-group, when ring formation can simultaneously occur.

o-Nitrophenylguanidine nitrate, pale yellow prisms, m. p. 160°, is obtained by the addition of 2*N*-nitric acid to the product of the action of concentrated hydrochloric acid on a mixture of *o*-nitroaniline and cyanamide. Should the latter contain dicyanamide, the white, amorphous *nitrate* of a condensation product of cyanamide and dicyanamide is also formed. *o*-Nitrophenylguanidine,

$$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}C(:NH){\cdot}NH_2,$$

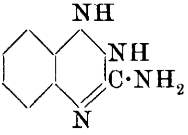
separates as a viscous oil when the finely powdered nitrate is treated with cold 2*N*-sodium hydroxide. It separates from its aqueous solution in orange-yellow needles which contain $1H_2O$, m. p. 53°.

Aminophenotriazoxine [3-*amino*-1 : 2 : 4-*benzotriazine* 1-*oxide*] (annexed formula), shining leaflets, m. p. 269°, is obtained in almost quantitative yield by the action of boiling sodium hydroxide solution on *o*-nitrophenylguanidine or on the crude reaction mixture obtained from *o*-nitroaniline, cyanamide and hydrochloric acid. The *hydrochloride, sulphate,* and *nitrate* were examined. The *silver* salt, $C_7H_5ON_4Ag$, was analysed.



Sodium nitrite and hydrochloric acid convert 3-amino-1 : 2 : 4-benzotriazine oxide directly into 3-*hydroxy*-1 : 2 : 4-*benzotriazine* 1-*oxide*, yellow leaflets, m. p. 219° (decomp.).

Aminobenzotriazine oxide is readily reduced by tin and hydrochloric acid; when 2*N*-nitric acid is added to the reaction product, 3-*amino*-



dihydro-1 : 2 : 4-*benzotriazine nitrate*, m. p. 195—197° (decomp.), is obtained. When an aqueous solution of this salt is treated with sodium carbonate, the free *base* (annexed formula) separates in white leaflets which rapidly become oxidised with formation of 3-*amino*-1 : 2 : 4-*benzotriazine*, yellow needles, m. p. 207°. The latter substance is best obtained by the action of potassium ferricyanide and sodium hydroxide on a solution of dihydroaminophentriazine nitrate.

For the preparation of o-*nitrophenylcyanamide*, $NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}CN$, an intimate mixture of *o*-nitroaniline hydrochloride and lead thiocyanate is allowed to remain at the ordinary temperature until a portion does not melt when placed in boiling water ; the mixture is then heated for six to seven hours on the water-bath, and subsequently boiled with 2*N*-sodium hydroxide ; after removal of lead sulphide, the solution is cooled, filtered from unchanged *o*-nitroaniline, and cautiously acidified with hydrochloric acid, when *o*-nitrophenylcyanamide, pale yellow needles, m. p. 152°, separates in poor yield. Boiling dilute hydrochloric acid transforms it into *o*-nitrophenylcarbamide, yellow needles, m. p. 183—184° (Schwartz [A., 1897, i, 411] gives 181°), which is converted by boiling potassium hydroxide into hydroxybenzotriazine oxide, identical with the product obtained from aminobenzotriazine oxide.

Attempts to prepare *o*-nitrophenylthiocarbamide were unsuccessful.

H. W.

A Mode of Decomposition of Halogenated Alkyl Derivatives of Hexamethylenetetramine. MARCEL SOMMELET (*Compt. rend.*, 1913, **157**, 852—854. Compare Hock, A., 1903, i, 465).—Derivatives of hexamethylenetetramine of the type $C_6H_{12}N_4RX$, where R is an alkyl group and X one of the halogens, are decomposed by boiling with water. This is particularly true of the derivative obtained from benzyl chloride, the products of the decomposition being benzaldehyde (70—80% yield) and a mixture of bases of which the following were characterised : ammonia, methylamine, dimethylamine, trimethylamine, and benzylamine. Benzaldehyde is similarly obtained by boiling benzyl chloride and hexamethylenetetramine together in aqueous alcoholic solution.

The three xylyl bromides combine directly with hexamethylenetetramine in chloroform solution to give the additive *compounds*, $C_6H_{12}N_4Br{\cdot}CH_2{\cdot}C_6H_4Me$, having melting points respectively, *ortho*, 198° ; *meta*, 215° ; *para*, 216°. Each of these are similarly decomposed by boiling with water, giving the corresponding tolualdehydes.

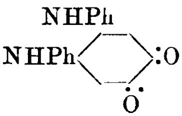
The course of this decomposition reaction is not yet clear, but the relatively abundant production of methylamine points to the possible primary production of benzylmethyleneamine, which undergoes isomerisation to benzylidenemethylamine :

$$CH_2Ph{\cdot}N{:}CH_2 \longrightarrow CHPh{:}NMe.$$

W. G.

Anilinoquinones and their Azine Derivatives. FRIEDRICH KEHRMANN and MARCELIEN CORDONE (*Ber.*, 1913, **46**, 3009—3014).—The authors have convinced themselves of the correctness of Willstätter's view as to the holoquinonoid nature of both modifications of *o*-benzoquinone, but believe that these merely represent dimorphous forms of the same substance. *o*-Benzoquinone is said to present an example of dichroism, on account of which the different crystalline forms appear to be of different colours; the less stable form is stated to be not colourless but green. Both forms of the substance are, therefore, of diketonic structure.

If catechol is oxidised in the presence of aniline by silver acetate in solution in cold acetic acid, a brown mixture of 4 : 5-*dianilino*-o-*benzoquinone* (annexed formula), brownish-red needles, m. p. 193°, with a little of the trianilino-compound separates; the former is easily extracted by sodium hydroxide, in which it is soluble.



When equimolecular quantities of the above dianilinobenzoquinone and *o*-phenylenediamine hydrochloride are heated together in concentrated solution in alcohol, condensation occurs to 2 : 3-*dianilinophenazine*,

$$C_6H_2(NHPh)_2 \ll\!\begin{smallmatrix}N\\N\end{smallmatrix}\!> C_6H_4,$$

orange-yellow, apparently rhombohedral crystals, m. p. 218—219°, which separate from alcohol with one C_2H_6O; the *hydrochloride*, which is the primary product, forms long, deep red needles.

A similar condensation could be effected between the dianilino-*o*-benzoquinone and phenyl-*o*-phenylenediamine hydrochloride, the product being 2 : 3-dianilino-10-phenylphenazonium chloride,

$$C_6H_2(NHPh)_2 \ll\!\begin{smallmatrix}N\\NPhCl\end{smallmatrix}\!> C_6H_4,$$

violet tablets, m. p. 235—237° (compare Fischer and Hepp, A., 1896, i, 50).

Under similar conditions to the above, 3-anilino-4-hydroxy-*o*-benzoquinone (Zincke, A., 1885, 787) condenses with *o*-phenylenediamine hydrochloride; producing long, deep red needles of the *hydrochloride* of 2-*anilino*-3-*hydroxyphenazine*; the free base forms brownish-red needles, decomp. above 200°. Condensation with phenyl-*o*-diphenylenediamine gave rise to two products which are probably 3-anilino-2-hydroxy-10-phenylphenazonium chloride and 2-anilino*apo*safranone,

$$C_6H_4 <\!\begin{smallmatrix}N\\NPh\end{smallmatrix}\!> C_6H_2(NHPh)O,$$

The constitution of the above dianilino-*o*-benzoquinone is demonstrated by hydrolysis with dilute solutions of alkali, which gives rise to the *s*-dihydroxyquinone of Nietzki and Schmidt (A., 1888, 1181). Of the three possible isomerides having the composition of a dianilinoquinone, two are already known, so that to this third isomeride is to be ascribed the remaining structure, 4 : 5-dianilino-*o*-benzoquinone.

D. F. T.

Purines. XII. CARL O. JOHNS and EMIL J. BAUMANN (*J. Biol. Chem.*, 1913, **15**, 515—521. Compare this vol., i, 774, 1000).—5-Amino-6-ethylamino-2-hydroxy-4-methylpyrimidine reacts smoothly with the reagents commonly used for the preparation of purines. Thus, when the formyl derivative is heated, *2-oxy-6-methyl-9-ethylpurine*, $\begin{array}{l}\mathrm{N{:}CMe{\cdot}C{-}{-}N}\\ \mathrm{CO{\cdot}NH{\cdot}C{\cdot}NEt}\end{array}\!\!>\mathrm{CH}$, is formed. This crystallises in a net work of silky needles, which begin to melt at 256°, m. p. 275° (decomp.).

Similarly, the corresponding acetyl derivative yields *2-oxy-6 : 8-dimethyl-9-ethylpurine*, which also forms a network of silky needles, m. p. 265° (decomp.) to a dark oil.

2-Oxy-8-thio-6-methyl-9-ethylpurine is formed when the diaminopyrimidine is heated with thiocarbamide; it crystallises in colourless sheaves, decomp. 295—300°. When the components are mixed in hot water, a thiocarbamide additive product of the pyrimidine is obtained; this has m. p. 204—206° (decomp.), and gives the thiopurine when heated.

The thiopurine reacts with monochloroacetic acid, forming *2-oxy-6-methyl-9-ethylpurine-8-thiolacetic acid*,

$$\begin{array}{l}\mathrm{N{:}CMe{\cdot}C{-}{-}N}\\ \mathrm{CO{\cdot}NH{\cdot}C{\cdot}NEt}\end{array}\!\!>\mathrm{CS{\cdot}CH_2{\cdot}CO_2H}.$$

This separates as a bulky mass of needles, which darken at 270°. It is stable in hot water, but boiling with concentrated hydrochloric acid hydrolyses it to 2 : 8-dioxy-6-methyl-9-ethylpurine.

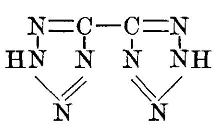
The action of thiophosphoryl chloride on 4 : 5-diamino-6-hydroxy-2-methylthiolpyrimidine converts it into *6-oxy-8-thio-2-methylthiolpurine*, $\begin{array}{l}\mathrm{NH{\cdot}CO{\cdot}C{\cdot}NH}\\ \mathrm{SMe{\cdot}C{-}N{-}C{\cdot}NH}\end{array}\!\!>\mathrm{CS}$. This separates in small globules, which begin to decompose at 275°, and give the murexide test. E. F. A.

Purines. XIII. 2 : 8-Dioxy-1 : 6-dimethyl-1 : 2 : 8 : 9-tetrahydropurine and 5-Nitro-3 : 4-dimethyl-1 : 2 : 3 : 6-tetrahydropyrimid-2 : 6-dione (α-Nitrodimethyluracil). CARL O. JOHNS and EMIL J. BAUMANN (*J. Biol. Chem.*, 1913, **16**, 135—142).—Methyl sulphate and an aqueous solution of the sodium salt of 5-nitro-6-amino-4-methyl-2 : 3-dihydro-2-pyrimidone react at the ordinary temperature to form, in 80% yield, *5-nitro-6-amino-3 : 4-dimethyl-2 : 3-dihydro-2-pyrimidone*, $\mathrm{CO}<\!\!\begin{array}{l}\mathrm{N{:}C(NH_2)}\\ \mathrm{NMe{\cdot}CMe}\end{array}\!\!>\mathrm{C{\cdot}NO_2}$, decomp. 170—195°, prisms containing $\frac{1}{2}H_2O$. The position of the new methyl group is established as follows. By heating with 25% sulphuric acid at 160°, the substance is converted into *5-nitro-3 : 4-dimethyl-1 : 2 : 3 : 6-tetrahydropyrimid-2 : 6-dione*, $\mathrm{CO}<\!\!\begin{array}{l}\mathrm{NH{-}{-}CO}\\ \mathrm{NMe{\cdot}CMe}\end{array}\!\!>\mathrm{C{\cdot}NO_2}$, m. p. 191°, slender prisms (the only other possible 5-nitrodimethyl-1 : 2 : 3 : 6-tetrahydropyrimid-2 : 6-dione is Lehmann's 5-nitro-1 : 4-dimethyl-1 : 2 : 3 : 6-tetrahydropyrimid-2 : 6-dione, m. p. 149°), which is oxidised by nitric acid, D 1·5, and concentrated sulphuric acid on the water-bath to 5-nitro-3-methyl-1 : 2 : 3 : 6-tetrahydropyrimid-2 : 6-dione-4-carboxylic acid, which cannot be

isolated, since it loses carbon dioxide and changes to Behrend's 5-nitro-3-methyl-1 : 2 : 3 : 6-tetrahydropyrimid-2 : 6-dione, m. p. 255°.

The reduction of 5-nitro-6-amino-3 : 4-dimethyl-2 : 3-dihydro-2-pyrimidone by aqueous ammonia and ferrous sulphate produces 5 : 6-*diamino*-3 : 4-*dimethyl*-2 : 3-*dihydro*-2-*pyrimidone*, $C_6H_{10}ON_4$, decomp. about 230°, colourless plates, in 40% yield; the latter and an equal weight of carbamide at 170—180° produce 2 : 8-*dioxy*-1 : 6-*dimethyl*-1 : 2 : 8 : 9-*tetrahydropurine*, $\begin{array}{l}\text{NMe·CMe:C·NH}\\ \text{CO—N}=\!=\text{C·NH}\end{array}\!\!>\!\text{CO}$, decomp. 260—265°, prisms containing H_2O; by evaporating the latter with nitric acid and treating the yellow residue with an alkali, a rose coloration is developed. C. S.

Bistetrazole and Isomeric Derivatives of Tetrazole. E. Oliveri-Mandalà and T. Passalacqua (*Gazzetta*, 1913, **43**, ii, 465—474. Compare A., 1912, i, 144).—When cyanotetrazole (*loc. cit.*) is further acted on with azoimide, or when cyanogen is passed into an aqueous solution of azoimide as in the experiment formerly described, but using a more concentrated solution, bistetrazole and the amide of tetrazolecarboxylic acid are produced in addition to cyanotetrazole, which still forms the chief product of the reaction. Saponification of the cyanotetrazole yields (by way of the unstable carboxylic acid) tetrazole, and this is the best way of preparing this substance. The preparation is conveniently carried out by heating the sodium salt described below with hydrochloric acid, evaporating to dryness, and extracting the tetrazole with warm acetone. *Bistetrazole* (annexed formula) forms prismatic crystals, m. p. 254—255° (decomp.). Bistetrazole and especially its *silver* salt are explosive. The substance has about the calculated molecular weight in freezing water. The *barium* salt, $C_2N_8Ba,3H_2O$, was prepared. Bistetrazole is decomposed by warm, concentrated sulphuric acid according to equation: $C_2H_2N_8 + 2H_2O + O_2 = 3N_2 + 2CO_2 + 2NH_3$, so that the sulphuric acid acts as an oxidiser.



The above-mentioned *tetrazole*-5-*carboxylamide*, $C_2H_3ON_5$, has m. p. 234° (decomp.). *Sodium* 2-*sodiotetrazole*-5-*carboxylate*, $C_2O_2N_4Na_2$, is obtained by saponification of the amide or of the cyanotetrazole. The *barium* salt has the composition $C_2N_4O_2Ba,3\frac{1}{2}H_2O$.

5-*Cyano*-2-*methyltetrazole*, $C_3H_3N_2$, b. p. 100—102°/16 mm., is obtained by boiling the silver salt of 5-cyanotetrazole with an ethereal solution of methyl iodide. When it is saponified with alcoholic sodium hydroxide, the *sodium* salt of the corresponding acid, $C_3H_3O_2N_4Na$, is produced, and from this the free 2-*methyltetrazole*-5-*carboxylic acid*, $C_3H_4O_2N_4$ (prisms, m. p. 204—205°, losing CO_2), can be prepared. When this acid is heated at its m. p., 2-*methyltetrazole*, $C_2H_4N_4$, b. p. 145—147°/759 mm., is obtained.

When the silver salt of tetrazole and ethyl iodide are heated in benzene solution for some hours, 2-ethyltetrazole and 1-ethyltetrazole are produced. 2-*Ethyltetrazole*, $C_3H_6N_4$, has b. p. 70—71°/35 mm., or

152—155° at ordinary pressure. 1-*Ethyltetrazole*, $C_3H_6N_4$, has b. p. 162—164°/30 mm. R. V. S.

The Hydrolytic Constants of Some Derivatives of Tetrazole. E. OLIVERI-MANDALÀ (*Gazzetta*, 1913, **43**, ii, 487—493. Compare preceding abstract).—Measurements of the catalysis of methyl acetate give the following values for the constants of hydrolysis: 2-methyltetrazole, 0·00026; 1-methyltetrazole, 0·000047; 2-ethyltetrazole, 0·00049; 1-ethyltetrazole, 0·00014. R. V. S.

Action of Nitrogen Peroxide on Aliphatic Diazo-compounds and on Tetrazens. HEINRICH WIELAND and CURT REISENEGGER (*Annalen*, 1913, **401**, 244—251).—Ethyl diazoacetate and nitrogen peroxide react in cold benzene to form ethyl dinitroacetate and nitrogen, ethyl furoxandicarboxylate being obtained as a by-product. Similarly, at the ordinary temperature, nitrogen peroxide and diazodeoxybenzoin yield ωω-dinitrotoluene, probably by the decomposition of the initially formed benzoyl derivative.

Nitrogen peroxide and diphenyleneazomethylene (Staudinger and Kupfer, A., 1911, i, 751) react in cold benzene in the absence of moisture to form nitrogen and 9 : 9-*dinitrofluorene*, $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>C(NO_2)_2$, m. p. 128° (decomp.), colourless needles, which yields fluorenone above its m. p.

Nitrogen peroxide and tetraphenyltetrazen in cold benzene yield a deep green solution of an additive compound, which decomposes at the ordinary temperature with the formation of pp′-*dinitrotetraphenyltetrazen*, $NO_2\cdot C_6H_4\cdot NPh\cdot N:N\cdot NPh\cdot C_6H_4\cdot NO_2$, decomp. 160°, orange-yellow crystals.

The substance is proved to be a tetrazen by the liberation of nitrogen and the production of an intensely blue solution by treatment with concentrated sulphuric acid; the positions of the nitro-groups are proved by reduction, whereby ammonia and *p*-aminodiphenylamine (2 mols.) are produced. In a similar reaction, nitrogen peroxide and diphenyldiethyltetrazen yield *di*-p-*nitrophenyldiethyltetrazen*, $C_{16}H_{18}O_4N_6$, orange-red needles, which is converted into *p*-phenylene-ethyldiamine by reduction. C. S.

The Real Nature of the So-called Artificial Globulin. HUBERT W. BYWATERS and D. G. C. TASKER (*J. Physiol.*, 1913, **47**, 149—158).—Several observers have stated that on keeping, the serum albumin in blood and urine is converted into globulin. The artificial product when analysed is found not to be identical with the natural globulin, but it is really alkaline meta-protein. W. D. H.

Colloidal Properties of Hæmoglobin. Modifications of the Viscosity and Surface Tension of Suspensions of Methæmoglobin by the Action of Hydrochloric Acid or Sodium Hydroxide. II. FILIPPO BOTTAZZI (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 263—270).—The viscosity and surface tension of aqueous suspensions of methæmoglobin (compare this vol., i, 1249), previously

purified by dialysis for four months or longer, differ little from those of distilled water. When the methæmoglobin is brought into solution by means of hydrochloric acid or sodium hydroxide, increased viscosity and diminished surface tension are shown by the liquid, which is at first a suspension solution and finally yields a perfect solution. Continued addition of acid or alkali does not lower the surface tension beyond a certain value, which seems to be independent of the concentration of the dissolved methæmoglobin so long as this lies within certain limits; neutralisation of the acid (alkali) with an equal volume of alkali (acid) causes precipitation of the methæmoglobin and increase of the surface tension.

The increased velocity caused by hydrochloric acid diminishes considerably when excess of acid is added, and tends to return to its original value, although no precipitation occurs. This seems to be due to the influence of the acid in lowering the dissociation of the methæmoglobin chloride, and hence the concentration of the methæmoglobin ions, on which the increased viscosity depends.

Addition of sodium chloride to solution of sodium methæmoglobinate produces a further small, constant diminution in the surface tension, although the salt has no appreciable effect on a solution of pure methæmoglobin (compare Bottazzi and d'Agostino, this vol., ii, 115).

T. H. P.

Action of Quinones on Wool and Other Protein Substances. LOUIS MEUNIER (*Zeitsch. angew. Chem.*, 1913, **26**, 616).—The results described by Scharvin (this vol., i, 661) have already been published by Meunier and incorporated in certain patents (compare A., 1908, i, 586, and D.R.-P. 240512). J. C. W.

Products of Hydrolysis of Thynnine and Percine. ALBRECHT KOSSEL and F. EDLBACHER (*Zeitsch. physiol. Chem.*, 1913, **88**, 186—189).—Thynnine yields an aminovaleric acid, proline, and tyrosine on hydrolysis. The same acids were obtained from percine. Acids of the C_5-series play the chief part in the constitution of the protamines, C_6-acids being only occasionally present. The latter play the more important part in the higher proteins. E. F. A.

The Stability of Invertase. CARL NEUBERG (*Biochem. Zeitsch.*, 1913, **56**, 495—497).—The invertase was found to be still intact in an expressed yeast juice which had been allowed to autolyse for 470 days. S. B. S.

Amylases. VI. A Comparison of Amyloclastic and Saccharogenic Powers. HENRY C. SHERMAN and M. D. SCHLESINGER (*J. Amer. Chem. Soc.*, 1913, **35**, 1784—1790).—In the investigation of the action of amylase on starch, the amount of reducing sugar produced is not always proportional to the amount of starch apparently digested.

The authors find that with specimens of pancreatic amylase the amount of starch apparently digested (amyloclastic power) is about twice the amount of maltose produced (saccharogenic power), whilst

with malt amylase the ratio of maltose formed to starch apparently digested is much higher; indeed, with some specimens of the latter, the amount of maltose exceeds the quantity of starch apparently digested. The application of the starch-iodine coloration is therefore evidently not well adapted for the measurement of the starch-digesting power of malt amylase. D. F. T.

Amylases. VII. The Forms of Nitrogen in Amylase Preparations from the Pancreas and from Malt, as Shown by the Van Slyke Method. HENRY C. SHERMAN and A. O. GETTLER (*J. Amer. Chem. Soc.*, 1913, **35**, 1790—1794).—Analysis has been made of various specimens of pancreatic and malt amylase by the Van Slyke method, and the results as to the nature and relative quantity of the hydrolytic products indicate that the amylase preparations used were essentially protein substances. All the eight forms of nitrogen recognisable by the Van Slyke method were present, the proportions being within the range of variation shown by typical protein substances. D. F. T.

The Partial Purification of the Esterase from Pig's Liver. GEORGE PEIRCE (*J. Biol. Chem.*, 1913, **16**, 1—3).—Pig's liver was ground up, strained, and water added, incubated at 37° for one day, and, after remaining several weeks at room temperature, was filtered. This crude enzyme solution was dialysed and filtered; dialysis removed about 90% of the solids, and the solution lost about 20% of its activity. Ammonium sulphate was then added nearly to half saturation and the liquid filtered. The precipitate was inactive. The filtrate was then fully saturated with the same salt, and filtered; the filtrate was inactive. The precipitate was then dissolved in water and dialysed until free from sulphate. This represents the most highly purified solution obtained; it was very active; no attempt was made to obtain a solid from it. W. D. H.

The Compound Formed between Esterase and Sodium Fluoride. GEORGE PEIRCE (*J. Biol. Chem.*, 1913, **16**, 5—18).—The compound formed between esterase (from pig's liver) and sodium fluoride has little if any action on ethyl butyrate. The formation of this compound is reversible. When the concentration of the fluoride is varied from 0·009 to 0·27 mg. per litre, the inhibition increases from 20 to 88%. The inhibiting effect hardly varies at all with the concentration of the enzyme. The conclusion is drawn that one molecule of the inactive compound contains 1 molecule of enzyme and 1 molecule of sodium fluoride. W. D. H.

The Stability of Carboxylase. CARL NEUBERG (*Biochem. Zeitsch.*, 1913, **56**, 497—498).—In a maceration juice prepared from an old dried yeast obtained by Lebedev's method, the carboxylase was found to be active when the zymase was no longer existent. The former ferment appears, therefore, to be the more stable. S. B. S.

Mercury Naphthalene Derivatives. JOHANNES GADAMER [with R. BRIEGER and WERNER SCHULEMANN] (*Zeitsch. angew. Chem.*, 1913, **26**, 627—631).—A lecture delivered before the Verein deut. Chemiker

at Breslau. Some mercury compounds of substituted naphthalenes are discussed, and it is shown how their unusual behaviour and inconstant composition may be explained by considering the residual affinities of the atoms and groups involved.

When the sodium salt of 8-amino-1-naphthol-3 : 5-disulphonic acid (*K*-acid) is digested with mercuric acetate, a bright red mercuriated substance is obtained. From its method of formation and its colour, it might be expected that the mercury is attached to a carbon atom, but the fact that ammonium sulphide causes precipitation of mercuric sulphide suggests that the metal is linked with nitrogen. The colour was destroyed by the addition of alkali or sodium chloride, but was reproduced on acidifying with a mineral acid. The varying mercury-content of the product suggested that not a chemical, but rather an adsorption, compound was present, but the fact that salt or strong acetic acid decolorised solutions of the substance is not in harmony with this view.

The influence of various substituents in the naphthalene nucleus was studied, and the following conclusions are drawn: the presence of $-OH$ or $-NH_2$ in the β-position hinders the fixation of mercury, only one atom of which enters the ortho-position; the presence of $-OH$ or $-NH_2$ in the α-position permits of the entry of two mercury atoms in the ortho- and para-positions, giving compounds which are stable towards ammonium sulphide, but tend to form unstable, coloured quinonoid compounds in the presence of reagents which reduce the acidity of their solutions; when attempts are made to introduce more mercury into naphthol derivatives, alkali is found to remove the excess of mercury as the hydrosol of the hydroxide, but the naphthylamines can loosely fix more mercury, giving substances which are turned deep red by alkalis and decomposed by ammonium sulphide; sulphonic acid groups render the mercury compounds more unstable.

In *K*-acid, the various effects indicated above are cumulative. These effects are discussed on theoretical grounds, and it is explained why these naphthalene derivatives can form compounds with indefinite quantities of mercury, in which there is no distinction between true chemical combination and adsorption. J. C. W.

Physiological Chemistry

Water in Expired Air. WILLIAM OSBORNE (*Proc. physiol. Soc.*, 1913, xii; *J. Physiol.*, **47**).—Galeotti states that the expired air is not fully saturated with aqueous vapour, but only about three-quarters saturated. Loewy and Gerhartz point out that this is incorrect, for the temperature of expired air is not 37°, but between 32·5° and 33·5°. The present experiments confirm the latter view, and the correct theoretical figures were obtained if the

temperature is assumed to be 33·9°. The experiments were made on men in whom loss of water by the skin was prevented by a rubber suit. Such experiments are only safe in winter, as a dangerous fever may arise if the external air is too warm.

W. D. H.

Acidosis. ERNEST L. KENNAWAY, MARCUS S. PEMBREY, and EDWARD P. POULTON (*Proc. physiol. Soc.*, 1913, x—xi; *J. Physiol.*, **47**).—In healthy men the value of the alveolar carbon dioxide pressure may fall below the normal (40 mm.) if carbohydrate food is withheld; in diabetes it may be normal; the determining factor is the extent of acidosis. It falls suddenly one or two days before the onset of fatal coma; a value of 25 is grave; one of 20 means that coma is imminent. Estimation of the acetone substances is not such a good guide, and suggestions are put forward to explain variations in the ratio between these substances. Their equilibrium point is probably connected with the degree of acidosis, and the high proportion of β-hydroxybutyric acid in marked cases may be due to a washing out of acetone from the blood by the increased pulmonary ventilation.

W. D. H.

The Carbon Dioxide and Oxygen Content of the Blood after Clamping the Abdominal Aorta and Inferior Vena Cava Below the Diaphragm. JOHN R. MURLIN, LEO EDELMANN, and B. KRAMER (*J. Biol. Chem.*, 1913, **16**, 79—101).—The changes found are consistent with the mechanical explanation of the altered respiratory quotient after clamping the vessels. When the quotient rose, the carbon dioxide of the blood fell; when it remained stationary, the carbon dioxide did not change; when it fell, the carbon dioxide rose. Clamping off the blood from the abdominal organs therefore does not alter the character of the metabolism.

W. D. H.

The Dissociation of Carbon Dioxide from Human Blood. JOHANNE CHRISTIANSEN, CLAUDE G. DOUGLAS, and JOHN S. HALDANE (*Proc. physiol. Soc.*, 1913, ii; *J. Physiol.*, **47**).—The experiments here briefly referred to show that the effect of oxygen on the carbon dioxide-carrying power of the blood is even more important than the well-known effect of carbon dioxide on its oxygen-carrying functions.

W. D. H.

The Combination of Hydrogen Arsenide in the Blood. RICHARD MEISSNER (*Chem. Zentr.*, 1913, ii. 705—706; from *Zeitsch. expt. Path. Ther.*, 1913, **13**, 284—300).—The absorption capacity of the various constituents of blood for the gas was estimated by Reckleben and Lockemann's method. All solutions or suspensions were shaken for the same period with the same amount of the arsenic compound. The various lipoids in suspension or in ether and chloroform solution have practically no combining capacity in quantities in which they occur in the blood. Even the brain can combine with no more hydrogen arsenide than can physiological

saline in which it is suspended. Of the other constituents, hæmatin possesses a marked combining capacity, and blood containing carbon monoxide is less liable to hæmolysis by the arsenic compound than normal blood. The combining capacity of the iron-free hæmatoporphyrin is much smaller than that of hæmatin. It appears that the iron plays some part in the combination of the various iron compounds investigated; only sodium nitroprusside evinced any marked combining capacity, for it yielded with hydrogen arsenide a solid substance containing both iron and arsenic. The antagonistic action of various substances to hydrogen arsenide poisoning was also investigated. Cholesterol and iodipin were without effect. Various colloidal silver and mercury preparations were also tried, but, although they combine with the arsenic compound, they were too toxic to the kidneys for *intra vitam* use. Of the other substances investigated, only cadmium chloride exhibited a high combining capacity. The *in vitro* action of the hydrogen arsenide on blood gives a product with a spectrum similar to thiomethæmoglobin. S. B. S.

The Fermentative Properties of Blood. II. The Peptolytic Ferments of Normal Animals. LUDWIG PINCUSSOHN and HELLMUTH PETOW (*Biochem. Zeitsch.*, 1913, **56**, 319—329).—In continuation of the work of Pincussohn (this vol., i, 788), many examples are given to illustrate the fact that the sera of animals are capable of degrading the peptones prepared (by sulphuric acid method) from the proteins of their own organs, but not from the organs of other animals and foreign proteins. An exception was found in the case of guinea-pig serum, and attention is called to the fact that this serum is used generally for supplying the complement in various hæmolytic systems. Guinea-pig's serum also degrades silk peptone. The serum also degrades peptones prepared from the organ proteins of closely allied species. Thus the serum from the fox also degrades peptones prepared from the organs of dogs, and dog's serum degrades peptones derived from fox tissues, but not from those of any other animals. The method may therefore be applied for determining the relationship of various species.

S. B. S.

Phosphatides of the Stromata of the Red Blood Corpuscles of Sheep and Man. M. BÜRGER and H. BEUMER (*Biochem. Zeitsch.*, 1913, **56**, 446—456).—The stromata of sheep were precipitated by carbon dioxide from the lysed blood and dried. They yielded an ethereal extract, which consisted, to the extent of 70%, of cholesterol The residue, after extraction with ether, was partly soluble in alcohol at 37°. Of the alcoholic extract, part remained insoluble after treatment with ether. This was obtained in the form of a white powder of stearin-like consistency, which swelled on treatment with water, and had m. p. 180—185°. Its analysis indicated a diaminomonophosphatide, similar in its properties to the myelins. Of the ether-soluble portion of the alcoholic extract, the greater part was precipitable by acetone, and of the acetone

precipitate, part was insoluble in hot alcohol, although soluble in ether and chloroform. This was a monophosphatide with the properties of a kephalin. The stromata of sheep's corpuscles contain therefore about 5% cholesterol and 12% phosphatides, of which about half is sphingomyelin, and kephalin is a constituent of the remainder. The blood of normal individuals and of carcinomatous individuals (drawn in the latter case from the cadaver) was examined in a similar manner to that employed in the case of sheep's blood. No essential differences in the chemical composition of the stromata of normal and cancerous individuals could be found, the ethereal extract containing 71·6 and 74% of cholesterol, and the alcoholic extracts 35 and 31% of sphingomyelin. There was isolated, in addition to kephalin, from the acetone precipitate from human blood small quantities of a phosphatide with 3·3% phosphorus and 4·33% nitrogen, which yielded a clear solution in water, but was insoluble in hot alcohol and ether. S. B. S.

Distribution of Ions in the Blood Serum. PETER RONA and PAUL GYÖRGY (*Biochem. Zeitsch.*, 1913, **56**, 416—438).—According to Zuntz and Hamburger, part of the sodium of the serum is non-diffusible, as it is in combination with the proteins. On treatment of the serum with carbon dioxide, part of this sodium should be convertible into sodium hydrogen carbonate. If therefore, serum treated with carbon dioxide is submitted to dialysis (by the compensation method repeatedly used by Rona), the outer liquid should contain more sodium hydrogen carbonate than the dialysate of a serum which has not been so treated. This was actually found to be the case, and the results confirm the statements of Zuntz. The carbon dioxide should, however, convert the serum proteins into a carbamic acid derivative. There would therefore exist in the dialysor sodium salt of a non-diffusible acid. Attention is called to the fact that, according to Donnan's theory (A., 1911, ii, 848), arrived at by thermodynamic considerations, the amount of sodium hydrogen carbonate on both sides of the dialysing membrane will not be the same when equilibrium is established, for on one side there is an electrolytically dissociated substance with a non-dialysable ion. The sodium hydrogen carbonate in the dialysor could not be estimated in a satisfactory manner by incineration. The contents were therefore submitted to ultra-filtration in a Bechhold apparatus, and the filtrate was analysed. The distribution of the chlorine was also investigated, when the $[H^{\cdot}]$ concentration of the serum was altered by the addition of acetic acid. In concentration above $H^{\cdot} = 10^{-5}$, equilibrium exists with a higher concentration of chlorine inside than outside the membrane, whereas in lower $[H^{\cdot}]$ concentrations the reverse is the case. The critical point of change is the isoelectric point, through which the protein changes from the anionic to the cationic state. The Donnan theory is also applicable in this case to the determination of the distribution of the chlorine. S. B. S.

Salts in the Coagulation of Blood. C GESSARD (*Compt. rend.*, 1913, **157**, 799—802).—A study of the influence of various salts

on the blood of a horse. The amount of salt necessary to prevent coagulation varied with the salt employed, and the plasma obtained could be made to coagulate according to the kind and amount of salt used either by dilution or by addition of a calcium salt, or by addition of serum. Magnesium chloride and sulphate are the most appropriate for the study of these phenomena, since they do not precipitate calcium salts, give no apparent reaction with the saline constituents of blood, and for small differences in weight give different types of plasma. W. G.

The Inactivation of Complement by Mechanical Agitation. HANS SCHMIDT (*J. Hygiene*, 1913, **13**, 291—313).—The complement in serum is inactivated by shaking. This does not seem to be associated with the precipitation of protein, which also occurs. No explanation of the inactivation is at present forthcoming.

W. D. H.

Complement Action in Regard to Surface Tension. HANS SCHMIDT (*J. Hygiene*, 1913, **13**, 314—334).—No relationship between the surface tension and complement action of serum was found.

W. D. H.

The Rate of Elimination of Nitrogen as Influenced by Diet Factors. I. The Influence of the Texture of the Diet. LAFAYETTE B. MENDEL and ROBERT C. LEWIS (*J. Biol. Chem.*, 1913, **16**, 19—36).—A standard diet was arbitrarily selected for dogs, and a constant curve of nitrogen elimination was obtained. This shows a rise reaching a maximum in the second three hours, and then a fall to the initial level early the next day. Delay in elimination is caused by adding indigestible materials, such as mineral oil, vaselin, bone ash, paraffin, filter paper, cork, agar-agar; the effect increases in the order these are enumerated. The last four cause a higher rate of elimination in the later periods. This is attributed to a slower rate of absorption, which in its turn may be produced by (1) rapid emptying of the stomach, and a consequent early exclusion of gastric digestion; (2) the indigestible material may make the digestible material less readily accessible to digestive enzymes; or (3) the final digestion products may be adsorbed by the indigestible substances. Sand gives exceptional results; it causes more rapid elimination of nitrogen during the first six hours. This is not due to increased excretion and reabsorption of digestive juices, for in starvation it has no effect. W. D. H.

The Rate of Elimination of Nitrogen as Influenced by Diet Factors. II. The Influence of Fats and Carbohydrates in the Diet. LAFAYETTE B. MENDEL and ROBERT C. LEWIS (*J. Biol. Chem.*, 1913, **16**, 37—53).—Carbohydrates delay the elimination of nitrogen when added to a protein meal; their effect increases in the order: starch, soluble starch, sucrose, dextrose. This may be explained by the tentative suggestion that it is due to the protein-sparing action of carbohydrates. In reference to fats, cottonseed oil delays

the elimination of nitrogen, but lard and "oleo-stearin" hasten it in the early periods. The last-named effect is, however, only due to removal of sucrose from the diet. W. D. H.

The Rate of Elimination of Nitrogen as Influenced by Diet Factors. III. The Influence of the Character of the Ingested Protein. LAFAYETTE B. MENDEL and ROBERT C. LEWIS (*J. Biol. Chem.*, 1913, **16**, 55—77).—Extracted meat lowers the rate of nitrogen elimination; the explanation advanced is that extracted meat contains relatively more connective tissue, and therefore is not so digestible. The curves following the ingestion of caseinogen, ovo-vitellin, edestin, "glidine," and gelatin show no more differences than those noted in the two meat products. Egg-white or albumin and soy bean give different curves due to rate of digestion and absorption, or, in the case of soy bean, to the presence of sucrose. Proteins do not differ materially in their rate of metabolism. The opposite findings of others are discussed. W. D. H.

The Metabolism of Infants During Starvation. ARTHUR SCHLOSSMANN and HANS MURSCHHAUSER [and, in part, KARL MATTISON] (*Biochem. Zeitsch.*, 1913, **56**, 355—415).—The authors, in confirmation of their previous investigations, show that the metabolism during starvation depends on the diet consumed in the period preceding the fast, and that the more nitrogen consumed during the period the greater is the amount of body protein decomposed during the first two or three days of starvation. Similar results were obtained in the case of infants. The breast-fed children metabolise less nitrogen than the artificially fed. There is, however, a marked difference between the metabolism of the two classes during starvation, for whereas the artificially fed children excrete less nitrogen during the period of fast than during the nutrition period, the reverse is the case with the breast-fed infants. In spite of this fact, however, the breast-fed children still excrete less nitrogen during the starvation period than the hand-fed children, and the authors draw the conclusion that the former are more capable of resisting the effects of deprivation of food. The excretion of the acetone substances during starvation was also investigated. The amount excreted rapidly increased in the second day of hunger, running nearly parallel with the increased output of nitrogen in the case of the breast-fed children. In the case of the hand-fed children, the acetone substances increased with diminishing nitrogen output. A few measurements of the respiratory exchanges were also made by the authors. S. B. S.

The Method and Places of Formation of Conjugated Glycuronates in the Organism. JUHO HÄMÄLÄINEN (*Chem. Zentr.*, 1913 ii, 1319—1320; from *Skand. Arch. Physiol.*, 1913, **30**, 196—198).—The small intestine of a rabbit under ether narcosis, after washing, was perfused with Ringer's fluid from the mesenteric artery to the portal vein. α-Santenol and dextrose were then injected into the intestine. After six hours' perfusion, the per-

fusion fluid and intestinal contents were examined, and a non-crystalline substance with the properties of α-santanolglucoside was isolated. Glucoside formation appears to take place therefore in the intestinal wall. S. B. S.

Fat Absorption by the Gastric Mucosa. CHARLES W. GREENE and WILLIAM F. SKAER (*Amer. J. Physiol.*, 1913, **32**, 358—368).—Evidence is adduced that absorption of fats occurs in the stomach of mammals (cats, dogs, rats). The gastric epithelium contains fat even in fasting; this is increased by feeding on fats. The fat in the gland cells, especially in the pyloric region, may be increased by fasting. This has no relation to absorption fat, but is due to mobilisation of the body fat. The observations throughout are histological. W. D. H.

The Processes of Absorption in the Intestine. N. A. DOBROWOLSKAJA (*Biochem. Zeitsch.*, 1913, **56**, 267—290).—The author discusses the various views as to the method of utilisation of the proteins in the organism, including those of Heidenhain, Hoffmeister, Abderhalden, etc., and attempts by various experimental methods to throw some light on the mechanism. In the first series of experiments, he analyses the serum of portal blood of dogs, estimating the changes of total non-protein nitrogen, and the amino- and peptide-nitrogen produced by the introduction of the chymus obtained from intestinal fistulæ of other animals into the small intestines. No definite results were obtainable by this method, as it was shown that the operative procedure alone, without introduction of digestion products, produced changes in the composition of the serum of the experimental animals. In a second series of experiments, the *in vitro* changes on the amino-nitrogen produced by serum, intestinal extracts, pancreas, etc., on amino-acids and digestion product of proteins, were investigated. The results again lead to no definite conclusions, in some cases indicating synthesis, and in others peptide degradation. In the third series of experiments, an anastomosis was made between the portal vein and the kidneys by the junction of the central end of the *vena lienalis* with the peripheral end of the renal artery. It was assumed that, in the event of introduction of digestion products in the intestine, and a consequent resorption of amino-acids into the portal vein, the excess would be eliminated by the kidneys. To increase the pressure in the kidneys, the portal vein was partly constricted above the junction with the *vena lienalis*. In the majority of cases, the kidney not connected with the portal vein was extirpated. In all of these cases, the animals died. In two cases, when the second kidney was left intact, a certain number of experiments were performed, and the nitrogen of the amino-groups, the hippuric acid, and ammonia nitrogen of the urine excreted were estimated. The introduction of nitrogen into the alimentary tract (by feeding) lead in many cases, especially that of alanine, to an increased amino-nitrogen in the urine. Owing to the fact that the second kidney was intact, these experiments could hardly be considered

satisfactory. In the fourth series of experiments, a portal vein fistula was made according to the method of London and the author, and blood was removed by way of the fistula at various periods after feeding. The results showed a periodic fluctuation in both the portal blood and the blood of the general circulation (removed from the jugular vein). The general result of the experiments is to indicate the difficulty of artificially increasing the amino-nitrogen of the portal vein under conditions approaching the normal physiological. S. B. S.

The Indispensability of Lipoids for Life. The Relation of the Necessary Substances to the Lipoid Extracting Agents. WILHELM STEPP (*Zeitsch. Biol.*, 1913, **62**, 405—407 Compare A., 1911, ii, 1002).—This is a continuation of the author's previous work on mice. A mixture of lecithin, cholesterol, kephalin, cerebron, and phytin added to a diet freed from lipoids by alcohol-ether extraction, does not supply the missing necessary material. If the primary acetone extract of egg-yolk is added to lipoid-free food, the result is that the necessary material is still lacking; the same is true for the secondary alcoholic extract. But the primary alcoholic extract restores the value of the lipoid-free food. The materials necessary for life are therefore soluble in alcohol, but not in acetone. If the material is extracted with acetone first, part only of the indispensable material goes into solution; the acetone-soluble substances are soluble also in alcohol. Extraction with ether does not remove the indispensable material; fat is therefore for the mouse not indispensable. Extraction of the food with alcohol entirely removes its power to support life. W. D. H.

Are there Substances at Present Unknown in Food-stuffs which are of Importance for the Maintenance of Life? EMIL ABDERHALDEN and ARNO E. LAMPÉ (*Chem. Zentr.*, 1913, ii, 522—523; from *Zeitsch. gesamte. expt. Med.*, 1913, **1**, 296—354).—As a result of a critical experimental investigation on a broad basis of the work of Suzuki, Shimamura and Odake, and of Funk and others, the authors draw the conclusion that up to the present time there has been no absolute proof of the existence of unknown substances in foods, of general significance, which are essential to the maintenance of life. They do not consider that the action of the so-called oryzanin of the Japanese authors, or of Funk's vitamine, has as yet been definitely established. S. B. S.

The Biological Significance of the Fat-content of Fish, with Special Reference to their Habitat. OSW. POLIMANTI (*Biochem. Zeitsch.*, 1913, **56**, 439—445).—Attention is called to the fact that during the development of fish embryos, the amount of visible fat diminishes, during which time the habitat gradually alters from that of an organism living on the surface of the water to one living deeper in the sea. It seemed therefore possible that the nectonic fish, which move rapidly about the surface, should contain more fat than the less active, more slowly moving, benthonic fish. Numerous analyses of various species were carried

out, which tend to confirm the above theory, the fat varying from 1·115 to 20·447% of the solid substance. S. B. S.

Proteins of Fish Sperm. ALBRECHT KOSSEL (*Zeitsch. physiol. Chem.*, 1913, **88**, 163—185).—The protamines from the sperm of a number of species of fish have been isolated and investigated. (The figures given are % of total nitrogen.)

Percine from the yellow perch (*Perca flavescens*) contains 85·5% of diamino-acid nitrogen, and 9·8% of monoamino-acid nitrogen, the former being mainly arginine (78·1%) with some histidine (5·6%). No lysine was present. The protamine from the pike perch (*Stizostedion vitreum*) proved to be identical with this.

That from the tunny (*Thynnus thynnus*) (compare Ulpiani, A., 1903, i, 215), which is termed thynnine, contains 80% of arginine nitrogen, no lysine or histidine, and 10% of monoamino-acid nitrogen. The sulphate, like that of other protamines, separates from aqueous solution as an oil. Thynnine also contains tyrosine. *Pelamys sarda* contains a very similar protamine.

The protamine of the sword fish contained 81·5% of arginine nitrogen, and 14% of monoamino-acid nitrogen. Neither histidine nor lysine were present.

The protamine of *Oncorhynchus tschawytscha*, the Chinook salmon (compare A. E. Taylor, A., 1909, i, 344), is identical with the salmine from Rhine salmon (Kossel and Dakin, A., 1904, i, 355, 702).

In the white fish (*Coregonus albus*) the proportions of arginine and monoamino-acid nitrogen are 87·3 and 9·4. In the lake trout (*Salvelinus*) they are 88·9 and 7·1, whilst in *Esocine*, the protamine of the pike (*Esox lucius*), they are 86·3 and 11·3.

In general, these protamines contain two molecules of arginine to one molecule of monoamino-acid—in a few protamines the proportion of monoamino-acids is larger. The protamines are thus to be expressed by the formula a_2m, where a is arginine, or $(alh)_2m$, when all three diamino-acids are present, the proportion of diamino-acid being again as 2 to 1.

A table is given of the known protamines and their formulæ. E. F. A.

The Lipoids of Nervous Tissue. CESARE SERONA and ANOTOINETTE PALOZZI (*Chem. Zentr.*, 1913, ii, 1064—1065; from *Arch. Farm. sperim.*, 1913, **15**, 375—384).—The composition of the brain (white and grey matter) of ox and calf was as follows: 14·25—16·13°/₀₀ cholesterol and the esters of cholesterinolic and palmitic acids, 39·8—44·1°/₀₀ oleic acid and palmitic acid lecithins, 14·6—14·8°/₀₀ cerebrin, and 3·76—5·8°/₀₀ homocerebrin or cerasin. To separate the constituents, the following process was employed. The brain was extracted with 5—6 times its weight of a mixture of equal parts of alcohol and ether. From the residue a substance could be extracted with hot alcohol with m. p. 164—165°, which had the properties of homocerebrin or cerasin. The alcohol-ether extract yielded, after evaporation of the ether, a flocculent mass *A*, and the alcoholic residue on evaporation, a waxy mixture *B*.

Each of these fractions was treated successively with cold acetone, cold ether, and hot alcohol. The acetone extract was fat-free, and contained, besides some phosphatic lipoids and cerebrin, which became insoluble on solution and reprecipitation with acetone, chiefly cholesterol and its fatty esters. The ethereal extract could be separated into two fractions, one, insoluble in cold alcohol, yielding a substance corresponding with Thudichum's and Koch's kephalin, which appears, on further investigation, to be an impure lecithin mixed with cerebrin, and a soluble fraction, consisting also chiefly of impure lecithin mixed with cerebrin. The alcoholic extract was also separated into fractions soluble and insoluble in cold alcohol. The former consisted of cerebrin, m. p. 190—192°, which on hydrolysis yielded a fatty acid, m. p. 74—75°, presumably cerebrotinic acid, and a reducing sugar with $[\alpha]_D^{25}$ +27·5°, and a substance which is possibly galactosamine. The part soluble in cold alcohol, m. p. 160—165°, is apparently impure homocerebrin or cerasin. S. B. S.

Influence of Activity on Automatic Rhythm in Heart Muscle. George R. Mines (*Proc. physiol. Soc.*, 1913, xiii; *J. Physiol.*, **47**).—If a frog's or mammal's heart is made to beat faster, the subsequent automatic rhythm is slowed; in the octopus the reverse occurs. In both cases, forced activity leads to formation of acid, but in different hearts, and different parts of the same heart, the optimum hydrogen ion concentration is different. In some cases the increase will be towards this value, in others away from it. W. D. H.

Hydrogen Ion Concentrations Limiting Automaticity in Different Regions of the Frog's Heart. (Miss) Dorothy Dale and C. R. A. Thacker (*Proc. physiol. Soc.*, 1913, i—ii; *J. Physiol.*, **47**).—The different heart chambers develop rhythm with varying degrees of hydrogen ion concentration. The sinus will beat in solutions which are too acid for the auricle, and the same holds between auricle and ventricle. Similar differences appear on the alkaline side. The actual figures are given in the paper. W. D. H.

Synthetic Sugar Formation in the Artificially Perfused Liver. Gustav Embden, Ernst Schmitz and Maria Wittenberg (*Zeitsch. physiol. Chem.*, 1913, **88**, 210—245).—The perfusion fluid employed was Ringer's solution, containing in it dog's blood-corpuscles washed by centrifugalising. If the liver (dog) is freed from glycogen by phloridzin poisoning, the perfusion leads to a slight but constant formation of sugar. If then dihydroxyacetone is added, the amount of sugar formed (dextrose) is increased. The addition of *dl*-glyceraldehyde to the perfusing fluid increases the sugar formation greatly; this sugar is in part *d*-sorbose. The aldehyde appears to be directly transformed into the sugar with previous rupture into short carbon chains. Glycerol forms dextrose less than the two trioses. W. D. H.

Formation of Acetoacetic Acid from Acetic Acid [in the Liver]. Gustav Embden and Adam Loeb (*Zeitsch. physiol. Chem.*, 1913, **88**, 246—258).—A study of the formation of acetoacetic acid

in the liver indicates that it is not formed from acetic acid by oxidative changes. The presence of *n*-valeric acid or of propionic acid prevents its formation from acetic acid. Formic acid is without influence, and is but little attacked on passing it through the liver. *dl*-Lactic acid has less effect on the reaction than propionic acid.

The conversion of acetic acid into acetoacetic acid is greatly retarded when the liver is full of glycogen. The addition of glycollic acid to the blood stream increases the formation of acetoacetic acid in the liver, although to a less extent than acetic acid.

E. F. A.

The Effect of Pituitary Extract on Renal Activity. C. E. KING and O. O. STOLAND (*Amer. J. Physiol.*, 1913, **32**, 405—416).—The view is disputed that pituitrin directly stimulates the renal epithelium; the vascular changes (vaso-dilatation) are considered sufficient to account for the diuresis. W. D. H.

The Heat-production of Fatigue and its Relation to the Production of Lactic Acid in Amphibian Muscle. RUDOLPH A. PETERS (*J. Physiol.*, 1913, **47**, 243—271).—By a modification of A. V. Hill's calorimeter it was found that the heat produced by the indirect stimulation of frog's muscles until fatigue set in has a maximum value of about 0·9 cal. per gram of muscle. The heat liberation is roughly exponential, and about 70—80% of it is liberated in the first two minutes. The figure 0·9 is about half of that obtained in chloroform rigor. No processes other than contraction arise in the production of rigor. The lactic acid figures agree with those of Fletcher and Hopkins; heat production and lactic acid liberation are intimately associated. W. D. H.

The Presence in the Vascular Walls of a Ferment Setting Free a Reducing Sugar at the Expense of the Virtual Sugar of the Blood, and Decomposing Phloridzin. RAPHAEL LEPINE and RAYMOND BOULUD (*Compt. rend.*, 1913, **157**, 627—628. Compare this vol., i, 1274).—The experiments show the presence of a ferment in the vascular walls of the kidneys, lungs, and aorta, capable of setting free a reducing sugar in the blood, a function previously ascribed to the liver alone. The ferment is also capable of partly hydrolysing phloridzin. W. G.

Amylogenesis and its Relation to Glycolysis in the Animal Organism. CESARE PADERI (*Chem. Zentr.*, 1913, ii, 1316; from *Arch. Farm. sperim.*, 1913, **16**, 54—96).—From his own results and those of other investigators, the author draws the conclusion that glycogen formation is a necessary preliminary process in the utilisation of sugar in the organism, and that a disturbance of this function results in diabetes mellitus. For the treatment of this condition, therefore, substances must be employed which assist the glycogen formation. Extract of muscles and of pancreas, both alone or combined, were found to be incapable of degrading dextrose at 37°. Disappearance of this substance under these

conditions can be attributed to bacterial action. Lactic and acetic acids were formed from the sugar under the combined action of pancreas extract and micro-organisms. The formation of these acids accounts for the fact that the addition of dextrose inhibits a far-reaching putrefaction of pancreas. No alcohol could be detected as a result of the combined action of pancreas and bacteria on sugar. A fasting animal exhibited appreciable formation of glycogen in the liver. Addition of extract of pancreas did not inhibit sugar formation in the transfusion of a surviving liver.

S. B. S.

A Comparison of the Observed and Computed Heat Production of Cattle. HENRY PRENTISS ARMSBY (*J. Amer. Chem. Soc.*, 1913, **35**, 1794—1800).—Experimental evidence that in the case of men and carnivora the usual equivalence exists between chemical energy, heat energy, and mechanical energy, is already forthcoming, but hitherto such investigations have not, as a rule, included an examination of herbivorous animals.

The present paper gives an account of results obtained during the last decade on cattle (steers), and in the aggregate of fifty-seven experiments the observed heat production differs from the computed by only 0·4%.

D. F. T.

Constituents of Animals Fats. The Fat of Cervus elaphus. ISIDOR KLIMONT and E. MEISL (*Monatsh.*, 1913, **34**, 1489—1492).—A lard from the red deer, with the following constants, has been examined: D 50°, 0·9066, acid number 20·5, saponification number 203·5, iodine number 19·3, m. p. 48° (Pohl), solidification point 47·5°. The fat was recrystallised eleven times from hot acetone, when β-palmityldistearin, m. p. 62·5—63·5°, was obtained (compare Bömer and Limprich, this vol., i, 442).

J. C. W.

The Organic Substance in the Skeletal Tissues of Anthozoa. IV. Isolation and Identification of Bromogorgonic Acid. CARL TH. MÖRNER (*Zeitsch. physiol. Chem.*, 1913, **88**, 138—154. Compare A., 1907, ii, 283; A., 1908, ii, 310).—3:5-Dibromo-*dl*-tyrosine has been identified as a product of the hydrolysis of *Primnoa* gorgonin with barium hydroxide. This is the first organic bromo-compound obtained by the hydrolysis of a naturally occurring protein. The whole of the bromine present in the gorgonin molecule is not dibromotyrosine. Other products of the hydrolysis of gorgonin are tyrosine, glycine, alanine, leucine, aspartic, glutamic, and oxalic acids.

E. F. A.

The Secretion of Cerebro-spinal Fluid. WALTER E. DIXON and WILLIAM D. HALLIBURTON (*J. Physiol.*, 1913, **47**, 215—242).—An intravenous injection of an extract of the choroid plexuses (choroid gland) produces an increased secretion of cerebro-spinal fluid, as tested by its rate of outflow through a cannula. The active principle is thermostable, soluble in water and in alcohol, and does not pass the pores of a Chamberland filter. Other effects of the

injection are increase of respiration, and a slight fall of blood-pressure. Extracts of brain produce the same effect, but less markedly; no other animal extracts act in the same way. Probably as a result of cerebral activity, some waste product acts as a hormone to stimulate the activity of the choroid cells, and from the richness of the cerebro-spinal fluid in carbon dioxide, it is suggested that one function of the fluid may be to enable the brain to get rid of this material. Reasons are given why this hormone is considered to act on the gland cells and not on secretory nerves. The hormone in question is not found in the cerebro-spinal fluid itself except in cases where catabolism is in excess, as in degenerative processes of the central nervous system.

Other agents which produce an increase of the fluid are excess of carbon dioxide in the blood, and drugs which interfere with respiration. The volatile anæsthetics have a similar action; these may act by interfering with oxygenation or by altering the physical condition of the secreting cells. A large number of substances were investigated, but all the remainder gave negative results, if respiratory and vascular effects were excluded. W. D. H.

The Comparative Composition of Human and Cow's Milk. EDWARD B. MEIGS and HOWARD L. MARSH (*J. Biol. Chem.*, 1913, **16**, 147—168).—Human milk differs from cow's milk in three important ways. It contains more lactose, less protein, and more substances of unknown nature. The following figures are averages in percentages of the whole milk:

	Fat.	Lactose.	Protein.
Human milk..............	2 to 4	6 to 7·5	0·7 to 1·5
Cow's milk	2 ,, 4	3·5 ,, 5	2·5 ,, 4

The unknown constituents are soluble in alcohol and ether; they contain little or no nitrogen, and are of importance as food. Some are crystalline, and the crystalline form of one is figured and described at length. (This contains sulphur, but is free from nitrogen.) They are most plentiful in early human milk (1%); as lactation proceeds they sink to 0·5%. Cow's milk at the latter period contains 0·3%. The paper contains analytical tables, and descriptions of methods. Much of the work was done by the late Arthur V. Meigs. W. D. H.

The Soluble Caseins of Milk. LÉON LINDET (*Bull. Soc. chim.*, 1913, [iv], **13**, 1001—1006. Compare this vol., i, 1116).—Further experiments are quoted in support of the author's views as to the presence of an α- and β-caseinogen in milk and the relationship between them. The sum of these two substances present is fairly constant in milk, but the proportions of each are very variable. W. G.

Solubility of the Proteins of Milk in the Elements of the Serum; Reduction of their Solubility under the Influence of Calcium Chloride. LÉON LINDET (*Bull. Soc. chim.*, 1913, [iv], **13**, 929—935). —The soluble proteins of milk include casein (distinguished as

α-casein), having $[\alpha]_D -116°$, and a second, called β-casein, which differs only in specific rotation, $[\alpha]_D -30°$. Milk serum, from which all the proteins had been removed by means of phenol, on evaporation and incineration yielded ash of the following composition, expressed in grams per litre of milk: alkali chlorides, 1·949; alkali citrates (calculated from the carbonate found), 0·765; alkali phosphates, 0·514; calcium phosphate, 0·638; magnesium phosphate, 0·458; iron and aluminium phosphates, 0·108; calcium sulphate, 0·341; undetermined, 0·387. An artificial serum containing lactose, 5; sodium chloride, 0·2; sodium citrate, 0·08; and sodium phosphate, 0·05 per cent., can dissolve 3·456 grams of casein per litre, and probably as much more of the β-casein. In milk, probably all the β-casein is in solution, and about 10% of the α-casein, the rest of the latter being in suspension. The addition of calcium chloride to milk before coagulation by rennet increases the nitrogen and phosphate content of the coagulum and accelerates the action, due to its converting the sodium salts into insoluble calcium salts, and thereby destroying the solvent action of the former on the casein. T. A. H.

Psychic Hyperglycæmia in Rabbits. IVAN BANG (*Zeitsch. physiol. Chem*, 1913, **88**, 44—46).—Hirsch and Reinbach (*ibid.*, 1913, **87**, 122) have described a hyperglycæmia and glycosuria in rabbits as the result of fright. The non-recognition of this condition produced by psychical causes renders much work on the general subject untrustworthy. The existence of such a psychic condition in rabbits and other animals is confirmed in the present paper.

W. D. H.

Pentosuria from the Chemical Point of View. ERNST ZERNER and RUDOLFINE WALTUCH (*Monatsh.*, 1913, **34**, 1639—1652).—In most cases of pentosuria which have been investigated, optically inactive urines have been encountered, from which osazones apparently corresponding with *i*-arabinose or *l*-arabinose have occasionally been isolated.

Two new cases of pentosuria have now been examined. The urines were inactive, which is taken as an indication of the absence of *l*-arabinose, since this has a very high specific rotation. The osazone obtained had m. p. 162—163°, and a small *d*-rotation, which was insufficient to distinguish it from *d*-arabinosazone. Diphenylmethanedimethyldihydrazine (Braun, 1910, i, 525) gave no indication of arabinose. A mixture with an equal weight of *l*-xylosazone had m. p. 208—210°, whereas *i*-xylosazone has m. p. 210—215° (Fischer, A., 1894, i, 566). The osazone from these urines is therefore *d*-xylosazone, and very probably the pentose is *d*-xylose. Further experiments are being carried out definitely to determine the nature of the sugar. J. C. W.

The Sugar in Pentosuric Urine. CARL NEUBERG (*Biochem. Zeitsch.*, 1913, **56**, 506—507).—Zerner and Waltuch (preceding abstract) have maintained that the sugar isolated by them in a

case of pentosuria was *d*-xylose, as the mixture of its osazone with that of the corresponding *l*-derivative has a higher melting point than the pure substance. A mixture of the *l*-form of osazone with the osazone obtained from the urine of the cases of pentosuria of the author did not produce a corresponding rise in the melting point. The author does not see, therefore, any reason to suppose that the sugar in his case is other than the *dl*-arabinose, as originally suggested. It is conceivable that various forms of pentosuria exist. S. B. S.

Physiological Action of Colloidal Carbon. GUIDO IZAR and C. PATANÈ (*Biochem. Zeitsch.*, 1913, **56**, 307—318).—The so-called mellogen, produced by the disintegration of a carbon anode by a galvanic current, was used in these experiments. It can be dispersed in water made slightly alkaline by sodium hydroxide, which mixture is afterwards neutralised by passing in carbon dioxide and heating. This preparation has no influence on the total autolysis of the liver. It increases the amount of uric acid formed by autolysing ox-spleen and liver, and inhibits the uricolytic action of ox-kidneys and washed pulp of dog's liver. Intravenous injections of large quantities into rabbits, white rats, pigeons, etc., produce dyspnœa, but only a few of the animals succumb. The intravenous injection has no appreciable effect on body temperature (rabbits), but increases the amount of carbon dioxide in expired air (as compared with control injection of distilled water). The amount of increase is approximately proportional to the amount of mellogen injected. S. B. S.

Action of Colloidal Sulphur on Autolysis. ANTONIO FAGIUOLI (*Biochem. Zeitsch.*, 1913, **56**, 291—294).—Colloidal sulphur increases the autolysis of liver tissue (ox, dog, and monkey), and to a still larger extent that of tumour tissue (rat sarcoma and human liver carcinoma). S. B. S.

Pharmacological Action of Ethyl Alcohol on the Isolated Mammalian Heart at Different Temperatures. GIUSEPPE BRANDINI (*Chem. Zentr.*, 1913, ii, 524; from *Arch. Farm. sperim.*, 1913, **15**, 178—192, 193—212).—The experiments were carried out on a rabbit's heart in a Langendorff perfusion apparatus. At normal temperatures the alcohol in small doses (1 in 50,000—1,150,000) exerts a stimulant action, in medium doses, the heart activity is depressed, but in higher concentrations ($30^0/_{00}$) the action is toxic. At lower temperatures (33°) the effect is weaker, and higher concentrations of alcohol are required to produce the same effects described as resulting at 37°. S. B. S.

The Scission of the Benzene Ring in the Animal Body. II. Behaviour of Muconic Acid and Benzene in Liver-perfusion Researches. MARIE HENSEL and OTTO RIESSER (*Zeitsch. physiol. Chem.*, 1913, **88**, 38—43).—When muconic acid is added to a fluid employed for perfusing the liver, the amount of acetone formed

by that organ is greatly increased, it may be fourfold. No certain result was obtained by perfusing the liver with benzene; this substance is strongly toxic. W. D. H.

The Conjugated Excretion Products of Bromobenzene and *p*-Iodophenol. ERBERTO ANGELO RABBENO (*Chem. Zentr.*, 1913, ii, 1070; from *Arch. Farm. sperim.*, 1913, **15**, 535—546).—It was presumed that it should be possible, by the estimation of the total sulphur, the conjugated sulphuric acid, and the rotation of the urine of dogs, to which bromobenzene and *p*-iodophenol had been administered *per os*, to ascertain whether the halogen derivatives of benzene undergo conjugation with glycuronic acid as well as with cystine and sulphuric acid. It was found as a result of the experiments that the bromine derivative is excreted conjugated only with cysteine and sulphuric acid, whereas the iodo-derivative is excreted conjugated with glycuronic and sulphuric acids, but not with cysteine. S. B. S.

The Influence of the Administration of Creatine and Creatinine on the Creatine Content of Muscle. VICTOR C. MYERS and MORRIS S. FINE (*J. Biol. Chem.*, 1913, **16**, 169—186).—The subcutaneous administration of creatine to rabbits causes a small increase in the creatine content of muscle (about 5% in five experiments). This is quite insufficient to account for the creatine, which does not reappear in the urine. The administration of creatinine exerts a similar effect, the creatine content of the muscles being 6% above the normal, an amount sufficient to account for the creatinine which was not eliminated by the kidneys. This apparent increase in the muscular creatine was not due to a retention of unchanged creatinine. Of the creatine given, 25—80% (the quantity depending on the amount injected) reappeared in the urine unchanged, whilst 2—10% was eliminated as creatinine. When creatinine was administered, 77—82% (average 80%) reappeared in the urine, and no elimination of creatine was detected. W. D. H.

Narcosis and Oxygen Consumption. JACQUES LOEB and HARDOLPH WASTENEYS (*Biochem. Zeitsch.*, 1913, **56**, 295—306).—The authors discuss the relationship between inhibition of oxidation and narcosis. When the embryos of *Fundulus* are not narcotised, they respond by rapid movement to a stimulus of $N/25$-hydrochloric acid. It was found that they only become insensitive to this stimulus when their oxidation rate has been reduced to 1/14 of the normal value by potassium cyanide; a reduction by this method to 1/9 is without influence on their response to the stimulus. On the other hand, they become unresponsive to chloroform treatment, without any appreciable reduction of the oxidation rate. Ethyl ether and butyl alcohol can produce insensitiveness to the strongest stimuli with the diminution of the oxidation rate by only 26%. Medusæ loose their mobility and reactivity to stimuli by direct reduction of oxidation by potassium cyanide only

when this reduction is 3—6 times as great as that which results when the motility and reactivity are destroyed by ethylurethane. The conclusion is drawn that narcosis cannot be due directly to reduction of oxidative capacity, and that the latter is a result either of inactivity of the tissues due to narcosis, or it is a secondary action of the narcotis, which stands in no direct relationship to the narcosis itself. S. B. S.

Biological Oxidation of Certain Glucosides. JUHO HÄMÄLÄINEN (*Chem. Zentr.*, 1913, ii, 1319; from *Skand. Arch. Physiol.*, 1913, **30**, 187—190).—After injection of the glucosides of certain terpene alcohols, the corresponding glycuronates appear in the urine. There is therefore no preliminary scission of the glucoside into sugar and alcohol, for neither in the blood nor in the organs could any terpene be detected. On the contrary, both glycuronate and the corresponding glucoside could be found. The facts confirm the theories of Fischer and Piloty and of Sundvik on the formation of conjugated glycuronates in the organism. Furthermore, more glycuronate is excreted after administration of the glucoside than after administration of the free substance. S. B. S.

The Influence of Certain Quinoline and Naphthaquinoline Derivatives on the Excretion of Uric Acid. RICCARDO LUZZATO and RICCARDO CIUSA (*Chem. Zentr.*, 1913, ii, 1318—1319; from *Arch. Farm. sperim.*, 1913, **16**, 6—40).—The following derivatives were investigated: 2-*p*-methoxyphenylquinoline-4-carboxylic acid, 2-*p*-dimethylaminophenylquinoline-4-carboxylic acid, 6-amino-2-phenylquinoline-4-carboxylic acid, 3-phenyl-β-naphthaquinoline-1-carboxylic acid, 2-*p*-dimethylamino-β-naphthacinchonic acid, 2-phenyldihydro-β-naphthaquinoline-4-carboxylic acid, 2-*o*-hydroxylphenyl-β-naphthacinchonic acid, 3-phenyl-β-naphthaquinoline, and 2-phenylcinchonic acid (atophan). Of these it was found that 3-phenyl-β-naphthaquinoline-1-carboxylic acid (the so-called diapurin) and atophan caused an intense excretion of uric acid, the action of the latter being somewhat less than that of the former. It caused, however, no turbidity of the urine, and was better tolerated, and a dose of 5 grams caused no bad symptoms in a dog of 12 kilos. weight, and could be taken by a man in doses of 2 grams for several days without ill effects. The action of diapurin is attributed to the mobilising effects on the uric acid, which already exist in the organism as a result of purine degradation, as the increased excretion of the acid is not accompanied by an increased phosphoric output, which should result if the nucleins are broken down. Furthermore, the increased output of uric acid ceases two or three days after administration of the drug. The particular action on the uric acid is due to the presence of a phenyl group in the 2-position, the quinolinecarboxylic acid group being inactive. The action is neutralised by the presence of the methoxyl and amino-groups in the 6-position. On the other hand, 2-phenyl-6-methylquinoline-4-carboxylic acid (paratophan) and 8-methoxy-2-phenylquinoline-4-carboxylic acid (isatophan) are fairly active. The introduction of the OH,

NMe_2, or OMe group into the 2-phenyl ring inhibits or weakens the action on uric acid. As hydroxyphenylquinoline-4-carboxylic acid is, according to Sk'orczewski and Sohn, a degradation product of atophan, the latter appears to exert its influence before oxidation. The reduction of the pyridine ring destroys or weakens the action. The general methods of Doebner, Kuntze, Lachs, and Steinert were employed in the preparation of the compounds, and the following substances were obtained: 2-p-*anisylquinoline*-4-*carboxylic acid*, m. p. 217°; 2-*dimethylaminophenylquinoline*-4-*carboxylic acid*; 6-*amino*-2-*phenylquinoline*-4-*carboxylic acid*, m. p. 160° (decomp.).

S. B. S.

The Behaviour of Certain Rhamnosides in the Animal Body. MARIO GARINO (*Zeitsch. physiol. Chem.*, 1913, **88**, 1—8).—Rutin, quercitrin, hesperidin, and hesperetin, after intravenous or oral administration, pass through the animal organism, and are excreted almost entirely unchanged. Hydrolysis of these substances appears to occur either not at all, or in the merest traces, in the body.

W. D. H.

The Action of Strophanthin on the Excised Frog's Heart. A. J. CLARK and GEORGE R. MINES (*Proc. physiol. Soc.*, 1913, vii—viii; *J. Physiol.*, **47**).—The effect of perfusing the heart with one part of strophantin in a million of Ringer's fluid is at first beneficial, and later toxic. The observations were made on the mechanical activity of the ventricle, the length of the A.V. interval, and on the electrical concomitant of activity. W. D. H.

Mechanism of the Biological Action of the Röntgen Rays. EUGEN PETRY (*Biochem. Zeitsch.*, 1913, **56**, 341—352).—The author has investigated the influence of Röntgen rays on the toxicity of various metals, following a similar line of research to that of Tappeiner and his pupils on the sensitising influence of eosin on actinic rays. Amœbæ obtained from hay-infusion were used as the objects of experiments, and these were submitted to the action of uranium nitrate, sodium tungstate, zinc sulphate, and colloidal zinc sulphide in the dark, in the presence and the absence of Röntgen radiation. As a result, it was found that the rays had no appreciable effect in increasing the toxicity of the metals. Compounds were purposely chosen which fluoresce when submitted to radiation. The rays exerted no action on the sensitising activity. Experiments were also carried out to ascertain whether organs which are highly sensitive to Röntgen rays contain substances which act as light-catalysts for these rays. Testicles and lymph glands were chosen, and the effect of radiated and unradiated extracts on hæmolysis, the mobility of amœbæ, and the milk-clotting by rennin, were investigated. The results were negative, and the author draws the conclusion that no substances have been discovered which act as catalysts for the Röntgen rays in the same way that eosin acts as catalyst for actinic rays. S. B. S.

Purine and Xanthine Bases as Intermediary Products in Poisoning by Nucleoproteins. HENRI DE WAELE (*Chem. Zentr.*, 1913, ii, 519—520; from *Zeitsch. Immun. expt. Therapie*, 1913, **18**, i, 410—422).—Just as, according to the author, the proteins use the amino-acids as intermediary products in developing their thromboplastic action, the nucleoproteins act by intermediation of the purine bases. Thus nucleoproteins, otherwise harmless, can be rendered toxic by degradation of their molecule, or by the addition to them of degradation products, or even amino-acids. Under these conditions, curves were obtained similar to those described by the author for proteins, showing, in an oscillatory manner, thromboplastic and antithrombic phases. The first of these is short, and may be overlooked. The nucleins produce a strong antithrombic secretion. The antithrombic phase is of short duration, but produces a distinct, although short-lasting, immunity. The nucleoproteins can be activated either by purines (affecting the nucleic acid part of their molecule) or by amino-acids (affecting the protein part). Nucleohistones, owing to the presence of the histone group, are directly toxic. For many nucleoproteins, such as those from the thymus, animals are directly anaphylactic, in the same way that carnivora are sensitive to peptones. S. B. S.

The Removal of the Poisonous Properties of Protein Cleavage Products by Substitution of the Cyclic Nucleus. GEORGE BAEHR and ERNST P. PICK (*Arch. expt. Path. Pharm.*, 1913, **74**, 73—91).—The proteins of horse- and ox-serum yield, on gastric digestion, poisonous products. But if these proteins are iodised, nitrited, or diazotised, the products of pepsin digestion no longer produce "peptone-shock," causing neither fall of arterial pressure nor loss of coagulability in the blood. The iodine, nitro- and diazo-groups in question enter the cyclic nucleus of the protein molecule. W. D. H.

Nature of the Coagulant of the Venom of Echis carinatus, a Small Indian Viper. J. O. WAKELIN BARRATT (*Proc. Roy. Soc.* 1913, [*B*], **87**, 177—190).—The effect of the intravenous injection of thrombokinase is essentially different from that of injection of thrombin. The latter causes an abundant intravascular formation of fibrin and a reduction of the amount of fibrinogen in the circulating fluid. Little or no fibrinogen is removed after the injection of thrombokinase, which thus has an essentially different action on blood plasma than on a solution of fibrinogen *in vitro* in presence of calcium chloride, which it causes to coagulate. The coagulant of viper venom, as exhibited by its effect in causing intravascular separation of fibrin when injected into the blood-stream and also indicated by its behaviour when heated, is a thrombin and not a thrombokinase. E. F. A.

Chemistry of Vegetable Physiology and Agriculture.

Biochemistry of Micro-organisms. VIII. Fermentation of Formic Acid by Bacillus Plymouthensis in a Medium of Constant Composition. HARTWIG FRANZEN and FRITZ EGGER (*Zeitsch. physiol. Chem.*, 1913, **88**, 73—102. Compare this vol., i, 322; A., 1912, ii, 669).—Further data are given obtained from experiments with *B. Plymouthensis*, made in the same way as previously with *B. kiliense* and *B. prodigiosus*. The results show the same divergence in different series of cultures. *B. Plymouthensis* ferments formic acid during the first twenty-four hours. The maximum amount of formic acid fermented was 9·95% at 17°, 16·8 and 26·47% at 21°, and 22% at 27°. No general conclusions are drawn. E. F. A.

Chemistry of Bacteria. II. SAKAE TAMURA (*Zeitsch. physiol. Chem.*, 1913, **88**, 190—198).—*Mycobacterium laticola* contains the same organic constituents whether it is grown on nutritive bouillon or on a medium lacking protein. The aromatic units in its composition are formed in quantity when only short open-chain carbon compounds are supplied as food—for example, lactic acid, glycerol, asparagine.

The inorganic constituents of the cells of *Bacterium tuberculosis* or of *Mycobacterium laticola* undergo considerable quantitative variation according to the nature of the environment in which the culture is made. E. F. A.

Violet Colouring Matter and its Production by a Certain Bacterium. W. J. HARTLEY (*Sci. Proc. Roy. Dubl. Soc.*, 1913, **14**, 63—73).—The pigment of a bright, violet bacterium obtained from a creamery water has been examined. The pigment turns green with acid, blue with alkali; it does not dye silk. The absorption spectrum has been characterised; it has no bands in the ultraviolet, absorbs continuously the rays in the red less refrangible than λ 6600, and transmits nearly all the rays from λ 6600 to λ 6439. The cultures, when macerated, gave a positive test with picrate paper for hydrogen cyanide. E. F. A.

Influence of Radioactivity on Nitrogen-fixing Micro-organisms or on those Transforming Nitrogenous Substances. JULIUS STOKLASA (*Compt. rend.*, 1913, **157**, 879—882).—Air activated by pitchblende has a markedly favourable influence on the fixation of atmospheric nitrogen by *Azotobacter chroococcum*, the influence being slightly more favourable with weak radioactive intensity than with a stronger intensity. On the other hand, the transformation of organic nitrogen into ammoniacal nitrogen and the fixation of free nitrogen is much weaker in solutions submitted to the influence of β- and γ-rays than in control solutions.

Soil submitted to air charged with radium emanations showed an increased nitrogen content of 0·021% over the control sample. The reduction of nitrates by denitrifying bacteria is considerably lessened under the influence of radium emanation, although there is ample development of the denitrifying bacteria. W. G.

Butylene-glycol Fermentation of Dextrose by Staphylococci and Tetragenes. M. LEMOIGNE (*Compt. rend.*, 1913, **157**, 653—655. Compare A., 1912, ii, 1199).—Staphylococci and tetragenes only attack carbohydrates slowly, and do not develop unless they have an abundant supply of organic nitrogenous food. The products of the fermentation of the sugar are dimethyl diketone, acetylmethylcarbinol, and butylene $\beta\gamma$-glycol. W. G.

The Optical Behaviour of Yeast Maceration Juice. CARL NEUBERG and P. ROSENTHAL (*Biochem. Zeitsch.*, 1913, **56**, 498—500).—The maceration juices from Lebedev's preparations were found to vary when freshly prepared from $-0·10°$ to $-0·42°$ in optical rotation. On keeping, the optical rotation of the juices diminished in some cases, whereas in others it increased. S. B. S.

Osmotic Pressure and Electrical Conductivity of Yeast, Beer, and Wort. HENRY H. DIXON and WILLIAM R. G. ATKINS (*Sci. Proc. Roy. Dubl. Soc.*, 1913, **14**, 9—12).—Pressed yeast gives higher values than wort, both in osmotic pressure and electrical conductivity. Comparing beer and wort, it is shown that whilst the electrical conductivity remains the same, the osmotic pressure becomes three times as great during fermentation. E. F. A.

Extraction of Zymase by means of Liquid Air. HENRY H. DIXON and WILLIAM R. G. ATKINS (*Sci. Proc. Roy. Dubl. Soc.*, 1913, **14**, 1—8).—Immersion of yeast in liquid air from ten to fifteen minutes renders the protoplasm permeable. On thawing, the yeast liquefies, and after centrifuging, the sap of the cells is obtained as a faintly opalescent, brown liquid. This contains zymase in as active a form as that prepared by Lebedev's maceration method. The amount of zymase extracted may be increased by dilution and maceration. The sap is practically free from glycogen, and does not show autofermentation.

The sediment froths actively, due to hydrolysis of the glycogen in the cells and fermentation of the sugar formed. E. F. A.

The Complete Hydrolysis of Yeast Albumin. HANS PRINGSHEIM (*Woch. Brauerei*, 1913, **30**, 399—400).—The hydrolysis of yeast furnished the following compounds, which were obtained by distillation in the form of esters (Fischer's method). The esters obtained from leucine and valine were the chief product; those from proline, phenylalanine, and glutamic acid were obtained in small quantities; the presence of serine is considered questionable, whilst alanine and glycine were not apparently present.

F. M. G. M.

Influence of Acids on Alcoholic Fermentation. M. Rosenblatt and (Mme.) M. Rosenblatt (*Bull. Soc. chim.*, 1913, [iv], **13**, 924—929. Compare A., 1909, ii, 752; 1910, ii, 643; Johannesohn, this vol., i, 143).—None of the acids tried has any accelerating action on the activity of yeast, and each of them begins to retard the activity at the concentrations quoted: Hydrochloric ($M/6000$), formic ($M/5000$), acetic ($M/300$), propionic ($M/250$), *n*-butyric ($M/200$); sulphuric ($M/6000$), tartaric ($M/1000$); phosphoric ($M/5000$), citric ($M/3000$). Potassium hydrogen sulphate behaves similarly. The following salts accelerate the activity, and the optimal concentrations are quoted: Potassium hydrogen oxalate ($M/200$), dipotassium hydrogen citrate ($M/10$), potassium dihydrogen citrate ($M/5$), sodium dihydrogen tartrate ($M/4$), potassium dihydrogen phosphate ($M/3$). T. A. H.

Formation of Acid by Fermentation. Ed. Moufang (*Zeitsch. f. ges. Brauwesen*, 1913, **36**, 297—299).—Dilute solutions of dextrose, lævulose, maltose, and sucrose were treated with yeast in the presence of malt, and the acids formed subsequently estimated by methods which have been described by Mösslinger. F. M. G. M.

Reduction of Chloral Hydrate by Yeast During Alcoholic Fermentation. Carl J. Lintner and H. Lüers (*Zeitsch. physiol. Chem.*, 1913, **88**, 122—123).—Living yeast in the act of fermenting sucrose reduces added chloral hydrate to trichloroethyl alcohol. E. F. A.

The Uselessness of Zinc for the Culture of Aspergillus niger. Charles Lepierre (*Compt. rend.*, 1913, **157**, 876—879).—*Aspergillus niger* will grow on a culture medium, free from all traces of zinc, providing the ratio, volume of liquid/surface exposed, is always greater than 2. If this ratio falls below 2, however, then the maximum growth is never obtained. This explains the difference between the author's results and those of Javillier (compare A., 1908, ii, 317), who grew the mould on liquid where the ratio v/s was 1·5. W. G.

Polyatomic Alcohols as Sources of Carbon for Lower Fungi. Ray E. Neidig (*J. Biol. Chem.*, 1913, **16**, 143—145).—Methyl alcohol and ethylene glycol are not capable of producing normal cultures of *Aspergillus* and other moulds when they are introduced into Czapek's medium in place of sugar. Glycerol is readily available, and gives cultures as good as when sucrose is employed. With increasing carbon, the availability does not increase; adonitol, for example, does not compare favourably with glycerol or even erythritol, and two of the hexatomic alcohols failed to yield cultures equal to those on glycerol. No connexion between availability and carbon asymmetry could be established. There may, however, be some relation between availability and the nature of the intermediate oxidation products, since all the substances which are available, including glycerol, yield oxidation products containing one or more asymmetric carbon atoms. W. D. H.

Attempts to Produce Citric Acid from Alcohol and Lactose by Fungi. CARL WEHMER (*Chem. Zeit.*, 1913, **37**, 1393—1394. Compare Mazé and Perrier, A., 1904, ii, 676; Herzog and Polotzky, A., 1909, i, 285; Wehmer, this vol., i, 229).—Unsuccessful attempts are recorded to produce citric acid from alcohol or from lactose by means of fungi. The author thus confirms Herzog and Polotzky's conclusion with regard to the non-formation of citric acid from alcohol (contrast Mazé and Perrier), but differs from them in finding that it is also not produced from lactose.

Two species of *Citromyces* were grown during several months in a nutrient solution containing ammonium nitrate, potassium phosphate, magnesium sulphate, calcium carbonate, and alcohol (2·5 and 5%). The latter exerts a marked retarding effect on the growth of the fungi, which differs in extent for the two species. Citric acid could not be detected.

Under similar conditions, a like result was obtained with lactose solutions, in which, however, growth of the fungi occurred readily.

H. W.

Disinfectants which Dissolve Lipoids. JOSEF GÖSSL (*Zeitsch. physiol. Chem.*, 1913, **88**, 103—108).—Overton and Meyer pointed out that certain anæsthetics owe their activity to the fact that they are soluble in the cell-lipoids. A large number of chemical substances are examined in the present research to see if this also holds for their disinfecting powers, with the result that the answer is in the affirmative. The experiments were made on yeast cells.

W. D. H.

Nitrate and Nitrite Assimilation. OSKAR BAUDISCH (*Zeitsch. angew. Chem.*, 1913, **26**, 612—613. Compare A., 1911, ii, 523; 1912. ii, 286; this vol., i, 324).—Some new experiments in support of the view that nitroxyl, NOH, plays an important part in the assimilation of nitrogen have been carried out, partly on the heights of Monte Rosa, where the activity of the light was nearly equal to that of a mercury lamp. It was found that the liberation of oxygen from solutions of potassium nitrite or nitrate was greatly accelerated by carbon dioxide. Nitric oxide in presence of formaldehyde or methyl alcohol soon produced formhydroxamic acid. Nitric oxide and water, with yellow phosphorus as catalyst, gave ammonium nitrate in sunlight, and ammonium nitrite in mercury light. Nitric oxide itself was detected in moist air which had been passed through dilute alkali and then exposed to brilliant sunlight. Substances of the nature of α-amino-acids were obtained by the action of mercury light on potassium nitrite in presence of carbon dioxide, with ferric chloride as catalyst. A new course for the photo-synthesis of organic substances from air, carbon dioxide, and water is thus indicated. Ammonia was oxidised to nitrous acid in presence of oxygen under the influence of mercury light.

A diagram is given which summarises the numerous photo-reactions between simple carbon, nitrogen, and oxygen compounds, which Baudisch, Piloty, and Stoklasa have already discovered.

J. C. W.

The Influence of Sodium Sulphate on the Growth of Plants. EMIL HASELHOFF (*Landw. Jahrb.*, 1913, **44**, 641—650).—An account of numerous culture experiments undertaken for the purpose of demonstrating the influence of sodium sulphate on the growth of *Vicia faba*, *Phaseolus vulgaris*, *Hordeum vulgare*, and *Zea mays*; the results are exhibited in tabular form.

F. M. G. M.

Uniformity of Structure of the Proteins. Their Changes in Vegetable and Animal Organisms. DMITRI N. PRIANISCHNIKOV (*Bied. Zentr.*, 1913, **42**, 679—682; from *J. exper. Landw.*, 1912).—Certain plants, such as barley, when supplied with ammonium chloride produce amides at the expense of proteins, whilst the ammonia is also converted into asparagine or glutamine. No accumulation of ammonium salt takes place. In the case of peas and vetches, ammonium salts do not increase the amount of asparagine, and may even diminish it. When, however, calcium carbonate is supplied along with an ammonium salt, the latter is converted into asparagine. With lupines, the presence of ammonium salts, both alone and with calcium carbonate, diminishes the amount of asparagine, whilst the plant accumulates ammonia, chiefly from cleavage products of the proteins.

Lower plants can accumulate ammonia without injurious effects. In lower animals proteins are degraded to ammonium salts, which are not completely converted into amides. N. H. J. M.

Effect of Chloroform on the Respiratory Exchanges of Leaves. D. THODAY (*Ann. Bot.*, 1913, **27**, 697—717).—Different varieties of leaves, when treated with small amounts of chloroform, showed increased absorption of oxygen and a similarly increased production of carbon dioxide. In starved leaves the stimulation was generally prolonged.

When the amount of chloroform was sufficient to cause visible disorganisation, the production of carbon dioxide was diminished, whilst the absorption of oxygen was no longer closely correlated with the production of carbon dioxide.

Leaves of *Tropaeolum*, which contain no tannin, showed a depression of oxygen absorption greater than that of the production of carbon dioxide. In leaves of cherry, Portugal laurel, and *Helianthus*, which contain tannins, the absorption of oxygen was very rapid for a short time, and, although quickly falling, remained at a much higher level than the production of carbon dioxide.

N. H. J. M.

Methyl Alcohol of Leaves. MAURICE NICLOUX (*Bull. Soc. chim.*, 1913, [iv], **13**, 939—943).—The author has applied his method (this vol., ii, 1080) to distillates from various leaves, and has found the following quantities of methyl alcohol: ivy, 0·36 gram; spindle-tree (*Euonymus*), 0·45 gram, per kilo. of leaves. In the case of the ivy leaves, the calculations give a negative quantity for formaldehyde, due possibly to the presence of a small quantity of

ethyl alcohol or some similar substance which consumes potassium dichromate without yielding carbon dioxide. It is suggested that methyl alcohol may originate in plants in accordance with the equation $CO_2 + 2H_2O = CH_3{\cdot}OH + O_3$. Such an action would require a chlorophyll coefficient above 1, and thus be in harmony with Maquenne and Demoussy's observations (this vol., i, 232 and 429). T. A. H.

Oxydases and their Inhibitors in Plant Tissues. WILLIAM R. G. ATKINS (*Sci. Proc. Roy. Dubl. Soc.*, 1913, **14**, 143—156. Compare Keeble and Armstrong, A., 1912, ii, 673; this vol., i, 325, 803).—The absence of a brown colour in the sap expressed from plant tissues may be due: (1) to the absence of organic peroxide; (2) to the presence of tannin, preventing the action of the oxydase; or (3) to the presence of some reducing agent or inhibitor. It is considered that oxydase is concerned in the production of cork and sclerenchyma. The distribution of oxydase and of a reducing agent in Iris species is described. The colours of Iris are due to the presence or absence of a yellow plastid pigment and an anthocyan pigment. A reducing substance active in aqueous solution may inhibit the production of anthocyan pigment. E. F. A.

The Presence of a New Diastase, Salicinase, in Almonds. GABRIEL BERTRAND and ARTHUR COMPTON (*Compt. rend.*, 1913, **157**, 797—799. Compare A., 1912, i, 592).—From a study of the temperature and the reaction of the medium, which, under definite conditions, favour the greatest activity of preparations of emulsin from almonds on salicin, the authors consider that their results point conclusively to the presence of a specific enzyme, *salicinase*, capable of hydrolysing salicin. W. G.

Flower Pigments of Antirrbinum majus. II. Pale Yellow or Ivory Pigment. MURIEL WHELDALE and HAROLD LLEWELLYN BASSETT (*Biochem. J.*, 1913, **7**, 441—444).—The pale yellow or ivory pigment present in each of the main classes of varieties of *Antirrhinum* with the exception of the white is identified as apigenin. In the plant it exists as a glucoside, and is present in the inner tissues. E. F. A.

The Trypsin of Calotropis procera R.Br. and the Poison which Accompanies It. C. GERBER and P. FLOURENS (*Compt. rend.*, 1913, **157**, 600—603).—The latex of *Calotropis procera* contains a proteolytic enzyme, which is very resistant to heat, and more active in alkaline than in neutral medium. It coagulates milk, and digests casein and fibrin. Separated from the latex by the usual methods, it is eight to ten times less active than the latex itself, owing to its lability towards the agents used in the separation.

Its physiological action varies according to the animal used, and is due to a poison which accompanies it. Subcutaneously injected into a white rat, a rabbit or a fowl, it produces only a local effect

on the skin and muscle, which disappears in a few days. In the case of the guinea-pig, pigeon, and certain cold-blooded animals, it is rapidly fatal. The deaths and premonitory symptoms are similar in character to those observed with the latex of *Broussonetia papyrifera*. The toxic substance can be extracted in the form of a brown solid, by maceration with alcohol. W. G.

Partial Decomposition of Yeast-nucleic Acid by the Press Juice of Cortinellus edodes. KWANJI TSUJI (*Zeitsch. physiol. Chem.*, 1913, **87**, 379—381).—The pressed juice of the fungus *Cortinellus edodes* produces guanosine from yeast-nucleic acid, indicating that it contains enzymes converting nucleic acid into nucleosides and hydrolysing the latter. E. F. A.

Capoc and Acon and their Bitter Constituents, Waxes, and Resins. HERMANN MATTHES and LOTHAR STREICHER (*Arch. Pharm.*, 1913, **251**, 438—452).—An examination of capoc and acon fibres. Java capoc, in contrast to cotton, contains cellulose 64·3%, lignin 13%, and pentosans 23—24%. Capoc and acon fibres are brittle, and contain 8·6% and 7·2% respectively of moisture, and about 5—10% of constituents soluble in water. Acon wax (4·63%), m. p. 30·5°, n_D^{40} 1·4682, acid number 65·09, ester number 106·43, saponification number 171·52, iodine number 70·52, Reichert-Meissl value 1·76, Polenske value 1·05, contains about 31% of unsaponifiable constituents, consisting of melicyl alcohol, a *hydrocarbon*, $C_{20}H_{42}$, m. p. 69° (probably laurane), and liquid and solid phytosterols; from the latter, a *phytosterol*, m. p. 136°, and another, m. p. 170° (probably stigmasterol), have been isolated. The fatty acids obtained from acon wax consist of about 20% of solid, and about 80% of liquid, acids. The solid acid consists only of palmitic acid; the liquid acids contain about 61% of oleic acid, 38% of linolic acid, and 1% of linolenic acid.

Capoc wax, m. p. 24°, n_D^{40} 1·4618, acid number 59·85, ester number 110·29, saponification number 170·14, iodine number 69·44, Reichert-Meissl value 2·02, Polenske value 0·97, contains about 28% of unsaponifiable constituents, and yields about 15% of palmitic acid, and 85% of liquid acids similar to those obtained from acon wax.

Capoc and acon possess a bitter taste. This is due to a substance which has been isolated from acon. It is a yellow substance, which is strongly poisonous, dissolves in water, reduces ammoniacal silver oxide and Fehling's solutions, develops with sulphuric acid and potassium dichromate a blue colour changing to green, and gives precipitates with the alkaloidal reagents, although it does not contain nitrogen. It resembles picrotoxin in being decomposed by boiling chloroform into a soluble and an insoluble component.

Acon fibres contain chlorophyll and a resin. C. S.

The Existence of a Cyanogenetic Compound in a Member of the Papaveraceæ (Papaver nudicaule). MARCEL MIRANDE (*Compt. rend.*, 1913, **157**, 727—729).—The author has examined the

leaves of plants of *Papaver alpinum*, of hybrids between this and *P. nudicaule*, and of nearly pure *P. nudicaule* for a cyanogenetic compound. The aqueous distillate of the leaves contains hydrocyanic acid in the case of the hybrids and *P. nudicaule*, but none in the case of *P. alpinum*. The plants with yellow flowers contain more of this compound than those with red or white flowers, and the nearer the plant is to the pure type, *P. nudicaule*, the higher is the yield of hydrogen cyanide. This is the first instance of a member of the Papaveraceæ containing a cyanogenetic compound. W. G.

Robin and the "Phasin" of Robinia Seeds. ROBERT KOBERT *Landw. Versuchs.-Stat.*, 1913, **79-80**, 176—181. Compare succeeding abstract).—The name "robin" was applied by Kobert to a protein first prepared from the bark of *Robinia pseudacacia* by Power in 1889 (*Pharm. Rundschau*, 1890, **8**, 29), and subsequently characterised more completely by the same author (A., 1901, ii, 679), who showed especially (1) that it was toxic, but lost its poisonous properties when heated; (2) that it hydrolysed amygdalin and sinigrin; and (3) coagulated milk like rennet ferment. These observations, especially as regards the physiological action of the substance, were confirmed and extended by Lau (*Diss.*, Rostock, 1906 (?1901)), Ehrlich (*Klin. Jahrb.*, 1898, **6**, 315), and others, including the present author. In the present paper it is shown: (1) that "robin" undoubtedly behaves as a agglutinant with blood of various kinds; (2) is not toxic when injected subcutaneously into rabbits in quantities of 1 to 10 c.c. of a 4% solution; (3) does not hydrolyse sinigrin; (4) does not coagulate milk; and (5) does not precipitate ricin-serum. The toxicity of the "robin" preparations examined by Lau is ascribed to impurity or to the use of abnormally large doses of the material. The toxicity of the bark, it is suggested, may be due to the alkaloid or the glucoside it contains. From Robinia seeds a similar "phasin," which agglutinates blood, but is not toxic and has no glucosidolytic activity, has been prepared. T. A. H.

Poisonous Constituent of the Bark of Robinia pseudacacia. FREDERICK B. POWER (*Amer. J. Pharm.*, 1913, **85**, 339—344. Compare *Pharm. Rundschau*, 1890, **8**, 29; A., 1901, ii, 679).—The author traverses the statements made by Kobert (preceding abstract) as regards the toxicity, glucosidolytic activity, and milk-clotting property of "robin." Repetition of some of his previous experiments with a sample of "robin" prepared in 1904 shows that the material is still poisonous, and is capable of hydrolysing sinigrin and amygdalin. T. A. H.

Hydrogen Cyanide in Salt-Grass (Triglochin). JAN J. BLANKSMA (*Pharm. Weekblad*, 1913, **50**, 1295—1302. Compare Greshoff, *ibid.*, 1908, **45**, 1167).—Greshoff's observation of the occurrence of hydrogen cyanide in salt-grasses is confirmed. The proportion is highest in the flowers and young fruit, and falls off as the fruit ripens. These grasses contain no acetone, but

maceration with water produces ethyl alcohol and acetaldehyde, even from varieties not containing hydrogen cyanide. The mode of combination of the hydrogen cyanide in the grasses is a matter of doubt. A. J. W.

The Presence of a Nitrogenous Substance in the Seedlings from Vicia Faba. TORQUATO TORQUATI (*Chem. Zentr.*, 1913, ii, 517—518; from *Arch. Farm. sperim.*, 1913, **15**, 213—223).—A *substance* of the approximate formula $C_{11}H_{15}O_5N$, m. p. 273—275°, was isolated from the seedlings in the following way. The disintegrated material was extracted with hot water acidified with acetic acid. The proteins and pectins were separated from the filtrate by lead acetate. The filtrate from these, on neutralisation with ammonia, yielded a light yellow precipitate. This was decomposed with hydrogen sulphide, and a substance precipitated from the solution thus obtained by basic lead acetate. On decomposing the precipitate thus formed by hydrogen sulphide and concentration of the solution, the above-mentioned substance separated in crystalline form. The substance is neutral and rapidly darkens, especially in the presence of alkalis. With potassium ferrocyanide and ammonia it yields a ruby-red solution, which rapidly darkens. Permanganate is quickly reduced by it in acid solution, and it also reduces various mercuric, silver, and copper salts. S. B. S.

The Presence of a Nitrogenous Substance in the Green Pods of Vicia faba. TORQUATO TORQUATI (*Chem. Zentr.*, 1913, ii, 518; from *Arch. Farm. sperim.*, 1913, **15**, 308—312).—In addition to tyrosine, discovered by Bourquelot and Hérissey, the author has succeeded in obtaining the same chromogenic substance as that got by him from the seedlings (see preceding abstract). This substance is not contained in the seeds themselves nor in the pods of *Pisum*.

S. B. S.

Calcareous Chlorosis of Green Plants. Rôle of the Root Excretions in the Absorption of Iron from Calcareous Soils. PIERRE MAZÉ, M. RUOT, and M. LEMOIGNE (*Compt. rend.*, 1913, **157**, 495—498. Compare A., 1912, ii, 1088).—The chlorosis, which is induced in plants grown in water cultures containing an excess of calcium carbonate in suspension or soluble calcium salts in solution, can be destroyed by the addition of small quantities of organic acid to the culture solutions, the green colour returning to the leaf. The appearance of chlorosis is accompanied by a pink coloration of the culture liquid, and this gradually disappears after the addition of the acid. W. G.

[The Lime-Magnesia Ratio.] JOHN A. VOELCKER (*J. Roy. Agric. Soc.*, 1912, **73**, 325—338).—Wheat was found to be benefited by the addition of magnesia to soil in which magnesia is deficient, provided that the magnesia does not exceed the lime. An excess of magnesia over lime has a toxic effect, and diminishes the yield. Addition of lime will then be beneficial, and an excess of lime does not possess the toxic effect which magnesia in excess has.

Both magnesia and lime are capable of modifying the growth of wheat, and altering the character of the root and the composition of the grain. N. H. J. M.

[Influence of Lithium, Zinc and Lead Salts on Wheat.] JOHN A. VOELCKER (*J. Roy. Agric. Soc.*, 1912, **73**, 314—325. Compare A., 1911, ii, 922).—The results of pot experiments showed that lithium salts are toxic when the soil contains 0·003% or more of lithium, whilst amounts not exceeding 0·002% have a stimulating effect. The best results are obtained with the nitrate (which is the most stimulating, as well as the most toxic of the different salts) when the amount of lithium does not exceed 0·001%.

Zinc salts have a slightly stimulating action on wheat when the soil contains less than 0·02% of zinc. Larger amounts of zinc have a toxic action.

Lead salts have no toxic effect when the soil contains as much as 0·03% of lead. The nitrate seems to have a stimulating effect.

It is worthy of note that much larger amounts of zinc than of lithium may be present in the soil without having any injurious action on wheat, the relative amounts being 10 : 1.

As regards the period in which the stimulating action takes place, the results so far obtained seem to indicate that it is during the germination of the seed rather than later. The action may result in considerable alterations in the development of the plant, in root production, and even in the character of the grain. N. H. J. M.

The Conditions which Affect the Activity of the Amylolytic Enzymes in Wheat Flour. C. O. SWANSON and JOHN W. CALVIN (*J. Amer. Chem. Soc.*, 1913, **35**, 1635—1643).—It is known that flour when mixed with water and allowed to digest for four hours at 60° shows great diastasic activity. The results of this investigation show that the optimum temperature for the production of the maximum amount of reducing sugars is near 65°, and that the best proportions of flour and water lie between 1 : 4 and 1 : 10, little difference being observable between these limits. The transformation is mainly effected in the first hour (approx. 88% of the total change), and under favourable conditions more than two-fifths of the flour undergoes conversion into soluble substances (calculated as maltose). Small quantities of sulphuric acid, sodium hydroxide, dipotassium hydrogen phosphate, and sodium chloride all exert an inhibitory effect on the action of the enzymes of the flour, the influence being most marked with sodium hydroxide, and least with sodium chloride. Although little difference is observable between the quantities of reducing sugars formed in the action of water on various grades of flour from the same wheat, the inhibitory effect of the chemicals named is less marked with a low grade than with a straight flour. D. F. T.

The Amounts of Sulphur and Chlorine in the Rice Plant. ALICE R. THOMPSON (*J. Amer. Chem. Soc.*, 1913, **35**, 1628—1634).—An investigation on the effect of fertilisers on the sulphur and

chlorine content of the plant grown in natural soil conditions and in sand cultures. The plant was analysed before flowering, the foliage and roots being examined separately; a second examination was made of the panicles, leaves, stems, and roots at the flowering period, and a third was made of the chaff, grain, leaves, stems, and roots at maturity. Analysis was also made of the soil of the rice field and of the water supplied.

The results of the analyses are tabulated in the original.

D. F. T.

Relationship between the Weight of the Sugar Beet and the Composition of its Juice. J. ARTHUR HARRIS and ROSS A. GORTNER (*Biochem. Bull.*, 1913, **2**, 524—529).—The wide-spread belief that large beets contain less sugar % than small beets is shown to rest upon very slender foundations. W. D. H.

The Influence of Growth in the Shade on the Various Constituents of Tobacco. ALBERT STUTZER and SAMUEL GOY (*Biochem. Zeitsch.*, 1913, **56**, 220—229).—Comparisons were made of the nicotine and potassium contents of the leaves from plants which were grown in pots in the shade, and from those grown under similar conditions in direct sunlight. There was less organic matter in those grown in the shade, but the percentages of nitrogen were higher. Both series of plants were richly fed with urea nitrate. In the lower leaves from the shaded plants the amount of nicotine was both absolutely and relatively higher than in the leaves of the other plant. In the upper leaves, however, the relative percentage of nitrogen in the form of nicotine in the shaded plants was less than that in the unshaded. The dried material of the shaded plants contained more potassium than that of the unshaded.

S. B. S.

Lævulose in the Leaves of Kentucky Tobacco Grown in Italy. FILIPPO TRAETTA-MOSCA (*Gazzetta*, 1913, **43**, ii, 428—430).—By dialysis of the leaves of this tobacco, the author has isolated a sugar which was identified as lævulose by means of its phenylglucosazone, rotatory power, and other properties. R. V. S.

The Ferments of Plants of Kentucky Tobacco Grown in Italy. FILIPPO TRAETTA-MOSCA (*Gazzetta*, 1913, **43**, ii, 431—437).—A glycerol extract of the green leaves of this tobacco appears to contain oxydases, peroxydases, catalases, invertase, amylases, lipases, emulsin, and proteolytic ferments. R. V. S.

Titanium and Rare Metals in the Ashes of Leaves of Kentucky Tobacco Grown in Italy. FILIPPO TRAETTA-MOSCA (*Gazzetta*, 1913, **43**, ii, 437—440).—In the leaves of this tobacco, the author has detected lithium, cæsium (both spectroscopically), titanium (spectroscopically and by colour reactions), and barium, as well as the other elements previously found in this plant.

R. V. S.

The Ethereal Extract of the Leaves of Kentucky Tobacco Grown in Italy. FILIPPO TRAETTA-MOSCA (*Gazzetta*, 1913, **43**, ii, 440—445).—That portion of the substances extracted with ether which is insoluble in cold alcohol yields a white *substance*, m. p. 62—63°, which gives the Liebermann-Burchard reaction for the ethers of the sterols, and contains 8·54% of oxygen (compare Thorpe and Holmes, T., 1901, **79**, 982). The resin of the leaves is a substance of high molecular weight (690), which yields a bromo-derivative, m. p. 118° (decomp.), and contains 64·89% of bromine but no oxygen. Oxidation of the resin with nitric acid yields a *substance*, $C_8H_{12}O_4$, m. p. 55—56°, possibly a hexahydrophthalic acid. Its *ammonium* salt yields colloidal solutions of a very typical character. R. V. S.

First Results of Manuring Vines with Manganese Sulphate. F. A. SANNINO and A. TOSATTI (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 237—242).—In one year's experiment the yield was considerably increased (possibly owing to the added sulphate), but the dextrose of the product was less than in the case of the unmanured vines, and the acidity was greater. In the second year the increase in yield was not so marked, and the dextrose and acid were present in about normal amounts. Details are given of the testing of the wines made from the manured and from the unmanured vines.

R. V. S.

Typical Peats. HERMANN MINSSEN (*Landw. Jahrb.*, 1913, **44**, 269—330).—A comprehensive study of different kinds of peat obtained from many localities, by which the author attempts to draw up a classification. Two great groups of peat formation are indicated, that is, the peats of "high" bogs and those in "low" positions, and between these many minor types exist. The different plants of which peats are formed are studied, and the results of numerous analyses tabulated, with a discussion on the possible significance of the facts observed. F. M. G. M.

Manurial Experiments with Calcium Cyanamide, Sodium Nitrate, and Ammonium Sulphate on Sand and Peat Soils. BRUNO TACKE and FR. BRÜNE (*Landw. Versuchs.-Stat.*, 1913, **83**, 1—100).—Frank's calcium cyanamide and Polzeniuss's calcium cyanamide (which contains calcium chloride) give similar results on sandy soils. On peaty soil the latter only had 81% of the value of Frank's manure.

Calcium cyanamide should be applied not with the seed, but at least a week beforehand; and it should at once be harrowed in. Different crops show different degrees of sensitiveness, rye being more sensitive than oats and potatoes when the manure is applied as top dressing, whilst oats is specially liable to injury when the manure is applied at the same time as the seed. As regards the utilisation of nitrogen, calcium cyanamide was far behind ammonium sulphate and sodium nitrate. N. H. J. M.

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART II.

General and Physical Chemistry.

The Band Spectrum of Mercury. ERNST LIESE (*Zeitsch. wiss. Photochem.*, 1912, 11, 349—375).—The banded spectrum of mercury is readily obtained when the uncondensed discharge from an induction coil is passed through a discharge tube in which mercury is distilled from one end to the other. In addition to the bands described by Eder and Valenta, which are situated at the more refrangible end of the spectrum, the author has observed other bands stretching from the green to the red end. These bands appear to be of an intermittent character, and although visual observations indicate that their structure is similar to that of the bands at the violet end of the spectrum, it has not been possible to obtain satisfactory photographs of them.

Wave-length measurements have been made in the case of four of the more refrangible bands, and the band structure thus indicated is discussed in reference to the formulæ of Deslandres and Ritz. In neither case do the calculated frequencies agree satisfactorily with those corresponding with the series of lines actually observed in the banded spectrum. H. M. D.

Magnetic Resolution of the Spectra of Nickel, Cobalt, and Iron. (Mlle.) I. M. GRAFTDYK (*Arch. Néerland*, 1912, [iii*A*], 2, 192—220).—The resolution of the lines which occurs when a

magnetic field is applied has been investigated in a quantitative manner. For iron, the spectral region examined extends from $\lambda = 4500$ to $\lambda = 6500$, for nickel from $\lambda = 2300$ to $\lambda = 6300$, and for cobalt from $\lambda = 3300$ to $\lambda = 4200$. If H denotes the strength of the applied field, then $d\lambda/\lambda^2 H$ affords a measure of the magnetic resolution, and if this is plotted against the number of the resolved lines, a curve is obtained which represents the frequency with which a given effect is produced. The great majority of the lines give rise to triplets, but the quantitative data afford no evidence of the existence of definite series of lines. In regard to the above-mentioned frequency curves, which are very irregular in character, there appear to be maxima for values of $d\lambda/\lambda^2 H$ equal to 10·75 and $14{\cdot}25 \times 10^{-13}$ in the case of iron, and when this quantity is equal to 10·50, 11·00, and $13{\cdot}25 \times 10^{-13}$ in the case of nickel. Between these values and the normal resolution of $9{\cdot}4 \times 10^{-13}$ there appears to be no simple connexion. The frequency curve for cobalt shows no very pronounced maxima. H. M. D.

Normal and Anomalous Zeeman Effects. FRIEDRICH PASCHEN and E. BACK (*Ann. Physik*, 1912, [iv], **39**, 897—932).—The resolution brought about by a magnetic field has been examined in the case of certain oxygen, helium, hydrogen, lithium, sodium, and potassium lines. The observations are discussed with reference to the general relationships which have been found in connexion with the magnetic resolution of series lines. H. M. D.

A New Proof of the Existence of Molecules. V. NILS PIHLBLAD (*Zeitsch. physikal. Chem.*, 1912, **81**, 417—430. Compare A., 1909, ii, 277, 561, 723; 1910, ii, 946).—A continuation of the work of Svedberg and Pihlblad. Colloidal solutions, suspensions, and molecular solutions of coloured dyes were made containing particles of varying sizes, and the light absorption investigated. The substances used were aniline blue-2B, indophenol-P, azobenzene, Bordeaux-R, and fast-red-A. The methods adopted for varying the size of the particles were: (1) addition of alkali, (2) addition of a protecting colloid (for example, rubber), (3) progressive mechanical sub-division, and (4) ageing the solutions. It is shown that here as in the former work (*loc. cit.*) that the light absorption curves of the disperse systems approach those for molecular solutions as the size of the particles is decreased. With increasing size of the particles the absorption curves show a flattening. J. F. S.

Relationship between Fluorescence and Chemical Constitution. JOHANNES STARK (*Zeitsch. Elektrochem.*, 1912, **18**, 1011—1014).—Polemical, and contains a survey of the publications of H. Kauffmann made at the "Deut. Bunsen-Ges. Vers." held at Karlsruhe (*ibid.*, 481). The author opposes the view that fluorescence is a property depending in any way on molecular constitution, and cites evidence to show that it is rather an atomic property. The interpretation of the luminous effects obtained, by Kauffmann, in gases by the use of Tesla oscillations is adversely criticised.

J. F. S.

A New Method for Examining Optically Active Compounds: Anomalous Dispersion. LEO A. TSCHUGAEV (*J. pr. Chem.*, 1912, [ii], **86**, 545—550).—A criticism of Deussen's work (A., 1912, ii, 510, 1020) on this subject.

The author refers to his own investigations, and points out that he has previously proposed that the rotatory dispersion of optically active compounds may be utilised for their analysis. F. B.

The [Chemical] Efficiency of Light Energy. FRITZ WEIGERT (*Zeitsch. wiss. Photochem.*, 1912, **11**, 381—394).—The author has collected and examined the available experimental observations relating to the chemical efficiency of the light which is absorbed in photo-chemical reactions. The values of the photochemical yield for the various reactions are summarised in the following table:

	Percentage yield estimated.	
Photochemical reaction.	Thermo-chemically.	Thermo-dynamically.
Carbon dioxide assimilation	98 and 14—20	—
Anthracene $\longrightarrow$ dianthracene	—	4·5
$S_\lambda \longrightarrow S_\mu$	0·24	—
Decomposition of ammonia	2·0	0—2
Formation of ozone	46·0	27·7

H. M. D.

Photo-electric Action of the Extreme Ultra-violet on Water, Aqueous Solutions, and Ice. W. OBOLENSKY (*Ann. Physik*, 1912, [iv], **39**, 961—975).—Experiments are described which show that water is photo-electrically sensitive to ultra-violet rays of very short wave-length. The ultra-violet light was obtained from the spark discharge between aluminium electrodes, and by the interposition of screens of fluorspar, quartz, air, calcspar, glass, and gypsum, it was possible to eliminate portions of the ultra-violet spectrum in a series of stages. In this way it has been found that the most active rays are those of the extreme ultra-violet region in the neighbourhood of $\lambda = 130\ \mu\mu$. For this group of rays, the photo-electric activity of water is about 1/400th of that of cupric oxide. As the wave-length increases, the exciting power of the rays falls off very quickly, and vanishes completely when λ exceeds 202·5 $\mu\mu$.

The addition of small quantities of acids, bases, and salts has no appreciable influence on the photo-electric activity of water. In larger quantities, chlorides diminish the effect, whilst sulphates, carbonates, and nitrates increase it. The presence of the dissolved salts also causes a displacement of the spectral position of the rays which exert the maximum effect.

Ice is much more photo-electrically sensitive than water. For the unfiltered rays from the aluminium spark discharge, its activity is about 0·7 of that of cupric oxide, and for the group of rays in the neighbourhood of $\lambda = 180\ \mu\mu$, it surpasses cupric oxide in its sensitiveness. Experiments with hoar-frost show that this behaves very similarly to ice.

The meterological significance of the observations is referred to.
H. M. D.

Photo-electric Effect of Some Compounds. R. S. WILLOWS (*Phil. Mag.*, 1912, [vi], **24**, 891—892).—According to Hughes (A., 1912, ii, 880), dry zinc chloride shows no photo-electric activity, although photo-electric currents of considerable intensity are obtained with the moist substance. This observation is probably connected with the fact that the moist halogen salts of zinc emit large quantities of positive and negative ions when heated to 300°, whereas the dried salts are inactive (compare Garrett, A., 1907, ii, 524). The halogen salts are evidently unstable, and ultra-violet radiation in presence of moisture represents one of several agents, the action of which suffices to bring about decomposition. H. M. D.

Inversion of Sucrose by Ultra-violet Rays. HENRI BIERRY, VICTOR HENRI, and ALBERT RANC (*Compt. rend.*, 1912, **155**, 1151—1153. Compare A., 1911, i, 524).—A claim for priority over Berthelot and Gaudechon (compare A., 1910, ii, 813; 1912, ii, 1120) for the discovery of the inverting action of ultra-violet rays on sucrose, the inversion being a direct result of the action of these rays. W. G.

Photolysis of Different Classes of Sugars by Ultra-violet Light. DANIEL BERTHELOT and HENRI GAUDECHON (*Compt. rend.*, 1912, **155**, 1153—1156. Compare A., 1912, i, 750; ii, 715, 1120).—The simple sugars can be divided into four classes according to their resistance to light; the ketoses are attacked by ultra-violet rays ($\lambda > 0{\cdot}30\mu$), the aldoses by the rays ($\lambda = 0{\cdot}30$ to $0{\cdot}25\mu$), the straight-chain polyhydric alcohols by rays ($\lambda = 0{\cdot}25$ to $0{\cdot}20\mu$), and the ring polyhydric alcohols only by the extreme ultra-violet rays ($\lambda > 0{\cdot}20\mu$). With light of slow vibrations, producing the first stage in the action, the liquid remains neutral, and does not reduce Fehling's solution in the cold. Then, with more rapid vibrations, decomposition increases, the liquid becomes acid, and carbon dioxide can be detected in the gaseous products; the amount of hydrogen evolved increases, the solution begins to reduce Fehling's solution in the cold, and finally methane is liberated. The volumes of carbon monoxide and hydrogen evolved in the first stage always bear a simple ratio to one another. The results of a series of comparative experiments are given, and it is found that, in the case of the ketoses, the solid sugars as well as their aqueous solutions undergo decomposition. W. G.

Secondary γ-Rays Excited by the β-Rays of Radium. FREDERICK SODDY (*Phil. Mag.*, 1912, [vi], **24**, 892).—Remarks on Chadwick's paper (A., 1912, ii, 1025) calling attention to a prior publication (A., 1910, ii, 474). F. S.

The Energy of the Groups of β-Rays from Radium. ERNEST RUTHERFORD (*Phil. Mag.*, 1912, [vi], **24**, 893—894).—In the paper by the author (A., 1912, ii, 1024) the energy of the β-particle was calculated from the formula $E = \frac{1}{2}m_0C^2\ (\beta^2/\sqrt{1-\beta^2})$, where m_0 is the "slow-

speed mass," C the velocity of light, and β the ratio of the velocity of the β-particle to that of light. The correct formula should have been $E = m_0C^2(1/\sqrt{1-\beta^2}) - 1$, which nearly agrees with the former for small values of β, but departs widely as β approaches unity. The $pE_1 + qE_2$ relation of the former paper holds with the new formula; only E_1 and E_2 have new values, namely, $E_1 = 1{\cdot}12 \times 10^{13}e$, and $E_2 = 0{\cdot}356 \times 10^{13}e$; p has values between 0 and 9, and q between 0 and 2. The twelve lines between Nos. 21 and 9 fit in, with the exception of No. 11. For lines Nos. 1 to 8, there is an approximately constant energy difference, $E_3 = 0{\cdot}173 \times 10^{13}e$, which is nearly $\frac{1}{2}E_2$. These lines are due probably to radium-B, whilst line No 9 may be due to either -B or -C. The calculated energy required to excite characteristic X-radiation in an atom of atomic weight 214 is for the "K" type $1{\cdot}27 \times 10^{13}e$, and for the "$L$" type $0{\cdot}19 \times 10^{13}e$ ergs, numbers which do not greatly differ from the values of E_1 and E_3. F. S.

The Ratio of the Intensities of the Hydrogen Canal Ray Lines. FRITZ LUNKENHEIMER (*Ann. Physik*, 1912, [iv], **39**, 1071).—In reference to Stark's criticism of the results obtained by the author (A., 1911, ii, 950), it is pointed out that these have been confirmed by Vegard (*Ann. Physik*, 1912, [iv], **39**, 111). H. M. D.

Luminosity of Gases under the Influence of Cathode Rays. II. ERNST GEHRCKE and R. SEELIGER (*Ber. Deut. physikal. Ges.*, 1912, **14**, 1023—1031. Compare A., 1912, ii, 517).—An improved form of apparatus is described for the study of the luminosity of gases subjected to the action of cathode rays of gradually diminishing velocity. The effect of the alterations which have been made is to increase the length of the path over which the cathode particles give rise to characteristic luminosity from a fraction of a millimetre to several millimetres. The colour effects obtained with nitrogen, hydrogen, helium, argon, mercury, carbon monoxide, and coal gas are described. In general, three differently coloured regions of luminosity are discernible, the best results being obtained in the case of hydrogen, whilst the regions are least sharply differentiated in helium. The spectra of the different regions have been examined for hydrogen, nitrogen, helium, and mercury, and these observations indicate that the colour changes brought about by the action of the retarded cathode rays are dependent on the specific characters of the luminous particles.

By comparison of the above luminous effects with those found in the positive column of the glow discharge, it is found that the sequence of colours is not always the same, although in many cases the individual colours are identical. H. M. D.

Spectra of Low Potential Discharges in Air and Hydrogen. GORDON S. FULCHER (*Physikal. Zeitsch.*, 1912, **13**, 1137—1142).—An examination has been made of the spectrum of the light emitted by the action of slowly moving cathode rays on the molecules of nitrogen, hydrogen, and oxygen. With a sufficiently hot Wehnelt cathode, with the electrodes about 5 cm. apart and a gas pressure of about 0·1 mm. of mercury, it has been found that discharge may be effected when the

potential difference amounts to 20 volts in the case of hydrogen, 27 volts in air, and 45 volts in oxygen. The spectra of the low potential discharge are compared with those obtained in the case of high speed cathode rays. The observations with air indicate that the small speed cathode rays give rise only to the emission of the positive nitrogen bands. Between 30 and 50 volts the relative intensity of the negative bands increases, however, very rapidly with the energy of the exciting rays, and at higher potentials the intensity becomes much greater than that of the positive bands. The difference in the behaviour of the two kinds of rays may be due to the more complete penetration of the molecules by the high speed rays. As an alternative explanation it is suggested that the positive bands are emitted by molecular aggregates which are dissociated by the high speed, but not by the low speed rays.

Similar differences are found when the low and high potential discharge spectra are compared, and the intensities of different lines in the two spectra are shown in a comparative table. H. M. D.

The Emission of Negative Corpuscles by Certain Salts which have Previously been Subjected to [Cathode] Rays. M. Volmer (*Zeitsch. Elektrochem.*, 1912, 18, 1086—1090).—The author has repeated the experiments of Henriot (*Ann. Chim. Phys.*, 1912, [viii], 26, 134) and finds that he is unable to confirm them, whilst at the same time the work of McLennan is confirmed (A., 1902, ii, 297). The power of emitting negative corpuscles, after treatment with cathode rays, is restricted to comparatively few salts, including K_2SO_4, Na_2SO_4, Li_2SO_4, $CaSO_4$, $BaSO_4$, and $SrSO_4$, whilst amongst those examined which did not possess this property are KCl, KBr, KI, $BaCl_2$, $KHSO_4$, Na_2SeO_4, $(NH_4)_2SO_4$, $MgSO_4$, $K_2Cr_2O_7$, KCN, CaO, and CaS. The author directs attention to the fact that, whereas McLennan (*loc. cit.*) got an effect with the alkaline earth sulphides amounting to one-fifth that obtained with K_2SO_4, he was unable to obtain any effect whatever, and he suggests that the sulphides used by McLennan contained sulphate. The rate at which the emission of corpuscles falls off does not follow the simple exponential law, but it is found to agree very well with an empirical law of Becquerel (*La lumière*, p. 295) for the decrease of phosphorescence. $J^n(c+t)=c$, in which n has value lying between $\frac{1}{2}$ and 1. An hypothesis is propounded to explain the action; it assumes that a decomposition of the salts is brought about by the cathode rays. Two cases are differentiated: (1) in which the components are driven apart and remain as isolated entities in the mass of the substance; (2) in which the components remain within the spheres of influence of one another. In the latter case the components combine instantaneously as soon as the rays are stopped and emit at the same time a negative corpuscle, whereas in the former case the components can only recombine as diffusion brings them within the spheres of influence of one another, and this would naturally occur more quickly, and consequently a more rapid emission of corpuscles would occur, at higher temperatures. The hypothesis certainly fits the experimental facts.

J. F. S.

Effect Produced by a Magnetic Field on Ionisation Currents. William Duane (*Le Radium*, 1912, 9, 342—347).—Experiments on the effect of magnetic fields on the movements of ions have been carried out with a view to deciding whether positive electrons exist in ionised gases. A narrow pencil of α-rays from a thin-walled tube of radium emanation passed between the plates of an ionisation chamber, placed between the poles of a magnet, such that the lines of force were normal to the path of the rays and to the electric force between the plates. The whole apparatus was capable of being exhausted very perfectly, so as to increase the free paths of the ions. There is always an enormous difference in the effect of the magnet on the positive and negative currents. For the currents carried by the negative ions the field diminishes the current even at pressures of several cm. of mercury, whilst at 0·06 mm., both in hydrogen and air, a field of a few hundred gausses reduces the current to a small fraction of 1%. For the positive current in air no effect is detectable at pressures above 0·03 mm. At pressures of a few thousandths of a mm. and an electric field not above 10 volts, a magnetic field of 1000 gausses diminished the current perceptibly in air, but, with an electric field of 25 volts, even a magnetic field of 2600 gausses produced no effect.

In hydrogen the effect of the magnetic field is more marked. From Sir J. J. Thomson's theory an estimate of the mass of the ions is formed from the experiments, although a precise measurement of e/m is not possible. All the negative ions are corpuscular, and none of them can be formed by the separation of a molecule into oppositely charged parts of molecular order of magnitude. In air the value of e/m for the positive ion is less than 740 and 500 in two experiments, which is in agreement with the view that the ions are atoms and molecules of oxygen and nitrogen, for which the values of e/m would be 612, 700, 306, and 350, assuming unit charge. For hydrogen the numbers are much greater than for air, and a large proportion have values for e/m greater than 700. F. S.

The Chemical Action of Penetrating Radium Rays. III. The Influence of the Penetrating Rays on Some Inorganic Compounds. Anton Kailan (*Monatsh.*, 1912, 33, 1329—1359. Compare A., 1912, ii, 522).—Under the influence of the penetrating radium rays the following reactions have been observed. Ferric sulphate is reduced, the reduction being considerably increased in the presence of sucrose (compare Ross, A., 1906, ii, 512). The formation of hydrogen peroxide from water takes place both in acid, neutral and alkaline solutions, the amount formed being greatest with acidified and least with alkaline water. No difference is observed whether the vessel containing the water be coated with paraffin or not.

In sulphuric acid solution, potassium bromide is decomposed with the liberation of bromine. The velocity of decomposition does not increase in direct proportion to the increase in concentration of the bromide or acid, since when the concentration of either the salt or the acid is increased ten-fold, the velocity of decomposition is only increased by about one-half. Under similar conditions, the rate of

liberation of bromine from solutions of potassium bromide is only about one-twentieth to one-hundredth of that of the liberation of iodine from solutions of potassium iodide (compare A., 1912, ii, 522), when the action of any hydrogen peroxide which may be formed is neglected. Any formation of hydrogen peroxide would lead to too great a difference in the observed rates of decomposition of solutions of potassium iodide and bromide. T. S. P.

The Chemical Action of Penetrating Radium Rays. IV. The Influence of the Penetrating Rays on Some Organic Compounds and Reactions. ANTON KAILAN (*Monatsh.*, 1912, 33, 1361—1377).—The influence of the penetrating radium rays has been studied in the following cases: the catalytic action of hydrochloric acid on the velocity of esterification of benzoic acid, either in absolute or aqueous alcoholic solution, is not affected, from which the conclusion may be drawn that there is also no effect on the dissociation of alcoholic hydrochloric acid.

The formation of acid from *o*-nitrobenzaldehyde is accelerated, both in alcoholic and benzene solution; the increase in the rate of reaction with increasing concentration of the aldehyde is hardly appreciable.

Neither in ethereal nor in alcoholic solution have 100 mg. of radium chloride any action on *p*-benzoquinone, nor is the light reaction accelerated.

Solutions of oxalic acid are not affected at 25°, but the rate of inversion of unsterilised solutions of sucrose is accelerated, the acceleration increasing with increasing length of time of the experiment. Acid is formed by the action of the rays, and the extent of the inversion corresponds approximately with the amount of acid formed. The growth of mould in unsterilised sucrose solutions seems to be favoured by the action of the rays. T. S. P.

Evidence that Sodium belongs to a Radioactive Series of Elements. F. C. BROWN (*Le Radium*, 1912, 9, 352—355).—The term "radioactive element" is employed to include, not only elements undergoing atomic disintegration, but also the products of such disintegration, such as helium, and the attempt is made to show from geological evidence that sodium is a member of a radioactive series. The data derived from the quantities of lead and of helium in radioactive minerals give estimates of the age of these minerals greatly in excess of the estimate, between 6·5 and 10×10^7 years, derived from the quantity of sodium in the ocean. Accepting the higher estimate from radioactive data, the small quantity of sodium can be explained by supposing either that a parent of sodium exists in the earth, but not in the ocean, or that the sodium in the ocean, in absence of its parent, is in process of diminution by disintegration. The hypothesis explains the fact that there is a great relative excess of chlorine over sodium in the ocean, whereas in the rivers the opposite is the case. The parent of sodium is to be sought among those elements more abundant in the earth than in ocean deposits. F. S.

Radioactivity of the Springs at Vichy and Other Places. A. Laborde and Adolphe Lepape (*Compt. rend.*, 1912, **155**, 1202—1204. Compare Curie and Laborde, A., 1904, ii, 461; 1906, ii, 515).—The authors have measured the radioactivity of the waters and gases from eight springs at Vichy, and springs at several other sources, and have also determined the quantity of radium in the deposits and residues from evaporation of these waters, the results being tabulated. The deposits from a number of the springs were further examined for thorium, it being absent in four cases and in two cases present to the extent of 0·11 to 0·50%, or about one hundred times more that in the common rocks. W. G.

The Action of the Silent Electric Discharge on a Mixture of Hydrogen and Titanium Tetrachloride. I. F. Böck and Ludwig Moser (*Monatsh.*, 1912, **33**, 1407—1429).—Pure dry hydrogen is passed through titanium tetrachloride, and the gas, charged with the vapours, is submitted to the action of a silent electric discharge in a specially designed apparatus. At the ordinary temperature the walls of the apparatus became coated with a dark brown deposit, the reactions of which showed it to contain titanium trichloride, although it was not the pure substance, containing also some tetrachloride. In different experiments the composition of the deposit varied considera-ably, but on heating in a vacuum at 100° the tetrachloride could be distilled off, leaving the trichloride as a brown substance, in which the tetrachloride had been probably occluded. This brown substance is probably a labile, allotropic form of the ordinary violet titanium trichloride, since it changes into the latter when heated at 150—200° in a vacuum.

For experiments at temperatures above 200°, neither glass nor porcelain apparatus could be used, since the electric discharge penetrated them. An apparatus was, however, designed in which the solid dielectric consisted of mica, which was wrapped in thin sheets round a glass tube. This could be used for temperatures between 200° and 400°, but not higher; at these temperatures the pure anhydrous violet trichloride was obtained, the stable modification apparently having no tendency to occlude the tetrachloride. T. S. P.

The Glow Discharge in Very Pure Gases. Georg Gehlhoff (*Ber. Deut. physikal. Ges.*, 1912, **14**, 960—969).—Experiments are described which show that the stratification of the positive glow which occurs in the passage of the discharge through nitrogen and the inert gases is dependent on the presence of traces of impurities. When these are removed, the positive glow is continuous. In the case of hydrogen, the formation of strata cannot, however, be eliminated by purification of the gas, and the phenomena would therefore appear to depend in the case of the pure gases on the electrical character of the gas molecules.

The changes which occur in the discharge potential and in the cathode potential when a discharge is passed through a tube containing potassium vapour have been found to be due to the purification of the residual gas by the alkali metal and to the covering of the cathode with a layer of metallic potassium. H. M. D.

An Attempt to Determine the Dielectric Cohesion of a Rare Gas, with Small Quantities of Material. EDMOND BOUTY (*Compt. rend.*, 1912, **155**, 1207—1208. Compare A., 1911, ii, 458).—By slightly altering his apparatus, the author has been able to make measurements on 5—6 c.c. of gas instead of the 200 c.c. ordinarily required. The relation of the apparent value, B, so obtained to the true value, b, for the dielectric cohesion is given by $B = 1{\cdot}165b + 6$, which calibration with helium, neon, and air shows to be applicable from $b = 7$ to $b = 419$. Provided that the volume of the gas is not too small and that the pressure is sufficiently great, the value, γ, of the field capable of producing visible illumination in the gas is a linear function of the pressure. The apparatus can be used in following the stages of purification of a rare gas. W. G.

Electrical Resistance Measurements of Mixtures of Copper and Mercury. A. P. SCHLEICHER (*Zeitsch. Elektrochem.*, 1912, **18**, 998—1000).—The alloys examined were made in the first series of experiments by threading a number of amalgamated copper wires through a long glass tube, the spaces between the wires being filled with mercury. In this way an alloy, in which the two components could be regarded as arranged like separate wires in close contact, was imitated. The results show that for alloys in which the components are longitudinally arranged, the resistance is a linear function of the volume composition. In the second series the alloys were imitated by placing a number of short pieces (1 cm.) of amalgamated wire into the tube and filling the interstices with mercury. This arrangement represents a more or less fine-grained crystalline alloy. The results show that the relation between the volume composition and the conductivity in a linear one, but it is regarded as unlikely that such a relationship will hold for the resistance. J. F. S.

Electrical Conductivity of Copper–Tin Alloys (a Correction). R. LEDOUX (*Compt. rend.*, 1912, **155**, 1249).—A correction of two temperature-coefficients for Cu–Sn alloys, the values of which, as given in a previous paper (compare A., 1912, ii, 727), were incorrect. W. G.

Variation of the Conductivity of Aluminium Anode Films with Temperature. G. E. BAIRSTO (*Trans. Faraday Soc.*, 1912, **8**, 232—252. Compare A., 1912, ii, 123).—Further experiments with aluminium anode films confirm the exponential law of variation of conductivity with temperature, $i = A\epsilon^{a\theta}$, the value of a being independent of the time of formation, the concentration of the electrolyte, and the nature of the cation, whilst A depends on these factors. The value of a varies with the anion, and serves as a measure of the equivalent of the anion. The conductivity of a film is about constant for voltages up to about one-half of the voltage of formation, and rapidly increases at higher voltages. At temperatures above 60°, the current-voltage curves have a maximum at a voltage below that of

formation. When log i is plotted against θ, the cooling curve lies above the heating curve, but becomes parallel with it. C. H. D.

Relative Electrical Conductivity and Ionisation of Aqueous Solutions of Hydrogen Chloride between 18° and 81°. JOSEPH A. MULLER (*Bull. Soc. chim.*, 1912, [iv], **11**, 1001—1006. Compare A., 1911, ii, 266).—The conductivity of aqueous solutions of hydrogen chloride has been determined at 18°, 51°, and 81°, the concentrations at the first temperature being accurately determined and those at the higher temperatures deduced from the coefficients of expansion of the solutions employed. In each case, a solution of maximum conductivity was observed, the molecular concentrations of which expressed with respect to the concentration of acid at 18° were respectively, $C_{18} = 5 \cdot 77$ at 18°, $C_{18} = 5 \cdot 88$ at 51°, and $C_{18} = 5 \cdot 98$ at 81°, corresponding approximately with 19·6 grams of hydrogen chloride in 100 grams of solution. The ionisation of aqueous solutions of hydrogen chloride was found to diminish rapidly with increasing concentration of acid, but, for a definite concentration, to vary but little with the temperature.

H. W.

Conductivity, Temperature-coefficients of Conductivity, and Dissociation of Certain Electrolytes in Aqueous Solution at 35°, 50°, and 65°. S. F. HOWARD and HARRY C. JONES (*Amer. Chem. J.*, 1912, **45**, 500—536).—In continuation of earlier work (Hosford and Jones, A., 1911, ii, 960; Winston and Jones, A., 1911, ii, 961), conductivity measurements have been made at 35°, 50°, and 65° of aqueous solutions of sodium ferrocyanide, potassium carbonate, potassium permanganate, dipotassium hydrogen phosphate, potassium sodium sulphate, potassium chromium sulphate (violet and green), potassium nickel sulphate, ammonium chromium sulphate (violet and green), calcium bromide, calcium chromate, zinc nitrate, zinc acetate, lead chloride, lead acetate, nickel acetate, uranyl chloride, uranyl nitrate, uranyl sulphate, uranyl acetate, hydrochloric acid, nitric acid, and sulphuric acid. The molecular conductivities, temperature-coefficients, and percentage dissociation are tabulated.

Jones and MacKay (A., 1897, ii, 396) found that the conductivities for certain of the alums were not constant, but changed with time. This explains certain discrepancies between some of the results of the present investigation and those obtained in the earlier work. It has been found that the time factor for hydrolysis is greater for concentrated than for dilute solutions, and that the temperature has but little effect on it. The observation that salts containing large amounts of water of crystallisation have large temperature-coefficients is confirmed. In the case of salts which do not undergo hydrolysis, the temperature-coefficients increase with dilution. The violet forms of ammonium and potassium chrome alum have smaller conductivities than the green forms, but the difference becomes less at higher temperatures. In several instances, hydrolysis was observed; dipotassium hydrogen phosphate had a time factor which extended over several days. With the exception of uranyl acetate and dipotassium

hydrogen phosphate, the percentage dissociation decreased with rise of temperature; the phosphate acted normally after being left for four weeks. E. G.

The Electrical Conductivity of Solutions in Methylamine and Ethylamine; The Fluidity of Ammonia, Methylamine and Sulphur Dioxide, and the Fluidity of Certain Solutions in these Solvents. FRED F. FITZGERALD (*J. Physical Chem.*, 1912, 16, 621—661. Compare Franklin, A., 1911, ii, 1052).—The abnormal conductivity-dilution curves given by solutions in methylamine, ammonia, and liquid sulphur dioxide have been further investigated in conjunction with the viscosities and densities of the solvents and a number of their solutions.

Solutions of silver nitrate and potassium iodide in methylamine at $-33·5°$, $-15°$, $0°$, and $+15°$ have a maximum of molecular conductivity at about normal concentration, followed by a minimum at $N/40$, and then a progressive rise on further dilution. There is no evidence that the molecular conductivity tends to approach a maximum value at high dilutions as in the case of aqueous solutions of these substances. Some hitherto unpublished conductivity measurements by D. H. Hoagland on solutions of potassium iodide, lithium nitrate, lithium chloride, sodium nitrate, mercuric iodide, and *m*-dinitrobenzene in methylamine are given. With the exception of the values given by *m*-dinitrobenzene his results are of the same general character.

Solutions of silver nitrate, ethylammonium chloride, and lithium chloride in ethylamine have a maximum of molecular conductivity at about normal strength, followed by an asymptotic diminution on dilution, but although the dilution was carried to $N/100$ in the case of silver nitrate the molecular conductivity showed no tendency to increase again.

The temperature-coefficient of conductivity of solutions in methylamine and ethylamine changes sign on passing from concentrated to dilute solutions, as has already been observed with certain solutes in sulphur dioxide and ammonia. The solvent and ionising properties of the amines are related to those of ammonia as the properties of the alcohols to those of water. On ascending the homologous series of solvents the ionising power and the solvent action on metallic salts decreases, but the solvent action on carbon compounds increases.

The densities and fluidities at 0° of solutions in methylamine and ammonia of potassium iodide, lithium chloride, sodium nitrate, silver nitrate, silver iodide, carbamide, sucrose, *m*-methoxybenzenesulphonamide, 2 : 4-dinitroaniline, ammonium bromide, and copper nitrate were measured in a special form of Ostwald viscometer. The viscosities of these solutions decrease progressively on dilution, and the author does not attempt to trace any connexion between his conductivity and viscosity measurements.

The viscosities, η, of the pure solvents methylamine, ammonia, and sulphur dioxide were also measured. The values of the product $\eta\Lambda_\infty$, where Λ_∞ is the molecular conductivity of potassium iodide at infinite dilution, fall between 0·9 and 1·1 with ammonia and sulphur dioxide, whereas with normal solvents Walden obtained the value 0·65.

Ammonia and sulphur dioxide must therefore be regarded as abnormal in the same sense as water is abnormal. R. J. C.

Electro-capillary Pulsation of a Mercury Meniscus. ALEXANDER P. ROSHDESTWENSKY and WILLIAM C. McC. LEWIS (*Trans. Faraday Soc.*, 1912, 8, 220—231).—The most sensitive solution for use in a capillary electrometer is the ordinary sulphuric acid solution, but in the course of experiments with various electrolytes it has been found that when mercuric cyanide is used regular pulsations of the mercury surface are observed within certain ranges of potential difference (above one volt, the mercury in the capillary being the cathode) and with concentrations of $N/10$ and upwards. The period is of the order of thirty seconds, suggesting that adsorption layers are built up and destroyed. C. H. D.

The Peltier Effect and the Iron-Mercury Thermo-electric Couple. E. OOSTERHUIS (*Arch. Néerland*, 1912, [IIIA], 2, 7—38).—The magnitude of the Peltier effect at the surface of contact between iron and mercury has been measured by a calorimetric method at a series of temperatures extending from that of the room to 182°. Corresponding determinations were also made of the thermo-electric potential difference, E, the influence of temperature on which may be expressed by the equation: $E.10^7 = 169{\cdot}53t - 0{\cdot}06336t^2 - 0{\cdot}00008918t^3$. The Peltier effect, π, representing the heat change due to the passage of one ampere for one second through the contact surface, increases from $116{\cdot}44 \times 10^{-5}$ cal. at 18·5° to $151{\cdot}1 \times 10^{-5}$ cal. at 182·3°. From the two series of data it is found that the relationship $\pi = T.dE/dT$ is satisfied within the limits of experimental error. On the other hand, the equation $\sigma_1 - \sigma_2 = -T.d^2E/dT^2$, in which σ_1 and σ_2 represent the Thomson effects for the mercury and iron respectively, is quite inconsistent with the experimental data. From this it follows that the energy of the thermo-electric current cannot be accounted for on the basis of the energy changes corresponding with the Thomson and Peltier effects. H. M. D.

Electro-chemical Behaviour of Tantalum. GEORG VON HEVESY and ROLAND E. SLADE (*Zeitsch. Elektrochem.*, 1912, 18, 1001—1002).—The potential differences between tantalum and a solution of tantalum pentafluoride (0·006 mol.) were measured both with passive tantalum and active tantalum. The values Ta (passive) | TaF_5 | $= +1{\cdot}537$ volt and Ta (active) | TaF_5 | $= +0{\cdot}165$ volt, were obtained ($H = 0$).

The authors arrive at the conclusions, that in its most passive condition tantalum has a nobler potential than silver of about 1 volt, whilst active tantalum has a potential close to that of copper.

J. F. S.

New Fuel Batteries. EMIL BAUR and H. EHRENBERG (*Zeitsch. Elektrochem.*, 1912, 18, 1002—1011. Compare A., 1910, ii, 573, 574).—Several new fuel batteries have been investigated with respect to their *E.M.F.*, current output, internal resistance, and polarisation. The batteries are constructed in porcelain U-tubes embedded in

magnesia and heated by an alternating current. The cells all consist of an oxygen electrode, maintained by leading oxygen or air continuously into molten silver. The fuel electrodes consist of carbon rods, or metal tubes (iron, nickel, platinum, or copper), into which hydrogen or carbon monoxide is continuously led. The electrodes dip into molten electrolytes, which in the various cases are: potassium carbonate, sodium carbonate, and mixtures of the two, also potassium metasilicate, cryolite and alumina, and borax.

The cell C | $NaKSiO_3+KF$ | O_2,Ag has an *E.M.F.* of 1·11 volt, which is raised to 1·24 volt by leading hydrogen into the carbon compartment of the cell; the internal resistance is approximately one ohm, and the cell is polarised to the extent of about 20% when furnishing a current of 500 amperes per sq. metre of carbon surface. The hydrogen cells H_2 | $Na_2B_4O_7$ | O_2,Ag gave at 1000° different values for the *E.M.F.*, depending on the nature of the tube through which the gas diffused; a copper tube gave 0·84 volt; an iron tube, 1·007 volt; nickel tube, 0·93 volt. Incidentally it is shown that 30 litres of hydrogen diffuse through 1 sq, metre of iron in one hour at 1000°, and 69 litres through nickel under the same conditions. The carbon monoxide cells CO | $Na_2B_4O_7$ | O_2,Ag at 1000° gave with a platinum tube for the intake of the gas an *E.M.F.* of 0·61 volt, with a copper tube, 0·65 volt, and a nickel tube, 0·80 volt.

The carbon cells were investigated on the large scale, since it was decided that the polarisation was due to the relatively small quantity of silver and, consequently, lack of oxygen for the process. The following results are given: Cell C | $Na_2B_4O_7$ | O_2,Ag at 1000° had an internal resistance of 0·5 ohm, of which 0·28 ohm is due to the carbon rod and the nickel wire connected to the silver. The *E.M.F.* on open circuit is 1·002 volt. A series of *E.M.F.* values for different outputs of current is given. The cell

C | 14%Al_2O_3 + 86%Na_3AlF_6 | O_2,Ag

at 1000° has an internal resistance of 0·29 ohm, of which 0·2 ohm is due to the electrolyte; the *E.M.F.* on open circuit is 0·73 volt. The cell C | Na_2CO_3 | O_2,Ag at 1000° has internal resistance, 0·165 ohm; *E.M.F.* on open circuit, 0·92 volt. The cell

C | 90%K_2SiO_3 + 10%KF | O_2,Ag

has internal resistance 0·46 ohm; *E.M.F.* 1·0 volt on open circuit. The whole of the large cells were free from polarisation after several hours' working at a comparatively large current output. Calculations are given to show that the observed *E.M.F.* values approach very nearly to those theoretically possible. J. F. S.

Self-induction in Concentration Cells. CHARLES M. VAN DEVENTER (*Chem. Weekblad*, 1912, 9, 973. Compare A., 1911, ii, 693).—A further contribution to the author's theory of the "leaking insulator," in which he deals with a private communication from J. J. van Laar. A. J. W.

The Elimination of Potential due to Liquid Contact. II. A Simple Equation for the Calculation of the Diffusion Potential. ALEXANDER C. CUMMING (*Trans. Faraday Soc.*, 1912, 8, 86—93. Compare A., 1908, ii, 253).—A modification of Henderson's

equation for the diffusion potential (A., 1907, ii, 426; 1908, ii, 665) is proposed, applicable in special cases, but it is not possible to simplify the equation in the same way when the anion and the cation of any salt in the system have different valencies. The mobilities of the ions are taken at the experimental concentrations instead of, as in the original equation, at infinite dilution. The only data required are the conductivities and the migration ratios. The equation is tested by comparison with experimental results. C. H. D.

New Experiments on the Super-tension of Hydrogen. ALFRED THIEL and E. BREUNING (*Chem. Zentr.*, 1912, ii, 1894; from *Festschr. med. naturwiss. Ges.*, 1912, 148—159).—By an elaboration of Caspari's method for the estimation of super-tension (A., 1900, ii, 7), the following values for hydrogen have been obtained. On blank platinum, 0·06—0·08; on platinised platinum, $0·0000 \pm 0·0001$; on gold, $0·0165 \pm 0·0005$; silver, $0·097 \pm 0·002$; nickel, $0·1375 \pm 0·0005$; copper, $0·1365 \pm 0·0005$; palladium, $0·0000 \pm 0·0001$. J. C. W.

The Polyiodides. II. Periodic Phenomena in the Electrolysis of Solutions of the Alkali Iodides. ROBERT KREMANN and R. SCHOULZ (*Monatsh.*, 1912, **33**, 1291—1304).—Küster (A., 1905, ii, 698) has observed periodic phenomena during the electrolysis of solutions of sodium sulphide, and explained them by the formation of insulating deposits of sulphur on the anode, which are dissolved off again when the current strength is low, with the formation of polysulphides; the current strength again rises, depositing sulphur, and so on. If such an explanation is correct, similar phenomena should be observed during the electrolysis of solutions of the alkali iodides, iodine being temporarily deposited on the anode and then dissolved with the formation of polyiodides.

Using a registering apparatus similar to that employed by Küster, it was found that solutions of cæsium and rubidium iodides gave sometimes regular and sometimes irregular periods of the current intensity; with potassium iodide very small periods were observed, whilst sodium and lithium iodides gave no periods. With solutions of ammonium iodide, it is doubtful whether periodicity occurs.

The tendency of the alkali iodides to form polyiodides decreases in the order: cæsium, rubidium, ammonium, potassium, and lithium or sodium (Abegg and Hamburger, A., 1906, ii, 747), which is in accordance with the above observations. T. S. P.

Electrolysis in Liquefied Sulphur Dioxide. LANCELOT S. BAGSTER and BERTRAM D. STEELE (*Trans. Faraday Soc.*, 1912, **8**, 51—67).—The sulphur dioxide is dried by distillation through a long column of phosphoric oxide. When potassium or sodium iodide is electrolysed in this solvent, sulphur is always deposited on the cathode, and potassium or sodium sulphite is also formed in its neighbourhood, corresponding with the formation of a hydroxide at the cathode in aqueous solutions. Gas is not evolved in the absence of moisture.

When a solution of tetramethylammonium iodide in sulphur dioxide is electrolysed at $-35°$ in a vacuum, a dark red solution is formed at

the cathode. A special form of apparatus is used for the purpose of examining the cathode and anode solutions separately. The dark liquid contains tetramethylammonium sulphite, together with an unstable reducing substance, the nature of which is unknown. When a zinc anode is used, mixing the cathode and anode solutions gives a yellow precipitate of *zinc tetramethylammonium sulphite*,

$$Zn_3(NMe_4)_2(SO_3)_4.$$

Solutions of hydrogen bromide in sulphur dioxide do not conduct, but conductivity is produced by the addition of water, only a little of which dissolves, the remainder falling to the bottom as a hydrate of hydrogen bromide. The conductivity is attributed to the formation of an oxonium compound. Hydrogen sulphide does not form a corresponding conducting solution. Experiments have been made in which substances capable of forming oxonium compounds with hydrogen bromide, such as ether and dimethylpyrone, are added to the solution, the results indicating that the compound is in most cases slowly formed. The electrode potentials of several metals when immersed in saturated solutions of their salts in sulphur dioxide have also been measured, lead, zinc, and cadmium salts being sufficiently soluble for the purpose. C. H. D.

The Thermo-electric Properties of the System Iron–Nickel–Carbon. EUGENE L. DUPUY and A. PORTEVIN (*Compt. rend.*, 1912, 155, 1082—1085. Compare Steinmann, A., 1900, ii, 523, 524).—The thermo-electric power of a number of nickel steels, annealed or tempered, has been measured between $-78\cdot5°$ and $0°$, and between $0°$ and $100°$, by Broniewski's method (compare A., 1912, ii, 258). Curves are given showing the variation of the *E.M.F.* with the percentage of nickel in the steel, and they exhibit a marked minimum corresponding to the change martensite $\longrightarrow$ austenite. This variation in thermo-electric power with nickel content could serve as a control for the chemical analysis. W. G.

Electric Furnace for Experiments in a Vacuum at Temperatures up to 1500°. ROLAND E. SLADE (*Proc. Roy. Soc.*, 1912, *A*, 87, 519—524).—The furnace consists essentially of a platinum tube, 2 cm. diameter, 17·5 cm. long, and with walls 1 mm. thick, each end of the tube being mounted in a water-cooled brass terminal. The tube is heated by the current from an accumulator battery of twelve cells arranged in six parallel sets of two, the furnace requiring about 350 amperes at 3 volts to raise the temperature to about 1400°. It is found that the temperature can easily be kept constant within 1° for several hours at any desired temperature up to 1500°.

In order to permit of the exhaustion of the strongly heated platinum tube, the furnace and its fittings are placed in an enclosure, the pressure in which can be adjusted so as to be nearly the same as that inside the furnace tube. H. M. D.

The Hall Effect in Metals at Low Temperatures and the Theory of Magnetism from the Point of View of the Theory of Quanta. HANS ALTERTHUM (*Ann. Physik*, 1912, [iv], 39, 933—960).—The influence of temperature on the Hall effect has

been investigated for a number of metals at temperatures varying from the ordinary temperature to that of liquid hydrogen. The effect of temperature varies according to the nature of the metal, maxima being exhibited by the curves representing the behaviour of copper, cadmium, antimony, and gold, minima by the curves for aluminium and platinum, whilst in the case of iron and nickel the Hall effect diminishes with fall of temperature to 83° abs., and then remains constant down to 20° abs.

These differences indicate that the Hall effect is very complex in character, and that it cannot be explained solely on the basis of the action of the magnetic field on the motion of the free electrons. The assumption that the Hall effect is dependent on the diamagnetic character of the metal is found to be at variance with some of the observations recorded. In the case of the ferromagnetic metals there also appears to be no essential connexion between the Hall effect and the internal magnetic fields.

It is further shown that the occurrence of the Hall effect in liquid metals is very improbable. H. M. D.

Magnetisation of Water and Oxygen. PIERRE WEISS and AUGUSTE PICCARD (*Compt. rend.*, 1912, **155**, 1234—1237).—The coefficient of magnetisation of water has been obtained by measuring the attraction or repulsion produced by a specially constructed electromagnet on a quartz tube, suspended from a delicate balance and filled in turn with hydrogen, water, and a solution of manganese chloride. The value obtained for the coefficient of magnetisation for unit mass of water was $\chi = -0{\cdot}7209 \times 10^{-6}$ at 20° with a temperature-coefficient $+0{\cdot}00013$ in the neighbourhood of 20°. The value for oxygen was obtained by measuring the alteration in level of water successively under hydrogen and oxygen, and found to be $\chi = +1{\cdot}0568 \times 10^{-4}$ at 20° for unit mass. W. G.

The Magnetic Properties of Alloys. SIR ROBERT HADFIELD, EDWARD COLVER-GLAUERT, SIEGFRIED HILPERT, PIERRE WEISS, H. KAMERLINGH ONNES, EDGAR WEDEKIND, FRIEDRICH HEUSLER, E. TAKE, ALEXANDER D. ROSS, and THEODOR DIECKMANN (*Trans. Faraday Soc.*, 1912, **8**, 94—210).—A series of papers on the general question of magnetic alloys, mainly summarising work previously published (compare following abstracts). C. H. D.

Magnetic Properties of Iron-Carbon and Iron-Silicon Alloys. ERNST GUMLICH and PAUL GOERENS (*Trans. Faraday Soc.*, 1912, **8**, 98—114).—The same percentage of carbon in the form of free cementite diminishes the electrical conductivity of iron less than when present as pearlite, and also produces much less magnetic hardening. In hardened steels, the saturation value diminishes regularly with increasing carbon. In the higher carbon alloys, therefore, the coercive force increases with increasing quenching temperature.

The improvement of the magnetic qualities of iron by small quantities of silicon is unexplained. With 3 or 4% of silicon, pearlite is decomposed into ferrite and temper-carbon, and, even with rapid

cooliug, the formation of the solid solution of carbon in iron is prevented. C. H. D.

The Magnetic Properties of Special Steels at Low Temperatures. JAMES G. GRAY and ALEXANDER D. ROSS (*Trans. Faraday Soc.*, 1912, **8**, 115—133).—Specimens of steels containing chromium, silicon, phosphorus, or tungsten in addition to carbon have been examined magnetically at the ordinary temperature and at $-190°$, after annealing and also after quenching from 450° and 900°. Cooling to $-190°$ usually lowers the permeability for low values of the magnetising force and raises it for high values, so that the magnetisation curves at 15° and $-190°$ cross. The crossing point moves to higher values of the field strength with increasing carbon, or with the increase of any other added element. This holds good for quenched as well as for annealed specimens. C. H. D.

The Heusler Alloys. A. A. KNOWLTON and O. C. CLIFFORD (*Trans. Faraday Soc.*, 1912, **8**, 195—206).—A description of the magnetic properties of nine different ternary alloys of copper, manganese, and aluminium under different conditions of thermal treatment. It is not yet known under what condition the alloy of maximum magnetisation may be obtained. The hypothesis preferred is that which regards the magnet units in Heusler alloys as complex molecular groups containing at least two different kinds of crystal molecules. C. H. D.

Magnetic Susceptibility of Ferric Salts. RUDOLF H. WEBER (*Chem. Zentr.*, 1912, ii, 695—696; from *Sitzber. naturf. Ges. Rostock*, 1912, [ii], 4. Compare A., 1906, ii, 331).—For comparison a solution of manganese sulphate (0·10273 gram, per c.c., D^{20} 1·0944) was used. The ferric sulphate used had the formula $Fe_2(SO_4)_3$; its solutions containing a few drops of sulphuric acid gave lower figures for atomic magnetic susceptibility than those previously recorded (Liebknecht and Wills, A., 1900, ii, 187). Addition of sulphuric acid raised the magnetic susceptibility, as did also gradual dilution. The lowest and highest values found for χ were 0·7521 and 1·008. The addition of 1—2% by volume of sulphuric acid raised the value in one case from 0·8673 to 0·9415, and further addition of hydrogen peroxide produced no effect. A solution having the mimimal value 0·7521 gave 0·9353 on addition of 1—2% sulphuric acid with hydrogen peroxide. The addition of this small amount of sulphuric acid changed the colour from brown to yellow. T. A. H.

Specific Heat of Substances at Low Temperatures. JACQUES DUCLAUX (*Compt. rend.*, 1912, **155**, 1015—1016).—A theoretical paper in which the author discusses the hypothesis that the diminution of specific heat of the elements at low temperatures, which is very rapid at $-200°$, is due to the fact that the elements undergo polymerisation at these temperatures. W. G.

The Dissociation Pressure and Melting Points of the System Copper–Cuprous Oxide. ROLAND E. SLADE and F. D. FARROW (*Proc. Roy. Soc.*, 1912, *A*, **87**, 524—534).—The investigation of the

melting-point diagram for mixtures of copper and cuprous oxide has shown that two liquid layers are formed at temperatures above 1195°. At this temperature, the co-existing liquids contain respectively 20·2% and 94·54% of cuprous oxide. From analyses of the two layers obtained by quenching mixtures heated to higher temperatures, it appears that the composition changes only to a small extent with rise of temperature. The actual change observed is in the direction of an increase in the mutual miscibility of the two layers.

With the aid of the tube furnace described previously (this vol., ii, 16), the authors have measured the equilibrium pressures determining the co-existence of the three phases—liquid 1, liquid 2, and gas. The values recorded are 4 mm. at 1205°, 10 mm. at 1240°, 12 mm. at 1260°, and 25 mm. at 1324°. From the data at 1205° and 1260°, the heat of dissociation is calculated to be −90060 cal., and from the data at 1260° and 1324°, −55890 cal. From these numbers it is obvious that the heat of dissociation varies with the temperature, a result which is to be expected in view of the change in composition of the two liquid phases. H. M. D.

Cryoscopic Determinations in Iodine. ERNEST BECKMANN (*Zeitsch. anorg. Chem.*, 1912, **77**, 200—208).—The material to be added is compressed to form tablets, either alone or with iodine. The constant found is 210, the value 253·5 (Timmermans, A., 1906, ii, 429) being too high. The theoretical value is found to be 201·4. The following molecular formulæ are found: SnI_4, SbI_5, AsI_5, HgI_2, Al_2I_6. Potassium iodide has a normal molecular weight in dilute solution, but polymerises at higher concentrations. Cæsium, sodium, and lithium iodides are polymerised at all concentrations.

C. H. D.

Polymorphism. EFISIO MAMELI and ANNA MANNESSIER (*Gazzetta* 1912, **42**, ii, 566—582. Compare Mameli, A., 1910, ii, 182).—The authors have determined the cryoscopic constants of the α- and β- modifications of chloroacetic acid, using naphthalene, *cyclo*hexanone, *o*-nitrobenzoic acid, butyric acid, propionic acid, *p*-xylene, *m*-cresol, safrole and acetic acid, and find them to be identical within the limits of experimental error (the means being K_α 52·41, K_β 51·67). Hence both have the value which, according to van't Hoff's formula, should belong to the α-form only.

The molecular weights of water, phosphoryl chloride, aniline, pyridine, and quinoline dissolved in the β-form have also been determined, the results being similar to those obtained with the α-form (*loc. cit.*). R. V. S.

Cryoscopic Researches. ÉMILE BAUD (*Bull. Soc. chim.*, 1912, [iv], **11**, 945—950).—The formula given by Luginin and Dupont (A., 1912, ii, 1040) implies that in paracetaldehyde the lowering of freezing point due to the solution of a second substance is proportional to the molecular concentration. This is only true for certain solvents within certain limits of concentration, and a study of mixtures of (*a*) toluene and ethylene dibromide and (*b*) toluene and bromoform shows

that the formula given by Baud and Gay (A., 1910, ii, 689) agrees better with the experimental results and is more generally applicable. Where heat changes occur on admixture, the heat of dilution must be taken into account, and for such cases an equation has been given already (A., 1912, ii, 233). Such cases are illustrated in this paper by curves for mixtures of acetic acid with (*a*) benzene and (*b*) ethylene dibromide. T. A. H.

Thermal Constants of Camphor. JOUNIAUX (*Bull. Soc. chim.*, 1912, [iv], **11**, 993—1001).—The author finds that the value, 500, previously adopted for the cryoscopic constant of camphor is slightly too high, and prefers the figure 495. From this, he deduces the value 8·24 cal. for the latent heat of fusion of camphor, whilst from considerations of the vapour tension of camphor at various temperatures, the number 8·23 cal. is obtained. Further, by the application of Trouton's formula, the latent heat of vaporisation is calculated to be 93·47 cal. This value is confirmed by two series of calculations, the one based on the vapour tension of liquid camphor, the other on the density of camphor vapour (compare Vanstone, T., 1910, **97**, 4). From the number so obtained, the ebullioscopic constant is calculated to be 49·7 by use of van't Hoff's formula, and confirmation of this value is deduced from Vanstone's experiments (*loc. cit.*) on the vapour tension of camphor and borneol and of the solid solution of these two substances. H. W.

Ebullioscopy of Iodine. ERNST BECKMANN (*Zeitsch. anorg. Chem.*, 1912, **77**, 275—281).—Ebullioscopic determinations may be made with liquid iodine by using a jacket of boiling aniline. Mixed platinum and silver beads are used in the inner vessel, silver beads alone becoming cemented by a layer of silver iodide. The mean ebullioscopic constant of iodine (b. p. 184°) is 105. Tin, antimony, and bismuth dissolve in the monatomic form, whilst aluminium and iron dissolve as Al_2I_6 and Fe_2I_6, whereas all other solutions indicate a molecule FeI_3. Alkali iodides give values which are more nearly normal than in the cryoscopic tests (this vol., ii, 19), but a tendency to give high values is still observed, especially in sodium and lithium iodides. C. H. D.

Vapour-Pressure of Concentrated Aqueous Solutions. EDGAR P. PERMAN and TUDOR W. PRICE (*Trans. Faraday Soc.*, 1912, **8**, 68—85).—The vapour pressure of concentrated aqueous solutions of carbamide, glycerol, sucrose, raffinose, potassium chloride, and calcium chloride has been determined over a range of concentration at temperatures of 70° and 90°. The air-current method (*Proc. Roy. Soc.*, *A*, **72**) is employed. The lowering of the vapour pressure is proportional to the concentration, except at very high concentrations. Babo's law holds good in many cases. Hydration is found to be a function of the concentration. C. H. D.

Triple Point of Methane. C. A. CROMMELIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 666).—The temperature and pressure at which solid, liquid, and gaseous methane co-exist have been found to

be $-183{\cdot}15°$ and $7{\cdot}0$ cm. of mercury. A previous determination by Olszewski gave $-185{\cdot}8°$ and $8{\cdot}0$ cm. H. M. D.

The Critical Coefficient and the Molecular Weight of Substances at the Critical Point. A. BOUTARIC (*Compt. rend.*, 1912, **155**, 1080—1082).—A mathematical paper in which the author discusses the relationship between the critical coefficient and the molecular weight of a substance. Taking the value $b/v = 1{\cdot}20$ as a mean of thirty determinations, where b is the constant in van der Waals' equation and v the molecular volume at the boiling point, he shows that if the value rises above $1{\cdot}2$, the substance must be considered as polymerised at its critical point. This is the case for water, alcohol, and thiophen. W. G.

The Limit of Formation of Endothermic Compounds at Very High Temperatures. EMIL BRINER (*Compt. rend.*, 1912, **155**, 1149—1151).—A theoretical paper in which the author, taking the values for the heat of formation of molecules from atoms as found for various elements by different observers, shows that compounds said to be endothermic will become exothermic at temperatures sufficiently elevated, and their concentration will reach a maximum and then diminish with further rise in temperature. Taking the case of nitric oxide and applying van't Hoff's equation : $(dlnK_1)/(dT) = -Q_1/(RT^2)$, he shows that, when the temperature is sufficiently high for the molecules of nitrogen and oxygen to be completely dissociated, then the concentration of the nitric oxide will diminish with rise in temperature. W. G.

The Behaviour of Iodine and Sulphur at Extremely High Temperatures, from Explosion Experiments. NIELS BJERRUM (*Zeitsch. physikal. Chem.*, 1912, **81**, 281—297).—The vapours of iodine and sulphur were investigated at temperatures between 3404° and 2299°. The experiments were conducted by mixing hydrogen iodide and hydrogen sulphide respectively with known amounts of electrolytic gas and exploding the mixture in a steel bomb of about 10 litres capacity. The maximum pressure generated by the explosion was determined by the displacement of a steel membrane, which was photographically recorded. Very full working details of the apparatus are given in the paper, and from the experiment with hydrogen iodide it is shown that the heat of formation of the molecule I_2 from its atoms is 35700 calories at temperatures in the region of 3000°, as compared with 34340 calories obtained by Bodenstein and Starck at 1000° (A., 1911, ii, 20). The atomic heat of iodine vapour is found to be slightly less than 3 at 3000°, the mean value obtained from many experiments and corrections, introduced for reasons given, is $3{\cdot}1 \pm 0{\cdot}3$ between 0° and 3000°. This value, being so near to the theoretical figure for monatomic gases, is held to show that, even at such high temperatures, the gaseous molecules have only translational energy, and no rotational energy as might have been expected for such a heavy atom as iodine. A series of results for sulphur is recorded, but it was found impossible to deduce

any trustworthy figures from them, since it is shown that at high temperatures a reaction occurs between sulphur vapour and water with the formation of sulphur dioxide. J. F. S.

Heat of Formation of Some Organic Fluorine Compounds. IV. FRÉDÉRIC SWARTS (*Bull. Acad. roy. Belg.*, 1912, 481—523).—A study of the heat of combustion of various fluorinated phenols, anilines, and aromatic nitro-compounds with a view to determining the influence of these groups on the variation of the internal energy of a compound produced by the replacement of hydrogen by fluorine. Owing to the difficulty of preparing *o*-fluoro-derivatives in any quantity, a complete study of the effect of position isomerism was not possible. The increase in heat of formation caused by the replacement by fluorine of one atom of hydrogen in benzene is 14 calories (compare A., 1907, ii, 9; 1908, ii, 354). The presence of a nitro-group has a depressing effect reducing this value to 8 to 9 calories. The introduction of a second nitro-group meta to the first still further reduces the figure to 7·2 calories, whereas *m*-dinitrobenzene shows an increase of 0·8 calorie over nitrobenzene, the fluorine being absent. The presence of an hydroxyl group causes an increase in this figure, the heat of formation of *m*-fluorophenol exceeding that of phenol by 23 calories, this being the value previously obtained with aliphatic hydrocarbons (*loc. cit.*). In the case of the phenols it was possible to study the effect of the position of the $-OH$ group relative to the fluorine atom. The meta-derivative shows the highest increase, the para- being second, whilst in the ortho-position the $-OH$ group has no effect whatever on the increase in the heat of formation. The replacement of the hydroxyl hydrogen by ethyl diminishes by 3 calories the increment value due to the $-OH$ group in the meta- and para-isomerides.

In the case of the substituted anilines, the amino-group causes a rise in the increased value of the heat of formation, the meta-isomeride again giving a higher value than the para. This difference, however, practically disappears in the case of the acetanilides.

A few tri-substituted benzene derivatives have also been examined, but no very definite conclusions could be drawn from the results, except that the nitro-group, in the ortho-position to the fluorine, still exerts a strong depressing effect on the heat of formation. Two aliphatic nitro-compounds were also examined, and a similar lowering in the heat of formation due to the nitro-group was proved in both cases.

Full numerical data are tabulated. A description of the preparation and properties of a number of new fluoro-compounds, used for this work but not as yet described, will shortly be published in a separate communication. W. G.

Thermochemical Researches on Solution. NICOLAS KOLOSOVSKI (*Bull. Acad. roy. Belg.*, 1912, 591—609 *).—The author gives a brief résumé of the various theories of solution, and then proceeds to a thermochemical examination of the problem by determining the heat of solution of sodium chloride in aqueous solutions of

* and *J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1659—1674.

alcohol, this solvent being his example of a binary mixture. The measurements were made in a Berthelot calorimeter, the alcohol used being purified by treatment with calcium oxide and potassium permanganate, followed by distillation. The sodium chloride was recrystallised, carefully dried, and introduced in a small silvered copper vessel. Measurements were made with mixtures of alcohol and water varying from 0 to 200 molecules of alcohol per 200 molecules of water, and a maximum absorption of heat was found for the solution containing about 33% alcohol. This value coincides approximately with that obtained by Dupré and Page (compare *Phil. Trans.*, 1861, **151**, 591) by the maximum heat of solution of alcohol in water. The author considers that his results support the theory of stable hydrates in solution. W. G.

Heat of Vaporisation of the Metals. ARTHUR WEHNELT and CHR. MUSCELEANU (*Ber. Deut. physikal. Ges.*, 1912, **14**, 1032—1034).—A strong current is passed through a discharge tube provided with a platinum cathode coated with calcium oxide and an anode of the metal the heat of vaporisation of which is to be determined. The current strength, anode fall of potential, time during which the current is passed, and the loss in weight of the anode are measured. From these data it is shown that the heat of vaporisation of the anode metal can be calculated. In this way the following values have been obtained: mercury, 63·6; cadmium, 181·0; zinc, 365·8; magnesium, 1700·0, and bismuth, 161·5. H. M. D.

Free Energy of Organic Compounds. I. Reversible Synthesis of Carbamide and of Ammonium Cyanate. GILBERT N. LEWIS and GEORGE H. BURROWS (*J. Amer. Chem. Soc.*, 1912, **34**, 1515—1529).—It is pointed out that a reaction is only possible thermodynamically when the total free energy of the products is less than that of the reacting substances, and that true equilibrium only exists when the difference of free energy between the factors and the products is zero. The free energy affords the only true measure of chemical affinity, and when the free energies of all the substances involved in a reaction are known, it will be possible to predict the direction and extent of the reaction. It is therefore desirable that the free energy of important compounds should be known with direct reference to the elements of which they are composed. In order to obtain the free energy of an organic compound, it is necessary that the compound should be synthesised from its elements by a series of processes in each of which a true equilibrium is investigated. In the present paper, an account is given of a study of the synthesis of carbamide and ammonium cyanate from ammonia, carbon dioxide, and water, the free energy for these three substances having already been determined.

A study of the equilibrium between carbamide, carbon dioxide, ammonia, and water was made by heating aqueous solutions of carbamide in sealed tubes at 132°, 111°, and 77°, and afterwards analysing the contents of the tubes. Similar experiments were made with solutions of ammonium carbamate. The free energy change of

the reaction $2NH_3 + CO_2 = CO(NH_2)_2 + H_2O$ being zero at equilibrium, it follows that if the free energies of ammonia, carbon dioxide, and water in this mixture are known, that of carbamide is also known. It was necessary therefore to determine the relations between the free energies of these substances in the equilibrium mixture and their free energies under normal conditions. This was effected by determining the vapour pressure of water, carbon dioxide, and ammonia above the equilibrium mixture; from the data so obtained the free energy of carbamide in that mixture could be calculated. The activity of carbamide in the equilibrium mixture was then ascertained in relation to that of solid carbamide by determining the distribution of carbamide between the equilibrium mixture and ethyl acetate. From the results obtained it is shown that for $CO_2(\text{gas}) + 2NH_3(\text{gas}) = CO(NH_2)_2(\text{solid}) + H_2O\ (\text{liquid}) : \Delta F = -1772$.

The relative activity of carbamide in the solid state and in dilute aqueous solution was next determined in an indirect way by means of a study of the vapour pressure of water at 25° over various aqueous solutions of carbamide, and it was found that for $CO(NH_2)_2(\text{solid}) = CO(NH_2)_2(\text{molal}) : \Delta F = -1562$. This when combined with the previous equation gives $CO_2(\text{gas}) + 2NH_3(\text{gas}) = CO(NH_2)_2(\text{molal}) + H_2O(\text{liquid}) : \Delta F = -3334$.

The equilibrium between carbamide and ammonium cyanate in dilute aqueous solution has been determined by Walker and Hambly (T., 1895, **67**, 746), Walker and Kay (T., 1897, **71**, 507), and Fawsitt (A., 1903, ii, 15). From their results and the value of the heat of the reaction, $CO(NH_2)_2 = NH_4^{\cdot} + CNO'$, recorded by Walker (A., 1903, ii, 136), it is found that for $CO(NH_2)_2(\text{molal}) = NH_4^{\cdot}(\text{molal}) + CNO^-(\text{molal}) + H_2O(\text{liquid}) : \Delta F = 2766$. This constant enables the free energy of formation of hydrogen cyanide to be calculated.

E. G.

New Forms of Whirling Gaseous Combustion and Their Analogy with the Appearance of Certain Astronomical Phenomena. JEAN MEUNIER (*Compt. rend.*, 1912, **155**, 1243—1246).—A further study of the "spiral flame" (compare A., 1912, ii, 432). By increasing the pressure on the gas supplying the wide flame to one-tenth of that supplying the jet, a different result is obtained, the narrow flame being bent back, and new phenomena appear. Diagrams are given showing the result, and a further analogy is drawn between these phenomena and star formation. W. G.

Polymerisation of Liquids and a General Method for Determining its Relative Value. MADISON M. GARVER (*J. Physical Chem.*, 1912, **16**, 669—678. Compare A., 1912, ii, 830).—The total pressure on a liquid (internal and external) is balanced by a kinetic pressure equal to that the liquid would exert if it were a perfect gas at the same temperature and density. This equilibrium is maintained by reason of the fact that the degree of polymerisation of the liquid is a function of the temperature and density, and thus polymerisation acts as a stabiliser to the system, that is to say, a "source and sink" of heat energy.

If H is the heat of polymerisation per gram of a vapour with molecular weight m, Hm is the heat of polymerisation per gram-molecule and is proportional to n, the number of molecules polymerised per gram-molecule on liquefaction, that is, $Hm = Kn$. The author assumes that K has the same value for all vapours at the same temperature and writes $H_1m_1/H_2m_2 = n_1/n_2$, where m_1 and m_2 are the molecular weights of the vapours of two different substances. It follows simply that $H_1m_1/H_2m_2 = x_2(x_1 - 1)/x_1(x_2 - 1)$, where x_1 and x_2 are the respective polymerisation factors of the two liquids.

Hence, knowing the amount of polymerisation which occurs in any one substance on passing from the gaseous to the liquid state, it is possible to calculate the amount of polymerisation of any other liquid at the same temperature from the relative values of H and m. If the absolute degree of polymerisation of the liquid is required, the value x must be multiplied by the polymerisation coefficient of the vapour.

The author calculates the values of x for water between 0° and 200° from the specific volumes, and, using these values, deduces x for thirteen organic liquids at their respective boiling points. It has already been suggested that the so-called "normal" liquids of Ramsay and Shields are polymerised and the values of x now obtained, ranging between 1·40 and 2·48, confirm this view. The apparently exceptional behaviour of acetic acid (*loc. cit.*) is shown to have been due to an error in calculation. R. J. C.

A Thermodynamic Measure of Polymerisation. MADISON M. GARVER (*J. Physical Chem.*, 1912, **16**, 679—681. Compare A., 1912, ii, 536).—The proof previously given that the degree of tension in a surface film is equal to the intrinsic pressure of the liquid referred to the density in the surface film involved the use of the function ϵ, the range of molecular action in the surface film.

The author's basic equation $\gamma/2\epsilon = \rho RT/m$ is now deduced without any assumption as to the meaning of ϵ, so that it constitutes "a secure foundation upon which to build a thermodynamic theory of the degree of polymerisation of liquid substances." R. J. C.

The Second Virial Coefficient for Monatonic Gases and for Hydrogen Below the Boyle Point. W. H. KEESON (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 643—648. Compare A., 1912, ii, 1138).—Assuming that the potential energy of the attraction between the molecules is proportional to r^{-q}, where r is the distance between the molecular centres and q a constant, the author has examined the behaviour of hydrogen, argon, and helium at low temperatures with the object of deducing the value of the exponent q. In the case of hydrogen the data agree with $q = 4$. For argon, the interval of temperature for which data are available is too small to allow of a definite conclusion being reached. At temperatures below $-100°$, the data for helium indicate also that $q = 4$, although the behaviour of the gas at higher temperatures is not in agreement with this value.

H. M. D.

Physical Constants of Certain Important Chlorinated Hydrocarbons Used as Solvents. WALTER HERZ and W. RATHMANN (*Chem. Zeit.*, 1912, **36**, 1417—1418).—Measurements have been made of the densities, coefficients of expansion, and vapour pressures of chloroform, carbon tetrachloride, trichloroethylene, tetrachloroethylene, *s*-tetrachloroethane, and pentachloroethane at a series of different temperatures. The densities at 25° and the coefficients of expansion are respectively:—chloroform, 1·4791, 0·001257; carbon tetrachloride, 1·5835, 0·001227; trichloroethylene, 1·4542, 0·001193; tetrachloroethylene, 1·6080, 0·001078; *s*-tetrachloroethane, 1·5881, 0·000998; pentachloroethane, 1·6712, 0·0009097. From the vapour-pressure data it is apparent that the six substances form a group for which the Ramsay-Young rule is valid, the value of the ratio $T^{\circ}_{760}/T^{\circ}_{300}$ being equal to about 1·085. From the variation of the boiling point with the pressure between pressure limits of about 0·5 and 1 atmosphere, the following molecular heats of vaporisation have been calculated—trichloroethylene 7436 cal., tetrachloroethylene 8554 cal., *s*-tetrachloroethane 9134 cal., pentachloroethane 8829 cal. These values are in agreement with Trouton's rule. H. M. D.

The Drawing Out of Metals. MAURICE HANRIOT (*Compt. rend.*, 1912, **155**, 971—974).—A study of the hardness, breaking strain, and elongation of metals when submitted to drawing-down. Metals only slightly hardened, although to different degrees, have practically the same breaking strain and elongation. Drawing out tempers metals much more highly, when they are almost completely annealed, whereas with metals possessing more than a certain degree of hardness it seems to exert a kind of annealing effect. Tempering by traction, as measured by increase in hardness, only commences after the metal has undergone a permanent deformation. W. G.

Viscosity Law for Liquids. ALEXIUS J. BATSCHINSKI (*Physikal. Zeitsch*, 1912, **13**, 1157).—If the specific volumes of a non-associated liquid at a series of different temperatures are plotted with reference to the fluidities at the corresponding temperatures, it is found that the points obtained lie very nearly on a straight line. From this relationship the author draws the conclusion that the viscosity of a liquid is determined by the specific volume. H. M. D.

Effect of the Transition Layer of a Liquid on its Surface Tension. RICHARD D. KLEEMAN (*Phil. Mag.*, 1912, [vi], **24**, 876—885).—It is shown that the formation of a transition layer at the surface of a liquid, in which the distribution of the molecules is different from that in the interior of the liquid, has the effect of decreasing the magnitude of the surface tension. A formula is deduced from which the value of the surface tension may be calculated for the case where no transition layer is formed. This is applied to the data for ethyl ether, carbon tetrachloride, methyl formate, and benzene. The surface tension values thus obtained are nearly twice as large as the experimentally determined surface tensions. Since the differences represent the external work done in the formation of the transition layer, it is

evident that the influence of the formation of the transition layer on the surface tension is very considerable. This influence is approximately independent of the temperature.

The formula referred to above may also be applied to liquid mixtures. In this case the difference between the calculated and observed surface tensions represents the external work during the formation of the transition layer, and in altering the relative proportion of the constituents. H. M. D.

The Laws of Surface Adsorption and the Potential of Molecular Attraction. J. R. KATZ (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 445—454).—The adsorption of water by finely divided quartz and anorthite has been examined. Weighed quantities of these substances, both obtained synthetically, were left for several days in contact with air exposed to the action of a 1% solution of sulphuric acid. The substances were then placed over mixtures of sulphuric acid and water of known vapour pressure until the weight had become constant. The loss of weight on ignition then gave the quantity of water adsorbed.

If the quantity of adsorbed water is marked off as abscissa and the relative vapour pressure p/p_0, where p_0 refers to pure water, as ordinate, characteristic curves are obtained. The first part of the curve is nearly horizontal, but when the adsorption reaches a certain value it rises very quickly and again becomes approximately horizontal.

This form of curve is supposed to be connected with the variation of the vapour pressure with the thickness of the water film on the surface of the solid. When the formula, $RT \ln p/p_0 = k$, which connects the vapour pressure p with the molecular attraction k is applied to the adsorption data, it is found that the attraction potential diminishes rapidly with increasing thickness of the film, but that there is a fairly well-defined radius of attraction, which in the case of water on the quartz surface amounts to $1{\cdot}3 \times 10^{-6}$ cm., and on the anorthite surface to $6{\cdot}2 \times 10^{-6}$ cm. H. M. D.

Adsorption by Clays. IV. PAUL ROHLAND (*Biochem. Zeitsch.*, 1912, **46**, 374—375).—The colouring matter of waters from sulphite cellulose factories is not adsorbable by clays unless treated with potassium ferrocyanide, when the pigment is converted into Prussian-blue. S. B. S.

Thermal Dissociation and Constitution of Readily Decomposable Salts. K. FRIEDRICH (*Centr. Min.*, 1912, 174—184, 207—220).—An electrical apparatus is described in which the tem-

Decomposition of	into	commencing at	Decomposition of	into	commencing at
$Fe_2(SO_4)_3$	Fe_2O_3	705°	$3ZnSO_4$	$3ZnO,2SO_3$	840 ca.
$CoSO_4$	CoO	880	$3ZnO,2SO_3$	$3ZnO$	935
$NiSO_4$	NiO	840	$MnSO_4$	?	1030
$2CuSO_4$	$2CuO,SO_3$	740	$Al_2(SO_4)_3$	Al_2O_3	770
$2CuO,SO_3$	$2CuO$	845	Ag_2SO_4	$2Ag$	1085
$4CuO$	$2Cu_2O$	1040 ca.			

perature of a substance can be gradually raised, during sixty minutes, up to 1350°. The temperatures are plotted against time, and heating (and heating-velocity) curves are given. The results obtained at atmospheric pressure and in a still atmosphere are shown on page 27.

$MnSO_4$ has m. p. 700°; transformation point 860°. Ag_2SO_4 has m. p. 660°; transformation point 410°. $ZnSO_4$ and $PbSO_4$ have the transformation points 740° and 850° (approx.) respectively.

L. J. S.

Thermal Dissociation and Constitution of Readily Decomposable Minerals. K. Friedrich and L. Garrett Smith (*Centr. Min.*, 1912, 616—626, 651—660, 684—693).—Various mineral carbonates were heated gradually during one hour up to 1130°, and the heating (and heating-velocity) curves plotted. The results obtained at atmospheric pressure and in a still atmosphere are tabulated below:

Substance.	Commencing decomposition.	Maximum decomposition.
Cerussite from Mies, Bohemia	about 315°	335°
Calamine from Thasos, Turkey	395	440
Chalybite from Ivigtut, Greenland	ca. 400 ?	460
,, ,, Neudorf, Harz		480
,, ,, Niederschelden, Westphalia		500
Rhodochrosite from Colorado	525	570
,, ,, Peru	510 ?	550
Magnesite from Kaiserberg, Styria	570	600
Calcite from Löwenberg, Silesia	895	910
Aragonite from Bilin, Bohemia	895	910
Strontianite from Hamm, Westphalia	over 1130	—
Witherite (locality ?)	,, 1130	—

In all cases, except for cerussite, strontianite, and witherite, the decomposition into oxide and carbon dioxide is complete. Cerussite alters into a basic carbonate at about 315—335°, and this is decomposed into lead oxide and carbon dioxide at 430—460°. Strontianite and witherite show an absorption of heat, corresponding with a transformation at 830—860° and 780—815° respectively.

In addition to these simple carbonates, various double carbonates (dolomite, ankerite, etc.) were also examined, and heating curves are given. Analyses are given for each mineral examined.

L. J. S.

Mechanism of Osmosis. Alf. Gillet (*Bull. Soc. chim. Belg.*, 1912, **26**, 502—503).—A mathematical amplification of some points discussed in a previous paper (A., 1912, ii, 1043). H. W.

The Kinetic Theory of the Osmotic Pressure of Concentrated Solutions, and the Agreement of Henry's Law for Concentrated Solutions of Carbon Dioxide in Organic Solvents at Low Temperatures. Otto Stern (*Zeitsch. physikal. Chem.*, 1912, **81**, 441—476).—The author deduces an expression, which shall represent the osmotic pressure of concentrated solutions, from theoretical considerations based on the van der Waals gas equation. The discussion of the formula leads to the conclusion than a given

substance will obey the osmotic laws much better than the same substance obeys the gas laws when it is in the gaseous condition. The second part of the paper is concerned with the experimental investigation of the formula deduced in the first part. This consists in examining solutions of carbon dioxide in ethyl alcohol, methyl alcohol, acetone, ethyl acetate, and methyl acetate at temperatures of $-78°$ and $-59°$, and at pressures from 50 mm. to 760 mm. of mercury. The experimental results show that Henry's law holds very exactly for concentrated solutions when expressed in terms of "solubility" (Ostwald), whereas in terms of the absorption coefficient (Bunsen) it does not hold. The osmotic pressure, calculated from the measurements, is in good agreement with that calculated from the theoretical formula deduced in the first part of the paper. The last portion of the paper consists of a consideration of Dolezalek's "Theory of Gaseous Solubility" (A., 1910, ii, 184) in connexion with the results obtained by the author. It is shown that the explanation given by Dolezalek for irregularities leads to results which are entirely opposed to those generally accepted.
J. F. S.

Activity of the Ions and the Degree of Dissociation of Strong Electrolytes. GILBERT N. LEWIS (*J. Amer. Chem. Soc.*, 1912, **34**, 1631—1644).—A review is given of the facts hitherto published bearing on the question of the degree of dissociation of electrolytes, and their probable theoretical significance is discussed. Attention is directed more particularly to the properties of strong uni-univalent electrolytes, as these afford the only data from which conclusions, free from ambiguity, can be drawn.

It is shown that many chlorides, bromides, and iodides are equally dissociated, whilst nitrates, chlorates, bromates, and salts of silver and thallium are somewhat less dissociated. The degree of dissociation of uni-univalent salts is probably much less than is usually supposed. If it is assumed that potassium chloride is dissociated to the extent of 74% at $0{\cdot}1M$, 82% at $0{\cdot}05M$, and 89% at $0{\cdot}02M$, then in most cases up to $0{\cdot}1M$ the activity of the ions is proportional to the concentration of the solution.

According to this view, the deviation of strong electrolytes from the mass law is to be attributed largely to a general increase in ionic mobility with the total ion concentration. This is in agreement with Jahn's theory (A., 1900, ii, 523), but differs from that advanced by Franklin and Kraus (A., 1905, ii, 298) and Lewis and Wheeler (A., 1906, ii, 650). According to the former explanation, it is the velocity of the ions which fails to obey the laws of the ionic theory, whilst, according to the latter, it is the degree of dissociation. Probably neither explanation is adequate by itself, but the evidence now adduced in support of the view that the ions in aqueous solution have a variable mobility renders further investigation desirable. E. G.

Neutralisation Curves and Dissociation Constants of Sulphuric and Citric Acids. JOHANNES E. ENKLAAR (*Zeitsch physikal. Chem.*, 1912, **81**, 481—482).—Polemical. An answer to the criticism of Drucker (A., 1911, ii, 687) on Enklaar's papers (A., 1911, ii, 1071; 1912, ii, 239). J. F. S.

The Absorption of Oxygen, Nitrogen, and Hydrogen in Aqueous Solutions of Non-electrolytes. CARL MÜLLER (*Zeitsch. physikal. Chem.*, 1912, **81**, 483—503).—The solubility of oxygen, nitrogen, and hydrogen is determined in aqueous solutions of sucrose, dextrose, glycerol, and chloral hydrate which vary in concentration from 10% to 60%. In the glycerol and chloral hydrate solutions the absorption coefficient decreases to a minimum and then increases with increasing concentration of the solutions, whilst in the sucrose and dextrose solutions the absorption coefficient increases steadily with increasing concentration. The relative decrease in the absorption coefficient at a given concentration of the solution is independent of the nature of the gas in the cases examined. The amount of gas absorbed can be represented by two straight lines which cut at the point of minimum absorption. The minimum absorption is found, for all the gases investigated, to lie at about the same concentration. The fact that the decrease of the absorption coefficient is independent of the nature of the gas can only be explained by the formation of hydrates in the solutions, and consequently it is to be regarded as a proof of the existence of hydrates in solutions. J. F. S.

Liquid Mixtures. I. Property-composition Curves and the Molecular Changes which take Place on Forming Binary Liquid Mixtures. ROBERT B. DENISON (*Trans. Faraday Soc.*, 1912, **8**, 20—34).—The existence of a chemical compound may be inferred with probability, but not with certainity, from the presence of a maximum or minimum in the property-composition curve. The deviation from a straight line is a maximum for the composition corresponding with that of the compound. This is independent of the dissociation of the compound. An approximate estimate of the extent of dissociation is obtained by examining the deviation-composition curve, a sharp maximum denoting a small dissociation. Changes of temperature may displace a maximum on the property-composition curve, but do not alter the position of the maximum on the deviation curve. It is thus possible to determine the equilibrium in a homogeneous solution by determining any suitable physical property of a series of binary mixtures.

C. H. D.

Liquid Mixtures. II. Chemical Combination in Liquid Binary Mixtures as Determined by a Study of Property-composition Curves. ROBERT B. DENISON (*Trans. Faraday Soc.*, 1912, **8**, 35—50).—The principles discussed in the preceding abstract are applied to several cases of contraction on mixing, and of the viscosity of liquid binary mixtures. The curves for mixtures of ethyl alcohol and water show a maximum deviation at 46% alcohol, corresponding with a compound $EtOH,3H_2O$. The position of the maximum is the same at 0° and 15·6°, but the maximum is sharper at the lower temperature, indicating dissociation as the temperature rises. The pyridine–water curves indicate in similar manner a compound $C_5NH_5,2H_2O$, whilst mixtures of lactic acid with water and of acetic acid with benzene, indicate compounds $C_3H_6O_3,2H_2O$,

and $C_6H_6,2C_2H_4O_2$ respectively. The method is also applied to aqueous solutions of salts, and a theoretical discussion follows.
C. H. D.

Systematics of the States of Aggregation of Matter. P. P. VON WEIMARN (*Koll. Chem. Beihefte*, 1912, 4, 65—100).—A further discussion of the author's orientation theory (compare A., 1910, ii, 1048; 1912, ii, 142, and other papers). The views of Lehmann are adversely criticised, and arguments advanced against the assumption of the amorphous state. H. M. D.

The Nature of Pseudo-solutions. BASIL KURILOV (*Zeitsch. anorg. Chem.*, 1912, 79, 88—96. Compare A., 1906, ii, 343).—The system studied is that of ferric hydroxide hydrosol and hydrochloric acid. The transition from pseudo-solution to true solution is observed in this system, the quantity of precipitate reaching a maximum for a certain concentration of the acid. The solid phase also alters in character as the change proceeds. Measurements of the optical extinction coefficient give the same result. The conclusion is confirmed, that the formation of a pseudo-solution depends on the formation of additive compounds. C. H. D.

The Theory of the Isoelectric Point. III. The Nature of Solutions of Colloids of the Character of Proteins. LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1912, 47, 250—259. Compare A., 1911, ii, 192, 577).—Sörensen has recently criticised the author's theory that the optimal condition for precipitation of substances from solution exists when the solution is isoelectric with the dissolved substance (*Ergebnisse der Physiologie*, 1912, 506). The author gives reasons for maintaining his position. He shows incidentally that the isoelectric points of phenylalanine and glycine, ascertained by determining the mixture of sodium acetate and acetic acid to which their concentrated aqueous solutions can be added without alteration of the hydrogen-ion concentration, agree accurately with isoelectric points calculated from their basic and acidic dissociation constants. He also calls attention to the fact that the peculiar properties of the protein colloidal solutions, as contrasted with those of amphoteric, slightly soluble crystalline substances, can be explained by the differences of the surface tensions of the interfaces, the surface tension in the case of crystalline substance and its saturated solution being great, whereas in the case of the protein colloids it is small. This last factor tends to cause dispersion of the colloid in solution, and to inhibit the tendency to crystallisation, which latter phenomenon, in the case of crystalline substances, is promoted also by the vectorial forces. S. B. S.

Theory of the Formation and Stability of Colloidal Solutions and Precipitates. II. P. P. VON WEIMARN (*Koll. Chem. Beihefte*, 1912, 4, 101—131. Compare A., 1910, ii, 835).—The theory of the so-called condensation methods for the production of disperse systems is further discussed.

Experiments are described which show the gradual change in the

character of precipitated sodium chloride when the conditions (nature of the solvent, temperature) under which the precipitation is effected are gradually altered. These structural changes are illustrated by photographs of the precipitated substance. Similar variations in structural character have been observed in the case of a large number of other substances. H. M. D.

Formation of New Colloids in a Colloidal Solution by Metallic Plates. MAURICE PHILIPPSON (*Bull. Acad. roy. Belg.*, 1912, 580—582. Compare A., 1912, ii, 914).—Colloidal copper, when prepared by Bredig's method, gradually undergoes a change when carefully cleansed plates of either zinc or platinum are introduced into the solution of the hydrosol. A study of Tyndall's phenomenon in these solutions shows that, whilst the copper is gradually precipitated, a new and not very stable colloid is produced. Contrary to the explanation previously put forward (*loc. cit.*), the precipitation is independent of the electrolytic solution pressures of the precipitating metals, and these metals, under the influence of the discharge of the colloidal particles during precipitation, are able in their turn to assume the colloidal state. W. G.

The Emulsoid Condition and the General Classification of Colloidal Forms. WOLFGANG OSTWALD (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 230—239).—The classification of colloidal forms of matter is discussed with special reference to the emulsoid condition. According to the author, emulsoid and lyophilic are not synonymous terms, the lyophilic colloids representing merely a special group of emulsoids, Since the term lyophilic is employed in reference to colloids in which the dispersive medium is combined to a greater or smaller extent with the disperse phase, it is suggested that such colloids may more conveniently be called solvated, the lyophobic colloids being then designated non-solvated.

As a direct test for the emulsoid condition, the formation of two distinct non-disperse liquid layers on coagulation is recommended. This type of coagulation has been observed in the case of gelatin, casein, soaps, lipoids, and silicic acid. H. M. D.

Jellies. P. P. VON WEIMARN (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 239—241).—Polemical against Zsigmondy and Bachmann (A., 1912, ii, 1149). The crystalline character of the ultra-microscopic particles exhibited by certain jellies had been previously demonstrated by the author. H. M. D.

Maximum and Minimum Equilibrium Pressure in Binary Systems. F. E. C. SCHEFFER (*Zeitsch. physikal. Chem.*, 1912, 81, 431—440).—A theoretical paper dealing with the conditions under which maximum and minimum pressures occur in $L+G$ and $S+G$ and $S+L$ surfaces. The work is a continuation of that of Smits (A., 1912, ii, 242). The author concludes, from theoretical considerations, that the systems HgI_2+HgBr_2, $d+l$ carvoxime, monochloro- and mono-bromo-quinol acetates, *p*-azoxyphenetole + *p*-methoxycinnamic acid,

and many binary metal systems ought to show curves of maximum and minimum pressure on the *SL* surface. J. F. S.

Examples of Bimolecular Reversible Reactions. WALTER HERZ and FRITZ KUNTZE (*Zeitsch. Elektrochem.*, 1912, **18**, 1015—1016). —A theoretical paper in which equilibrium constants are calculated from experimental results of F. Kuntze on the reaction between chloral alcoholates and alcohols (compare A., 1908, i, 322). The following constants are given: chloral-amyl alcoholate + ethyl alcohol, $k_1/k = 0{\cdot}444$; chloral-amyl alcoholate + propyl alcohol, 0·444; chloral propyl alcoholate + *l*-amyl alcohol, 0·121; chloral butyl alcoholate + *l*-amyl alcohol, 0·121; chloral amyl alcoholate + benzyl alcohol, 0·298. J. F. S.

Gaseous Mineralisers in a Magma. II. PAUL NIGGLI (*Zeitsch. anorg. Chem.*, 1912, **77**, 321—334. Compare A., 1912, ii, 632).—A further theoretical discussion of ternary systems including a gaseous phase. C. H. D.

Equilibria in Quaternary Systems. V. Completely Isomorphous Quaternary Mixtures. NICOLA PARRAVANO (*Gazzetta*, 1912, **42**, ii, 305—326).—The study of the phenomena of crystallisation of quaternary systems by the tetrahedral method of representation (compare A., 1911, ii, 973) involves the erection, at the angles of the tetrahedron, of ordinates in space of four dimensions. The author treats the problem mathematically, and shows how it is possible to obtain the results required in spite of the impossibility of drawing such ordinates. Four typical cases present themselves and these are considered in turn. T. H. P.

Distribution of Dyes between Two Solvents. The Theory of Dyeing. WILLEM REINDERS and D. LELY, jun. (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 482—495).—The influence of concentration on the distribution of a number of dyes between *iso*butyl alcohol and water has been examined. Denoting the corresponding concentrations in the alcohol and water by c_a and c_w respectively, it is found that the ratio c_a/c_w decreases in all cases as the concentration increases. For some dyes, the observations can be satisfactorily represented by means of the adsorption formula: $\log c_a = 1/n \log c_w$, but for others this is by no means the case, and in order to obtain approximate agreement between the calculated and observed values, it is necessary to assume larger values of $1/n$ for the more concentrated solutions. For the dyes examined, the value of $1/n$ varies from 0·3 for erythrosine-*A* to 1·0 for alkali-blue and crystal ponceau.

The increase of $1/n$ with the concentration may be explained on the assumption that the absorption of the dye by the alcohol is mainly dependent on the concentration of the non-ionised and hydrolytically dissociated molecules.

This view accords with the fact, that in the case of basic dyes, the transition from the water to the alcohol layer is increased by the addition of bases, whilst in the case of acid dyes the addition of acids has a similar effect. This influence of acids and bases has been

examined in the case of acid, basic and substantive dyes, and the observed changes in distribution, together with the accompanying change in colour, are recorded in each case.

When the facts relating to the distribution of dyes between water and *iso*butyl alcohol and between water and fibrous substances are compared, there can be no doubt that a close similarity exists, and the authors conclude that the absorption of dyes by fibres is essentially dependent on the formation of solid solutions. The assumption of a surface adsorption is in many cases quite unnecessary.

H. M. D.

The Calculation of Equilibrium Constants from Cryoscopic Measurements. J. B. GOEBEL (*Zeitsch. physikal. Chem.*, 1912, 81, 298—307).—A continuation of the work described in previous papers (compare A., 1910, ii, 268; 1911, ii, 1078). The present paper deals with the calculation of the dissociation and association constants of binary electrolytes and with the first and second dissociation constants of ternary electrolytes. The results show that, in general, these electrolytes follow the law of mass action. Equations are given for the calculation of the conductivity of ternary electrolytes. A number of printer's errors in the previous papers (*loc. cit.*) are corrected. For the deduction of the numerous equations, the original paper must be consulted. Among the general conclusions arrived at, the following may be noted: (1) The weak organic acids are all polymerised to about the same extent in aqueous solution, and have, approximately, the same polymerisation constant, 0·5; (2) of salts in aqueous solution the sulphates are the most strongly polymerised, the nitrates somewhat less, and the chlorides least of all; (3) generally the weaker the electrolyte, so far as salts are concerned, the more strongly is it polymerised; (4) the potassium salts are more strongly polymerised than the corresponding sodium salts. J. F. S.

[Reciprocal Salt Pairs.] OTTO MENGE (*Zeitsch. physikal. Chem.*, 1912, 81, 377—378).—A reply to criticisms made by Jänecke (A., 1912, ii, 762) on a previous paper of the authors (A., 1911, ii, 982). J. F. S.

Theory of the Efflorescence of Saline Hydrates. CH. BOULANGER and GEORGES URBAIN (*Compt. rend.*, 1912, **155**, 1246—1249).—For the efflorescence of salts in a dry atmosphere the authors deduce the equation $\log(m_\theta - m_t) = \log a + A\log(\theta - t)$, where θ is the total time necessary for efflorescence, m_θ the corresponding loss in weight, and m_t the loss at any given time t. a and A are constants, the value of the latter being 1·6 for most hydrates. Results are given for sodium sulphate, $Na_2SO_4,10H_2O$, and the values obtained experimentally are in close accord with those calculated. This agreement is less satisfactory in the case of salts which in the anhydrous form retain traces of water except at high temperatures. W. G.

Saturation of the Ethylenic Bonds of Oleic Acid by means of Iodine and the Molecular Weight of Dissolved Iodine. JOSEPH A. MULLER (*Bull. Soc. chim.*, 1912, [iv], 11, 1006—1009. Compare A., 1911, ii, 266).—The author has measured the velocity of

the addition of iodine to oleic acid in carbon tetrachloride and in ethyl acetate solution at different dilutions. In each case, the reaction is found to be bimolecular, and the molecule of dissolved iodine thus appears to be diatomic. The difference in colour of the two solutions is attributed to the probable existence of free molecules of iodine in carbon tetrachloride solution and to a combination of iodine with ethyl acetate when dissolved in the latter solvent. H. W.

Hydrolysis of Metallic Alkyl Sulphates. GEORGE A. LINHART (*Amer. J. Sci.*, 1912, [iv], **34**, 539—542).—The velocity of hydrolysis of calcium and strontium ethyl sulphate under the catalytic influence of hydrochloric acid has been measured at 60° in order to ascertain the influence of the replacement of barium in barium ethyl sulphate (A., 1912, ii, 927) by calcium and strontium. The rate of decomposition of the salts decreases as the weight of the metal decreases, the values of the velocity coefficient for *N*-hydrochloric acid being 0·0083, 0·0078, and 0·0073 for the barium, strontium, and calcium salts respectively. T. S. P.

The Alkaline Decomposition of Chlorohydrins. L. SMITH (*Zeitsch. physikal. Chem.*, 1912, **81**, 339—376).—The rate of decomposition of neutral and acid chlorohydrins by means of alkalis, both with and without the addition of neutral salts, is investigated in the present paper (compare Evans, A., 1891, ii, 796, and Senter, A., 1910, ii, 276). The following neutral chlorohydrins were used: ethylene chlorohydrin, α-monochlorohydrin, propylene chlorohydrin, *iso*butylene chlorohydrin, β-methyl-Δ^{β}-butylene chlorohydrin, α-dichlorohydrin, and epichlorohydrin. In all cases it is shown that the influence of the different alkalis is the same. The author was unable to prove the presence of glycerol in the product of the reaction with monochlorohydrin and alkali, which was stated by Senter (*loc. cit.*) to be formed. It is shown in the case of α-chlorohydrin that the results are more in accord with a termolecular reaction than with a bimolecular change. The addition of neutral salts has a slight effect on the velocity of the reaction, which, however, is too small to be attributed to a metallic ion catalysis. In the reaction between baryta and epichlorohydrin the case is somewhat different, for here an addition of barium chloride causes an increase in the rate of the reaction, which is larger the smaller the concentration of the hydroxyl ion present. The following chlorohydrins of acids were investigated: chloromalic acid, β-chlorolactic acid, and α-chloro-β-phenyl-β-lactic acid. The reactions were studied with sodium hydroxide, potassium hydroxide, baryta, and calcium hydroxide, and in all cases are shown to be bimolecular; there is, however, a catalytic influence exerted on the velocity of the reactions by the metallic ions present. The Holmberg constant, *d* (see Holmberg, A., 1912, ii, 443, 1048), and the catalysis constant for chloromalic acid with different bases are as under:

	$Ca(OH)_2$.	$Ba(OH)_2$.	KOH.	NaOH.
Catalysis const.	55	42·9	11·4	10·6
d..	1/12	1/3	1/4	1/4

With β-chlorolactic acid the values are:

	$Ca(OH)_2$.	$Ba(OH)_2$.	KOH.	NaOH.
Catalysis const.	3·8	1·79	0·74	0·74
d	1/4	1/4	1/7	1/7

Similar results are also given for α-chloro-β-phenyl-β-lactic acid, in connexion with which the existence of two isomerides is shown, m. p. respectively 94° and 103°. J. F. S.

Inorganic Ferments. VI. Catalytic Decomposition of Formic Acid by Rhodium. THOMAS BLACKADDER (*Zeitsch. physikal. Chem.*, 1912, 81, 385—416. Compare Bredig and co-workers, A., 1900, ii, 213; 1901, ii, 441, 442; 1909, ii, 389; 1910, ii, 284).—The velocity of the decomposition of formic acid by means of rhodium has been investigated by the author, together with the influence of changes in the various conditions of carrying out the decomposition. The most active rhodium is produced by allowing rhodium sponge to lie in contact with potassium sulphide for several hours, or by electrolytically depositing rhodium black on to platinised platinum from a solution of rhodium in 60% sulphuric acid by a current of 0·02 ampere at 180°. Rhodium is only capable of effecting the catalysis when it contains either sulphur or oxygen. In the latter case, the activity is of short duration, whilst in the former case it persists for several days. Formic acid is practically quantitatively decomposed into hydrogen and carbon dioxide, and a small amount of hydrogen sulphide, amounting to 0·02%, is evolved at the same time. The reaction is complicated, as shown by the constant, which, when calculated from the equation for reactions of the first order, increases with decrease of the formic acid concentration. The temperature-coefficient of the reaction between 85° and 95° is rather more than 2 per 10° rise of temperature. The effect of more rapid stirring is slight, and this, taken in conjunction with the temperature-coefficient, indicates that the process is to a large extent purely chemical and does not depend on diffusion. The addition of sodium formate increases the velocity of the reaction, whilst the addition of sufficient alkali to make the solution alkaline entirely stops the reaction. Dilution of the formic acid and sodium formate mixture brings about an increase in the velocity of the change. The addition of hydrochloric acid decreases the velocity of the reaction, which indicates that the increase brought about by sodium formate is due to a decrease in the concentration of the hydrogen ions. Active rhodium has a more positive potential than inactive rhodium when measured in formic acid solution.

J. F. S.

Catalysis on the Basis of Work with the Imino-esters: the "Salt Effect" JULIUS STIEGLITZ (*J. Amer. Chem. Soc.*, 1912, 34, 1687—1695).—Investigations of the action of ammonia on imino-esters (A., 1908, ii, 168) indicated that, in addition to the reaction of the anion of the imino-ester with a high velocity coefficient, a second accelerating force is involved, the imino-ester itself exerting a "salt effect" on its own catalysis. In more recent work on the velocity of

the rearrangement of acid chloroamides through salt and ion formation in alkaline solutions, it has been found that not only do the anions of the salts formed undergo the rearrangement, but that possibly both the anions and the non-ionised salts suffer the rearrangement simultaneously, and that probably the anions are the rapidly reacting components.

In view of these results, the work on the decomposition of imino-esters by water has been re-investigated in order to ascertain whether a parallel action of water on the non-ionised imino-ester, proceeding simultaneously with the main action on the imino-ester ion, could be inferred. In referring the velocity of the action to the ion as the sole reacting component of the imino-ester, it was necessary to assume a considerable acceleration of the action in the more concentrated salt solutions, analogous to the "salt effect" in other catalytic actions. The effect of adding neutral salts was generally found to be in harmony with the assumptions made.

Acree has advanced the theory that the accelerations beyond the theoretical effect of a catalyst could be due to a parallel decomposition of ions and non-ionised molecules, and that accelerations occur in which the reacting components are salt molecules and not their ions.

It is shown that the numerical data obtained in some of the author's experiments agree as well with the hypothesis of a parallel decomposition of the non-ionised salt molecules by water as with the assumption of a "salt catalysis." Further work is therefore being undertaken with a view to determining the salt factor for other reactions in which water is involved. E. G.

The Natural System of the Elements. A. KLEINER (*Ann. Physik*, 1912, [iv], **39**, 1070).—A claim of priority in respect of certain views expressed by Laemmel (A., 1912, ii, 1048) in reference to the influence of temperature on the specific heats of the elements.

H. M. D.

The Theory of Radicles as an Interpretation of Mendeleév's System. DAN RADULESCU (*Chem. Zentr.*, 1912, ii, 1418—1420; from *Bul. Soc. Ştiinte Bucareşti*, 1912, **21**, 59—71).—The structure of an element is considered to be somewhat similar to that of organic compounds; it is built up of a characteristic radicle, the "characteristic" and an indifferent carrier, the "nucleus." The characteristic is the bearer of the valency, the specific and unalterable analytical properties of the element and of the colour, and its weight does not exceed nine times the atomic weight of hydrogen. The nuclei are whole multiples of the three radicles, $R = 22$, $R' = 21 \cdot 27$, and $R'' = 22 \cdot 27$; metallic nature increases from R to R″. Nuclei that approach 10R are radioactive; greater than these are unknown. The characteristics are attached to the nuclei like the various groups to the carbon skeletons in organic compounds. They are seven in number and are equal to: 1 for alkali metals (basic, univalent, coloured flames, few spectral lines, colourless salts); 2·07 for the magnesium group (weak bases, stable salts, bivalent, affinity for carbon); 4 for

characteristics of stable quadrivalence; 5 for tervalence and boron; 8 for sexavalence (blue, green, and red salts, polyammino-compounds and complexes); 7 for quinquivalence, and 5·48 for halogens and manganese. A periodic table shows that from the "constitutional formulæ" based on these theories, the important properties of the elements are made apparent, and that the calculated atomic weights agree very closely with the experimental data. J. C. W.

Some Considerations Regarding Werner's Theory. ITALO BELLUCCI (*Gazzetta*, 1912, **42**, ii, 532—539).—The author discusses the views of Briggs (T., 1908, **93**, 1564; 1911, **99**, 1019) in regard to the nature of the linking of the ionisable radicles in complex compounds. He is of opinion that the experimental evidence is quite insufficient to justify this modification of Werner's theory, and in particular he points out that Briggs' hypothesis would require the existence of enormous numbers of isomerides among complex compounds, whereas Briggs adduces only a few instances, and in the author's opinion even these require further investigation. R. V. S.

Laboratory Apparatus. ERNST BERLIN (*Chem. Zentr.*, 1912, ii, 889; from *Zentr. Physiol.*, 1912, **26**, 219—222).—Two pieces of apparatus are figured and described. The first is for use in the preparation of hydrogen chloride by adding sulphuric acid to hydrochloric acid. The second provides for the automatic extraction of substances from one liquid by means of a heavier liquid, for example, extraction of substances from an aqueous solution by means of chloroform.

T. A. H.

Lecture Experiment on the Explosion [and Production] of Electrolytic Gas by Alternating Currents. FRITZ FICHTER (*Zeitsch. Elektrochem.*, 1912, **18**, 1080).—The experiment is designed to show that both products of electrolysis are liberated at a single electrode by an alternating current, and that a large production of gas at an electrode is only possible with large current density when using alternating current. The experiment also demonstrates the explosion of electrolytic gas in a perfectly safe manner. The apparatus consists of a short length of thick-walled glass-tubing, 8 cm. long and 2 cm. diameter; this is fitted with a rubber stopper, which supports a glass stopcock and a platinum wire. The wire serves as one electrode, and projects 3—4 cm. into the tube. The whole is attached to a wooden rod and placed in a beaker of dilute sulphuric acid, so that the tube is filled with the liquid. The tap is then closed. The other electrode consists of a large piece of gas carbon. A current of 7 amperes is passed through, which rapidly fills the tube with electrolytic gas and consequently drives out the solution. Just before the solution has finally left the platinum wire the current density on the wire is great enough to produce a glowing layer of gas which fires the mixture, and allows the tube to refill with solution. The process then repeats itself. J. F. S.

Photochemistry. IV. Photochemical Lecture Experiments. OSKAR BAUDISCH and ROSE FÜRST (*Ber.*, 1912, **45**, 3426—3428).—The explanation given in a previous paper (A., 1911, ii, 952) of the

formation of α-hydroxyazonaphthalene from ammonium α-nitrosonaphthylhydroxylamine has been confirmed by extracting the yellow dye from the fibre. It was identified as α-azoxynaphthalene, and the methyl-alcoholic solution, on exposure to sunlight, deposited glistening, brownish-red needles of α-hydroxyazonaphthalene.

If filter paper is treated with ammonium α-nitrosonaphthylhydroxylamine so as to obtain the yellow dye, and then exposed to the rays from a quartz-mercury lamp, it is turned red, whether screens of glass, glass coated with gelatin, starch solution, or egg-albumin solution, are interposed or not. Such screens, however, prevent the liberation of iodine on paper treated with potassium nitrate and starch iodide, showing that it is the long rays which are active in the first case, and the short rays in the second. The fact that these long rays will penetrate colloidal solutions is discussed in connexion with the utilisation of light energy by the colloidal plasma of plant cells.

By acidifying an aqueous solution of ammonium α-nitrosonaphthylhydroxylamine with metaphosphoric acid, an almost white, curdy precipitate of the *free acid* is obtained; white needles from light petroleum, m. p. 54—55°. In chloroform solution the free acid is reduced to α-naphthalenediazonium chloride. T. S. P.

Inorganic Chemistry.

The Behaviour of Water as a Liquid and in Five Solid Modifications Under Pressure. P. W. BRIDGMAN (*Zeitsch. anorg. Chem.*, 1912, **77**, 377—455).—The behaviour of water has been examined under higher pressures than in previous experiments, liquid water being studied between $-20°$ and $+80°$ up to 12,000 kilograms per sq., cm., and solid water between $-80°$ and $+78°$ up to 20,500 kilograms per sq. cm. Two new modifications of ice, one of which is capable of existing above 0°, have been discovered. Five of the six stable triple points have been found, and ten of the eleven transformation lines have been followed. In addition to the five stable solid modifications, two exist which have no range of stability. All, with the exception of ordinary ice, are denser than water.

The temperature of maximum density of water is independent of the pressure, but the maximum disappears at high pressures ; a new anomaly appears, however, between $-15°$ and $-20°$ at a pressure of 5000 kilograms. The increased compressibility at high pressures suggests a possible compressibility of the atoms as well as of the molecules, but the data are still insufficient to construct an equation for the behaviour of liquid water.

The results with the solid phases confirm and extend those of Tammann. The equilibrium curve between ice II and III, which was not found by Tammann, has now been determined. The water is

enclosed in a vessel filled with light petroleum, and the pressure is measured by the change in resistance of a manganin wire. In order to determine the curve II—III, along which the volume changes are very small, a different method has to be adopted, the temperature being varied at constant volume, and the changes of pressure observed.

Ice VI, which is formed at temperatures above 0° under high pressure, has the greatest range of existence, as regards both temperature and pressure, and the form of the curve is such as to indicate that further modifications are not formed. The existence of two modifications having no range of stability is inferred from the occurrence of volume changes which do not lie on any of the equilibrium curves.

The observations confirm the impossibility of superheating a solid phase with respect to the liquid, whilst undercooling readily takes place, and many of the curves have been prolonged into the region of instability, but an unstable triple point has not yet been realised, and indications of a metastable limit have not been found. Nuclei of a previously existing phase appear to persist even in a solid phase. The velocity of transformation, even in solid phases, is extremely high in the neighbourhood of a triple point, but diminishes rapidly with falling temperature. The bearing of these results on the theory of the solid state is discussed. C. H. D.

A New Modification of Sulphur. A. H. W. Aten (*Proc. K. Wetensch. Amsterdam*, 1912, **15**, 572—583; *Zeitsch. physikal. Chem.*, 1912, **81**, 257—280).—If a solution of rhombic sulphur in sulphur chloride, saturated at the ordinary temperature, is heated at about 150° and then cooled, it is found that a further and considerable quantity of sulphur may be dissolved in the liquid. It is shown that this cannot be due to the formation of S_μ from S_λ, for the solubility of S_μ in sulphur chloride is very small at the ordinary temperature, and if solutions saturated with S_μ at a higher temperature are cooled down, this separates out quite readily.

In order to ascertain whether this phenomenon is due to the formation of a new modification of sulphur or to the combination of sulphur with the sulphur chloride, systematic determinations have been made of the solubility of rhombic sulphur in sulphur chloride which has been heated with varying proportions of sulphur at a definite temperature and then cooled to either 25°, 0°, or −60°. The data thus obtained point to the formation of a new variety of sulphur. If this conclusion is correct, it should be possible to obtain some indication of its formation in the absence of sulphur chloride. This is actually the case, for if sulphur is heated alone to 125° and rapidly cooled, and its solubility in sulphur chloride examined, it is found that the solubility is distinctly greater than that of unheated rhombic sulphur.

H. M. D.

The Relation between the Sulphur Modifications. H. L. de Leeuw (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 584—593). —If the sulphur contained in a dilatometer tube is heated to its boiling point, and then rapidly cooled so that a large proportion of the

S_μ formed remains intact, it is found that the temperature of conversion of rhombic into monoclinic sulphur is lowered from 95·45° to about 71°. As the proportion of S_μ present decreases, the transition temperature rises until it reaches 95·45°, which must be regarded as the true unary transition point. Kruyt's work (A., 1911, ii, 879; 1912, ii, 1051) on the dynamic allotropy of sulphur is criticised adversely, and in particular it is shown that there is no evidence for the assumption of a region of partial miscibility in the liquid phase.

The occurrence of two liquid layers is due to differences in temperature, and when the thermal conductivity is increased by the introduction of platinum wire or gauze, the phenomenon in question is only observed very indistinctly or not at all. H. M. D.

Alleged Complexity of Tellurium. WILLIAM C. MORGAN (*J. Amer. Chem. Soc.*, 1912, **34**, 1669—1675).—Flint (A., 1910, ii, 845; 1912, ii, 1051) has stated that by fractional hydrolysis of tellurium tetrachloride, he obtained two fractions, one giving the atomic weight 124·3, and the other, which was still impure, the atomic weight 128·85. This work has now been repeated with a large quantity of material, but the results do not show progressive diminution of the atomic weight, and thus fail to confirm Flint's conclusion. In view of these experiments and those of other investigators, the author considers that the evidence for the homogeneity of tellurium is quite convincing. E. G.

[Compounds of Tellurium and Iodine.] FRANS M. JAEGER and J. B. MENKE (*Zeitsch. anorg. Chem.*, 1912, **77**, 320. Compare A., 1912, ii, 344).—It is not possible to determine the freezing point of mixtures containing more than 70% of tellurium in an open vessel, and mixtures rich in iodine boil. The compound TeI_4 dissociates when heated in carbon dioxide. C. H. D.

The Ternary System Tellurium Tetra-iodide–Hydrogen Iodide–Iodine, and the Estimation of Tellurium by means of Hydrazine Hydrate. J. B. MENKE (*Zeitsch. anorg. Chem.*, 1912, **77**, 282—288. Compare Jaeger and Menke, A., 1912, ii, 344).—Tellurium tetra-iodide, prepared by melting together its components, is heated with hydriodic acid and iodine in a sealed glass tube, ten days being allowed for the attainment of equilibrium in each experiment. The only solid phases found are $TeI_4,HI,8H_2O$ and iodine. A hexa-iodide is thus not obtained either by fusion or from solution. The double compound resembles iodine in appearance.

For analysis, the free iodine is titrated with thiosulphate after neutralisation with sodium hydrogen carbonate; the total iodine is estimated as silver iodide after removal of most of the tellurium by alkali sulphite. The method of Gutbier and Flury (A., 1902, ii, 653) is not applicable to tellurium tetra-iodide, and the reduction of tellurium by means of sulphur dioxide is not exact, as the fine, amorphous tellurium readily oxidises. Precipitation by means of hydrazine hydrate is usually incomplete, as the filtrate contains colloidal tellurium. In acid solution the precipitation is almost complete, but the excess of acid must be neutralised before filtration, otherwise the precipitate partly redissolves. C. H. D.

The Validity of Werner's Theory of Subsidiary Valencies for Ammoniates. WALTER PETERS (*Zeitsch. anorg. Chem.*, 1912, **77**, 137—190).—The addition of ammonia to inorganic salts has been studied by means of the apparatus of Ley and Wiegner (A., 1905, i, 749). After saturating the solid with ammonia, it is weighed, transferred to a vacuum until the weight is constant, and again saturated. Addition takes place more readily the second time, and in some cases a further quantity of ammonia is added.

The number of molecules added depends on the degree of saturation of the salt molecule and on the residual affinity of its ions, and when salts with the same anion but different cations are compared, analogies corresponding with the periodic system are observed. The number of molecules of ammonia is most frequently six or a multiple of six, which is in accordance with Werner's hypothesis.

The following new compounds have been prepared: $CuCl,3NH_3$; $CuBr,3NH_3$; $CuI,3NH_3$; $CuCN,\frac{1}{2}NH_3$; $Cu(NO_3)_2,5NH_3$; $AgCl,3NH_3$; $AgBr,2\frac{1}{2}NH_3$; $AgI,\frac{1}{2}NH_3$; $AgCNO,NH_3$; $AgCNS,2NH_3$; $AgNO_3,3NH_3$; $KAuCl_4,3NH_3$; $KAu(CNS)_2,5NH_3$; $ZnSO_4,H_2O,6NH_3$; $K_2HgI_4,2NH_3$; $BaHgI_4,8NH_3$; $Cu_2HgI_4,6NH_3$; $CdHgI_4,6NH_3$; $Hg(CNS)_2,4NH_3$; $Hg(C_2H_3O_2)_2,4NH_3$; $Hg(C_3H_5O_2)_2,4NH_3$; $CrCl_2,6NH_3$; $UCl_4,3NH_3$; $UO_2Cl_2,2NH_3$; $MnCl_2,6NH_3$; $MnI_2,6NH_3$; $MnSO_4,6NH_3$; $MnSO_4,H_2O,5NH_3$; $FeSO_4,H_2O,5NH_3$; $Zn_2Fe(CN)_6,7NH_3$; $Mn_2Fe(CN)_6,2NH_3$; $Cd_2Fe(CN)_6,7NH_3$; $Co_2Fe(CN)_6,3NH_3$; $Ni_2Fe(CN)_6,7NH_3$; $Zn_3[Fe(CN)_6]_2,12NH_3$; $Mn_3[Fe(CN)_6]_2,6NH_3$; $Cu_3[Fe(CN)_6]_2,16NH_3$; $Cd_3[Fe(CN)_6]_2,12H_2O$; $Co_3[Fe(CN)_6]_2,8NH_3$; $Na_2FeNO(CN)_5,2NH_3$; $Ni(SCN)_2,6NH_3$,; $NiS_2O_6,6NH_3$; $Co(CN)_2,2NH_3$; $Co(SCN)_2,6NH_3$; $RuCl_3,3NH_3$; $RuBr_3,3NH_3$; $RhCl_3,4NH_3$; $PdCl_2,5NH_3$; $PdI_2,6NH_3$; $Na_2PdCl_4,5NH_3$; $(NH_4)_2PdCl_4,5NH_3$; $PtCl_2,5NH_3$; $PtI_2,6NH_3$; $Na_2PtCl_4,4NH_3$; $Ag_2PtCl_4,6NH_3$($7\frac{1}{2}NH_3$ at low temperatures); $K_2Pt(CN)_4,NH_3$; $KNaPt(CN)_4,2NH_3$; $CuPt(CN)_4,4NH_3$; $Ag_2Pt(CN)_4,5NH_3$; $MgPt(CN)_4,4NH_3$; $BaPt(CN)_4,6NH_3$; $ZnPt(CN)_4,4NH_3$; $CdPt(CN)_4,6NH_3$; $MnPt(CN)_4,4NH_3$; $FePt(CN)_4,4NH_3$; $NiPt(CN)_4,6NH_3$; $CoPt(CN)_4,6NH_3$; $CaPt(CN)_4,3NH_3$; $K_2Pt(SCN)_4,2NH_3$; $CuPt(SCN)_4,8NH_3$; $Ag_2Pt(SCN)_4,6NH_3$; $PtCl_4,6NH_3$; $PtBr_4,6NH_3$; $Na_2PtCl_6,6NH_3$; $Ag_2PtCl_6,8NH_8$ ($10NH_3$ at $-10°$); $CuPtCl_6,18NH_3$; $CaPtCl_6,12NH_3$; $BaPtCl_6,6NH_3$; $ZnPtCl_6,11NH_3$; $CdPtCl_6,18NH_3$; $MnPtCl_6,11NH_3$; $NiPtCl_6,12NH_3$; $CoPtCl_6,12NH_3$($18NH_3$ at $-20°$; $Na_2PtBr_6,6NH_3$; $K_2Pt(SCN)_6,12NH_3$; $(NH_4)_2Pt(SCN)_6,15NH_3$; $CuPt(SCN)_6,15NH_3$; $Ag_2Pt(SCN)_6,14NH_3$; $Au_2[Pt(SCN)_6]_3,30NH_3$; $BaPt(SCN)_6,12NH_3$; $ZnPt(SCN)_6,15NH_3$; $CdPt(SCN)_6,18NH_3$; $Tl_2Pt(SCN)_6,9NH_3$;

$MnPt(SCN)_6,18NH_3$; $NiPt(SCN)_6,18NH_3$; $CoPt(SCN)_6,14NH_3$; $K_2Pt(SeCN)_6,6NH_3$.

Hydrogen chloride and hydrogen phosphide are not absorbed by any inorganic salts under similar conditions.

The absorption spectra of aqueous solutions of the compounds $CuCl_2,6NH_3$ and $CuPtCl_6,18NH_3$ show that both the long visible waves and the ultra-violet are absorbed, the transmitted band being narrower in the case of the double salt.

Determinations of the vapour pressure of several of the compounds have been made by means of a tensimeter. C. H. D.

Revision of the Atomic Weight of Phosphorus. III. Analysis of Phosphorus Trichloride. GREGORY P. BAXTER and CHARLES J. MOORE (*J. Amer. Chem. Soc.*, 1912, **34**, 1644—1657).—In earlier papers (Baxter and Jones, A., 1910, ii, 288; Baxter, Moore, and Boylston, A., 1912, ii, 347), accounts have been given of determinations of the atomic weight of phosphorus by the analysis of silver phosphate and phosphorus tribromide. The investigation has now been extended to the analysis of phosphorus trichloride.

Phosphorus trichloride was prepared and analysed by methods similar to those employed in the case of the tribromide. The product was freed from the pentachloride by distillation in a vacuum. Two series of fractions were collected, and analysed in the usual way after decomposition with water and oxidation of the phosphorous acid produced.

From the average of twenty-four analyses, the value for the atomic weight of phosphorus was found to be 31·018 (Ag = 107·880; Cl = 35·457), as compared with 31·04 obtained from the analysis of silver phosphate and 31·027 from that of phosphorus tribromide. The average of the results from the tribromide and trichloride is 31·023.

E. G.

The Density of Phosphorus Vapour. ALFRED STOCK, GEORGE E. GIBSON, and ERICH STAMM (*Ber.*, 1912, **45**, 3527—3539).—A membrane-manometer, which is a special modification of the spiral manometer of Ladenburg and Lehmann (*Ber. Deut. physikal. Ges.*, 1906, **4**, 20), and is to be described in another paper, was used to determine the vapour density of phosphorus; the manometer is sensitive to 0·5 mm. difference in pressure. Purified red phosphorus, which can be obtained in a purer condition than colourless phosphorus, was used in the experiments, at the temperature of which it was completely transformed into vapour.

At temperatures between 500° and 700° the vapour density corresponds exactly with the formula P_4. At higher temperatures dissociation takes place, but even at 1200° it is only 61% under a pressure of 175 mm. Calculations made on the assumption that the dissociation which occurs is in accordance with the equation: $P_4 \rightleftarrows 2P_2$, give a very good agreement between theory and experiment. Under atmospheric pressure the degrees of dissociation at 800°, 1000°, and 1200° are respectively 0·01, 0·1, and 0·33; under a

pressure of 0·25 atmos. the degree of dissociation is almost 0·66 at 1200°.

Calculation of the heat of dissociation gives values varying from − 49,200 to − 50,300 cals.

The above results do not agree with previous measurements, but various measurements were so concordant that there is every probability of their accuracy. The experiments of Preuner and Brockmöller (A., 1912, ii, 1146) are probably untrustworthy because they used ordinary, commercial phosphorus. T. S. P.

Boron Hydrides. ALFRED STOCK and CARL MASSENEZ (*Ber.*, 1912, **45**, 3539—3568).—The boron hydrides obtained by the authors have been prepared by the action of hydrochloric acid on magnesium boride.

Full details are given of the conditions needful for the preparation of a satisfactory sample of magnesium boride from magnesium and boron trioxide.

The decomposition of the boride with acid was carried out in an apparatus similar to that used in the preparation of antimony hydride (A., 1904, ii, 246), the boride being dropped continuously into the acid whilst a slow stream of hydrogen is passed through the apparatus. The decomposition is carried out at 50°, using 4*N*-hydrochloric acid. The evolved gases are passed through U-tubes immersed in liquid air, a snow-like deposit forming, whilst hydrogen passes on. The first portions of gas escaping from the U-tube smell strongly of boron hydride, but as soon as the solid forms it prevents the escape of any more hydride. The deposit consists of boron hydrides, together with silicon hydrides and carbon dioxide from impurities in the materials used. It is fractionally distilled at varying pressures and temperatures in order to remove the impurities. Hydrogen and traces of silicon hydride are removed by evacuating at the temperature of liquid air. The temperature is then raised to − 80°, when the solid melts to a colourless, strong refracting liquid, having a pressure of 250 mm. The pressure can be rapidly diminished to a few millimetres, whereby silicon hydrides, carbon dioxide, and any traces of hydrogen phosphide or sulphide which may be present are removed. As soon as the gas is free from silicon hydride, it is collected separately at a pressure of less than 3 mm., the temperature of the room in which the distillation is being carried out being maintained above 20°, otherwise liquid hydride would be condensed in the mercury pump used. The gas collected at this pressure and temperature consists of the *boron hydride*, B_4H_{10}. The residue is then warmed to − 40° and distilled until the pressure falls to $1\frac{1}{2}$ mm., the temperature further raised to 0°, and distillation proceeded with until the pressure falls to 9—10 mm., in order to remove all the hydride B_4H_{10}. The remaining liquid on further distillation gives the *boron hydride*, B_6H_{12}, the pressure falling below 5 mm. Two hundred grams of magnesium boride give about 100 c.c. of the pure hydride B_4H_{10}, and 60 mg. of the hydride B_6H_{12}.

Owing to the fact that these hydrides possess compositions very

different from what was to be expected, they were analysed by a number of different methods.

The hydride B_4H_{10} was analysed as follows: (1) a known volume was decomposed by passing slowly through a weighed quartz tube at 500° and the hydrogen collected. The boron was weighed directly, and also oxidised to boric acid and estimated volumetrically; (2) at room temperature the gas is slowly decomposed by water, with liberation of hydrogen and formation of boric acid. The results are in accordance with the equation: $B_4H_{10} + 12H_2O = 4B(OH)_3 + 11H_2$. (3) Decomposition also takes place in the presence of sodium hydroxide, the results according with the equation: $B_4H_{10} + 4NaOH + 4H_2O = 4NaBO_2 + 11H_2$. The vapour density agrees with the formula B_4H_{10}.

The boron hydride B_4H_{10} is a colourless liquid, b. p. 16—17°/760 mm., m. p. *ca* −112°, of a peculiar and most disagreeable odour. A few bubbles of the gas affect respiration and cause headache. It is a very unstable substance, decomposing at the ordinary temperature after a few hours, and quicker at higher temperatures, giving rise to a whole series of new hydrides which await investigation. It is similarly decomposed by electric sparks. It takes fire spontaneously in the air or in oxygen, burning with a green flame. Water and dilute hydrochloric acid decompose it, and it is oxidised by concentrated nitric acid with explosive violence. It is rapidly absorbed by aqueous sodium hydroxide, the solution slowly evolving hydrogen in accordance with the equation already given. It is probable that an intermediate hypoborate, corresponding with the oxide B_4O_5 (compare Travers and Ray, A., 1912, ii, 938), is formed, since when brought into contact with solid potassium hydroxide the latter becomes coated with a thick layer of a white salt in the form of a loose powder.

Ammonia gives a solid light brown substance, insoluble in water, whilst alcohol decomposes the hydride with evolution of hydrogen. The solution in benzene is very stable towards oxygen.

The hydride B_6H_{12} was analysed similarly to the hydride B_4H_{10} by decomposing it by heat. The vapour density corresponds with the formula B_6H_{12}. It is a colourless liquid, b. p. 10°/15 mm., *ca* 100°/760 mm., possessing a highly disagreeable odour and taking fire spontaneously in the air. It is more sensitive towards water and moisture than the hydride B_4H_{10}. With aqueous alkalis, hydrogen is immediately evolved.

The composition of the above hydrides is not in agreement with that of the boron alkyls, nor with the results obtained by Jones and Taylor (T., 1881, **39**, 213), Sabatier (A., 1891, 979), and Ramsay and Hatfield (P., 1901, **17**, 152). A critical examination of the experiments of these various investigators shows that no trustworthy conclusion can be drawn from them as to the composition of boron hydride. T. S. P.

Condition Diagram of Carbon Dioxide. GUSTAV TAMMANN (*Chem. Zentr.*, 1912, ii, 598; from *Nachr. K. Ges. Wiss. Gött.*, 1912, 446—452).—The author had observed previously that liquid carbon

dioxide at temperatures ranging from $-56{\cdot}7^\circ$ to $-7{\cdot}5^\circ$ and pressures between 5·1 atm. and 2800 kg. per sq. cm. deposited a different crystalline species from that obtained at higher pressures. Repetition of the experiments up to 4000 kg. pressure showed that a triple point does not occur in the melting curve (compare A., 1912, ii, 29).

T. A. H.

Carbon Subsulphide, C_3S_2. ALFRED STOCK and PAUL PRAETORIUS (*Ber.*, 1912, **45**, 3568—3578).—In the preparation of carbon telluride (A., 1911, ii, 722) a substance possessing a very penetrating odour was always an accompanying product. This has proved itself to be the tricarbon disulphide, C_3S_2, first obtained by Lengyel (A., 1894, ii, 90), which the authors propose to call carbon subsulphide from analogy to carbon suboxide.

Lengyel's method of preparation (*loc. cit.*) is not a convenient one, and the authors have sought for a better. The compound is produced when an arc is formed between carbon electrodes under liquid carbon disulphide, but it is accompanied by many by-products. It is also produced when carbon disulphide is passed through a heated quartz tube, the most favourable temperature being 1000—1100°; carbon is deposited in the tube at the same time, and diminishes the yield of subsulphide. If the quartz tube is filled with a spiral of iron wire, the formation of subsulphide takes place below 800°, but it soon ceases owing to the formation of iron sulphide. The action of metals led the authors to investigate the formation of subsulphide by the disintegration of metals by means of an arc under liquid carbon disulphide, the disintegration of the anode exposing fresh, hot surfaces continually to the carbon disulphide. Iron, copper, and aluminium electrodes gave no subsulphide, whilst electrodes of arsenic, bismuth, lead, tin, antimony, cadmium or zinc yielded the required compound, large quantities of the metallic sulphides being formed at the same time. The best results were obtained with a carbon cathode and an anode consisting of antimony mixed with 7% of carbon. The brownish-red solution obtained is filtered, and then shaken with mercury and phosphoric oxide to remove sulphur and polysulphides and water. A solution of carbon subsulphide in carbon disulphide is thus obtained, from which by distillation, finally under a high vacuum, the pure substance is obtained in a receiver cooled to -40° as a yellowish-red solid. At the ordinary temperature, it forms a bright red, strongly refracting liquid, the vapour density of which corresponds with the formula C_3S_2; the m. p. is $-0{\cdot}5^\circ$, and the substance possesses normal molecular weight in carbon disulphide solution.

The alcoholic solution decomposes after a short time. Dilute solutions in carbon disulphide are salmon-coloured, stronger solutions, yellowish-brown; above 1% strength the solutions gradually deposit black, polymerisation products, even in the dark; solutions below 1% strength are stable in the dark, but not in sunlight. Carbon disulphide solutions have no action on copper or mercury, but are decomposed by the sulphides of these metals, owing, probably, to the formation of additive products.

The polymerisation at 90° is a reaction of the second order, and

can be readily measured by observing the diminution in pressure; the reaction takes place at the surface of the containing vessel.

Carbon subsulphide can be considered as the anhydride of thiomalonic acid (compare carbon suboxide), since with aniline it readily gives thiomalonanilide. Its constitution may therefore be expressed as S:C:C:C:S.

The black polymerisation product is not affected by water, sodium hydroxide, hydrochloric acid, or chlorine water. Heated in a vacuum it gives carbon disulphide and a black residue which still contains 39% of sulphur. T. S. P.

The Reduction of Silica. H. VON WARTENBERG (*Zeitsch. anorg. Chem.*, 1912, **79**, 71—87).—Platinum is often attacked when heated in a silica vessel in a reducing atmosphere, even if not in contact with the silica, indicating the formation of either silicon vapour or silicon hydride. The dissociation of silicon hydride (prepared by the action of alcohol on purified silicon-chloroform, followed by decomposition of the ester by sodium) has been studied. It is necessary to use a catalyst, and the nickel used in Sabatier's method of reduction has proved to be suitable. Without a catalyst, decomposition is hardly measurable below 350°, even after several days. Measurements up to 380° give the result $SiH_4 = Si + 2H_2 - 8700$ cal. From 100° to 150° the pressures observed are higher than would be expected, probably owing to the occurrence at the lower temperature of the reaction $2SiH_4 = Si_2H_4 + 2H_2$.

The volatilisation of crystallised silicon in a stream of hydrogen has been measured up to 1315°. Silicon hydride is not to be detected in the issuing gas. The experiment has been repeated with argon in place of hydrogen, with similar results, the diminished loss of silicon being accounted for by the formation of a thin protecting layer of the nitride, Si_3N_4, as nitrogen is not completely removed from argon, even by passing over heated lithium. The value $SiH_4 = Si$ (vapour) $+ 2H_2 - 44{,}000$ cal. is calculated.

The reduction of silica by hydrogen has been studied at 1350—1400°, at which temperature silica is not volatile. The observed sublimation at lower temperatures is therefore due to reduction followed by oxidation. Carbon monoxide and graphite are also capable of reducing silica. C. H. D.

The Velocity of Crystallisation and Crystallising Power of Silicates. ERWIN KITTL (*Zeitsch. anorg. Chem.*, 1912, **77**, 335—364).—The crystallisation of a number of silicates has been examined in relation to the viscosity. Crystallisation takes place on the heating stage of a microscope, and the growth of the crystals, which usually form radiating groups of needles, is measured by means of a micrometer eyepiece. The linear velocity of crystallisation varies with the undercooling in the manner described by Tammann for organic substances. The horizontal maximum of the curve is often very short, or diminished to a point, and is best marked in silicates of low viscosity. Olivine, bronzite, and hypersthene show sharp maxima, whilst polysilicates show a low, flat curve. The maximum is usually 20—30° below the initial temperature of crystallisation. Metasilicates

form the longest needles, the larger number of centres in orthosilicates causing interference.

Orthosilicates of the alkalis form glasses without crystallising, with the exception of lithium orthosilicate, which crystallises if cooled slowly. Simple and mixed magnesium, calcium, ferrous, and manganous silicates crystallise readily. Alkali metasilicates, with the exception of lithium, form only glasses. The simple metasilicates of the metals mentioned above crystallise readily, whilst the mixed metasilicates remain partly glassy. Polysilicates, especially those of complex constitution, tend to form glasses. C. H. D.

The Proportion of Potassium Chloride in Potassium Chlorate, and the Nephelometric Control. FRIEDRICH MEYER and ARTHUR STÄHLER (*Zeitsch. anorg. Chem.*, 1912, **77**, 255—256. Compare A., 1911, ii, 881; Guye, A., 1912, ii, 552).—The criticism of Guye overlooks the fact that the solution in the nephelometer is not one of silver chloride in pure water, but contains an excess of either silver or chloride, considerably diminishing the solubility. In the case of potassium chlorate, the error cannot affect more than the sixth decimal place in the atomic weight of chlorine or potassium.

C. H. D.

Molten Carnallite. KURT ARNDT and HEINRICH HUGO KUNZE (*Zeitsch. Elektrochem.*, 1912, **18**, 994—998).—Determinations of the density, electrical conductivity, and freezing point of carnallite and mixtures of carnallite and potassium chloride are given. The carnallite used was prepared artificially by mixing magnesium chloride and potassium chloride in the requisite proportions. In all experiments decomposition of the magnesium chloride was prevented by the constant and careful addition of small quantities of ammonium chloride. The freezing points were deduced from cooling curves obtained by the use of a thermocouple, and are as follows: pure carnallite, 496°; carnallite + 6% KCl, 493°; carnallite + 12% KCl, 484°; carnallite + 18% KCl, 470°; carnallite + 24% KCl, 460°, and carnallite + 30% KCl, 436°. The density determinations were made by weighing a platinum sinker in the molten mixture (compare Brunner, A., 1904, ii, 244). Tables of results are given which show that at 550°, 650°, and 750° the addition of potassium chloride up to 30% causes a slight decrease in the density of the mixture. Pure carnallite has the density at 570°, 1·711; 600°, 1·698; 650°, 1·678; 700°, 1·658; 750°, 1·638, and 780°, 1·625. It is shown from the density determinations that carnallite and potassium chloride form no definite compounds. The conductivity measurements were made by the method described by Arndt (A., 1906, ii, 418), and the following specific conductivities obtained:

	%-Excess of potassium chloride.		
Temp.	20·3—20·5.	10·4—10·7.	0·8—1·0.
550°	0·96	0·92	0·87
600	1·07	1·03	0·98
650	1·18	1·14	1·09
700	1·29	1·25	1·20
750	1·40	1·36	1·31

By extrapolation from the above figures the specific conductivity of pure carnallite was deduced. The values are at 570°, 0·92; 600°, 0·97; 650°, 1·08; 700°, 1·20, and 780°, 1·37. J. F. S.

Thermal Analysis of Binary Mixtures of Alkali Nitrites with Other Salts of the Same Metals. D. MENEGHINI (*Gazzetta*, 1912, **42**, ii, 472—479).—The paper deals with the thermal analysis of the systems KNO_2–KNO_3, $NaNO_2$–$NaCl$, and $NaNO_2$–$NaBr$. Fused mixtures of potassium nitrite and nitrate, in the interval from 10% to 100% of nitrate, give an uninterrupted series of mixed crystals, whilst at the ordinary temperature between the same limits of concentration there is no miscibility. It is impossible to obtain nitrite free from nitrate.

The experiments with sodium nitrite were carried out with a nitrite containing 1·5% of nitrate. The diagrams of the systems $NaNO_2$–$NaCl$ and $NaNO_2$–$NaBr$ belong to Roozeboom's type III. R. V. S.

The Action of Ozone on Alkali Hydroxides. WILHELM TRAUBE (*Ber.*, 1912, **45**, 3319—3320. Compare A., 1912, ii, 844).—The previous work of Manchot and Kampschulte (A., 1908, ii, 101) on the same subject is acknowledged. T. S. P.

The Electrolytic Preparation of Sodium Hypochlorite. PAUL H. PRAUSNITZ (*Zeitsch. Elektrochem.*, 1912, **18**, 1025—1080).—After careful consideration of the theory of the electrolytic production of sodium hypochlorite from sodium chloride the paper deals first with an experimental examination under laboratory conditions, with enclosed cells, of the various factors which influence the reaction. In the second part the results are applied to the technical conditions, the author using in this connexion working models of the best known technical electrolysers. The experiments were all made, except where the contrary is stated, with $5N$-solutions of sodium chloride to which a $0·2N$-solution of potassium chromate had been added. The reactions were studied with regard to the maximum concentration of available bleaching chlorine obtainable and the current efficiency. The first section includes: (*a*) The influence of the anode current density (D_a) and the anode shape. The best results were obtained with a short bright platinum anode in the form of a wire, in which case a maximum concentration of 88 grams per litre of available bleaching chlorine was obtained with a current density $D_a = 14·3$ amperes per sq. cm. Massive platinum anodes (sheets or wires) are far more efficient than gauze electrodes. Platinised platinum anodes showed a slight superiority over bright anodes for current densities up to $D_a = 0·44$ ampere per sq. cm., but above this value there was no advantage gained by platinising the electrodes. With $D_a = 0·44$ ampere per sq. cm. using platinised electrodes a maximum concentration of 48 grams per litre available bleaching chlorine was obtained with a current efficiency of 91%. The platinised electrodes showed their superority, especially when they had been previously cathodically polarised. Grey platinum electrodes behaved similarly to the platinum-black electrodes.

(*b*) Influence of temperature. The best results were obtained at the ordinary temperature. At 30° the concentration of hypochlorite was diminished, whilst at 0° and 15° the formation of chlorine hydrate ($Cl_2,10H_2O$) on the anode interfered with the process. (*c*) Influence of stirring the electrolyte. The effect of stirring is to reduce the maximum concentration of the hypochlorite. (*d*) Influence of dilution of the electrolyte. The salt concentration was changed from 5*N* to 2*N* and 1·1*N*; in each case there was a decrease in the maximum concentration of the hypochlorite and of the current efficiency. (*e*) Influence of the addition of various substances to the electrolyte. The object of the addition was to prevent cathodic reduction. The experiments were carried out with carbon anodes in addition to platinum which had hitherto been used. The results are: (I) Potassium chromate prevented reduction almost entirely; (II) the addition of calcium chloride and Turkey-red oil (sulphonated castor oil) allowed a reduction of 20%, although a 30% higher maximum concentration of hypochlorite could be obtained. The action of the Turkey-red oil is probably the formation of an anode coating which causes a great increase of the current density. The best results are obtained by combining the chromate and Turkey-red oil additions; in this way, for example, 62 grams per litre of available bleaching chlorine was obtained with a 62% current efficiency. By using Portland cement to make the cell walls of, from which something is dissolved, an improvement of both anode and cathode actions was effected. Wheat starch and soluble starch gave much inferior results. The author experimented with models of the apparatus used in the old Kellner process, the new Kellner process, the Schuckert process, and the Weichert process. Working with the old Kellner process it was found that the highest concentration of hypochlorite obtainable was 12—20% below that given in closed vessels. This is attributed to the influence of the carbon dioxide from the air and to the circulation of the electrolyte over the anode. In the new Kellner process it was found that the maximum hypochlorite concentration was independent of the current density and the rate of flow of the electrolyte. The anode in this process must be placed beneath the cathode for the best results. The yield is increased by the addition of potassium chromate and Turkey-red oil to the electrolyte, and in this case a concentration of 68 grams per litre available bleaching chlorine was obtained from a 5*N*-solution of sodium chloride with a 41% current efficiency. In the Schuckert process the current density has but little influence on the concentration of the product; the best results were achieved by adding potassium chromate to the electrolyte. The addition of calcium chloride and sodium resinate gave less favourable results. In the Weichert process, using a dilute sodium chloride solution (5·5° Be) with the addition of 0·2% potassium chromate, a yield of 8—10 grams per litre of available bleaching chlorine was obtained when working with a current of 14 amperes at 95 volts, and with the electrolyte flowing through the cell at 40 litres per hour.

J. F. S.

Crystallographic Study of Lithium Chlorate. (Mlle.) H. Bruhl (*Bull. Soc. franç. Min.*, 1912, **35**, 155—165).—Lithium chlorate

was prepared by mixing solutions of lithium sulphate and barium chlorate. It is extremely deliquescent and is very soluble in alcohol, the latter property affording a means of purifying the salt. Under the microscope the anhydrous salt, $LiClO_3$ (m. p. 125—127·5°), was observed in three different crystalline modifications. There is also the hydrate, $Li,ClO_3,\frac{1}{2}H_2O$ (m. p. 63—65°), which forms plates with secondary twin-lamellæ. L. J. S.

The Binary System Li_2SiO_3–$Al_2(SiO_3)_3$. REZSÖ BALLÓ and EMIL DITTLER (*Zeitsch. anorg. Chem.*, 1912, **77**, 456. Compare A., 1912, ii, 758).—The biaxial modification of lithium metasilicate previously described is already known, and is probably monoclinic. Its properties persist in its solid solution with aluminium metasilicate. C. H. D.

The Carbonic Acid of Natural Waters which is Able to Attack Calcium Carbonate. J. TILLMANS and O. HEUBLEIN (*Chem. Zentr.*, 1912, ii, 1395—1396; from *Gesundheits-Ing.*, 1912, **35**, 669—677).—A certain amount of carbonic acid is necessary to protect calcium hydrogen carbonate from decomposition, so that, although "free," it does not attack calcium carbonate. Thus a soft water will attack limestone far more than a hard water containing the same amount of free carbon dioxide. A curve has been made, connecting calcium hydrogen carbonate with the carbon dioxide which is necessary for its protection. Having found the amount of combined carbon dioxide and the total free carbon dioxide in a water, it is thus possible to say how much of the latter is capable of attacking calcium carbonate. Small amounts of magnesium carbonate do not seriously affect the results. J. C. W.

Physical Action of Neutral Reagents on the Tribasic Alkaline Earth Phosphates. Investigation of the Colloidal State. WILLIAM OECHSNER DE CONINCK (*Rev. Gen. Chim. Pure Appl.*, 1912, **15**, 285—286).—If the normal phosphates of calcium, strontium, and barium are shaken up with water, methyl alcohol, or ethyl alcohol for several days, colloidal solutions are obtained which can be separated from the excess of phosphate by filtration through filter paper. In this way the author has prepared colloidal solutions of calcium phosphate in water and methyl alcohol and of strontium phosphate in methyl and ethyl alcohol. The solutions are unstable, and on this account the solutions of barium phosphate, which appear to be formed in methyl and ethyl alcohols, are coagulated during the process of filtration. H. M. D.

The Ternary Alloys of Magnesium, Zinc, and Cadmium. GIUSEPPE BRUNI and CARLO SANDONNINI (*Zeitsch. anorg. Chem.*, 1912, **78**, 273—297).—The portion of this system which includes the constituents Zn–Cd–$MgZn_2$ has been described previously (A., 1910, ii, 954). Cadmium retains up to 2 atomic % of zinc in solid solution. The crystallisation-interval is very small throughout the magnesium–cadmium series. A transformation curve for the compound MgCd is

drawn, showing a eutectoid point near 80 atom. % Cd, traces of a eutectoid structure being recognisable in slowly-cooled alloys having about this composition.

The compounds $MgZn_2$ and MgCd form a simple eutectiferous series. The entire triangular diagram is divided into two parts by a continuous eutectic curve, connecting the two eutectic points of the magnesium–zinc system, and separating the $MgZn_2$ area from that of solid solutions and from that of zinc. This curve passes through a maximum. The curves of secondary and eutectic crystallisation have been completely traced. It appears that the β-solid solutions retain zinc in solution at high temperatures, but that its solubility disappears at about 250°.

The alloys are best etched by means of nitric acid in amyl alcohol. The photo-micrographs illustrate the whole series of ternary alloys, and serve to fix the limits of stability of the solid solutions.

C. H D

Action of Potassium Amide on Thallium Nitrate in Liquid Ammonia Solutions. EDWARD CURTIS FRANKLIN (*J. Physical Chem.*, 1912, **16**, 682—703).—The author describes in detail the preparation and properties of thallium nitride and potassium ammoniothallite which have already been briefly mentioned (A., 1912, ii, 452).

The interaction in liquid ammonia solution of thallium nitrate and potassamide according to the equation: $3TlNO_3 + 3KNH_2 = Tl_3N + 3KNO_3 + 2NH_3$ yields a a dense black precipitate of thallium nitride which is readily soluble in excess of potassamide and also in liquid ammonia solutions of ammonium nitrate. In the latter case the thallium nitride is reconverted into nitrate, thus: $Tl_3N + 3NH_4NO_3 = 3TlNO_3 + 4NH_3$.

From the solution in excess of potassamide well formed, golden-yellow crystals are deposited. These consist apparently of isomorphous mixtures of potassamide and dipotassium ammoniothallite with ammonia of crystallisation. The potassamide may be eliminated by contact with excess of thallium nitride or by repeated crystallisation.

Dipotassium ammoniothallite, when freed from excess of ammonia in a vacuum at $-40°$, has the formula $TlNK_2,4NH_3$ or

$$TlNH_2,2KNH_2,2NH_3.$$

At $+20°$, in a vacuum, ammonia is given off and the yellow substance, $TlNK_2,2NH_3$ or $TlNH_2,2KNH_2$, results. On further deammoniation at $+100°$ the substance turns black and approximates to the composition $TlNK_2,1\frac{1}{3}NH_3$, alternatively written $Tl_3N,6KNH_2$ or as a simple mixture ($Tl_3N + 6KNH_2$).

The alternative formula for dipotassium ammoniothallite,

$$TlNH_2,2KNH_2,2NH_3,$$

is more reasonable in view of the isomorphous mixed crystals with potassamide, but, on the other hand, thallium amide is unknown in the free state. The extreme composition observed in the mixed crystals was $TlNK_2,4NH_3 : 3{\cdot}6KNH_2$, and the higher the proportion of potassamide the greater the solubility. The ammonia of crystallisation was always proportional to the thallium content, the proportions being $Tl : 4NH_3$ and $Tl : 2NH_3$ in preparations dried at $-33°$ and $+20°$ respectively.

Thallium nitride and potassium ammoniothallite and its mixtures

explode with great violence when subjected to heat, shock, or the action of water or dilute acids. They were hydrolysed for analysis by means of water vapour.

No evidence could be obtained of the formation of an amide or imide of thallium even at $-33°$. R. J. C.

The Quaternary System $KCl-CuCl_2-BaCl_2-H_2O$. FRANS A. H. SCHREINEMAKERS and (Miss) W. C. DE BAAT (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 467—472).—The equilibria occurring in this quaternary system have been examined at 40° and 60°. The choice of these temperatures is determined by the fact that the ternary system $KCl-CuCl_2-H_2O$ is characterised by the formation of only one double salt, $2KCl,CuCl_2,2H_2O$, below 57°, whereas a further double salt, $KCl,CuCl_2$, may occur between 57° and 92°.

The experimental data may be conveniently represented by means of a tetrahedron, the four apices of which correspond with the four components. The spacial model for 40° shows saturation surfaces corresponding with KCl, $BaCl_2,2H_2O$, $CuCl_2,2H_2O$, and

$$2KCl,CuCl_2,2H_2O,$$

whereas that for 60° shows an additional surface corresponding with $KCl,CuCl_2$.

The temperature corresponding with the disappearance of this surface has been found to be 55·7°, and this temperature corresponds with the reversibility of the change represented by $BaCl_2,2H_2O + CuCl_2,2H_2O + 2KCl,CuCl_2,2H_2O \rightleftharpoons KCl,CuCl_2 +$ solution.

H. M. D.

Mutual Solubilities of Cuprous Chloride and Ferrous Chloride, as also of Cuprous Chloride and Sodium Chloride, and the Transformation Point of $FeCl_2,4H_2O \rightleftharpoons FeCl_2,2H_2O + 2H_2O$. ROBERT KREMANN and F. NOSS (*Monatsh.*, 1912, **33**, 1205—1215).—At 21·5° the solubility of cuprous chloride is increased by the addition of ferrous chloride, as also that of ferrous chloride by the addition of cuprous chloride, the solid phases in equilibrium with the solution being respectively cuprous chloride and ferrous chloride; there is no formation of a double salt. The solution saturated with respect to both the salts contains 73·20 grams of ferrous chloride (anhydrous) and 23·20 grams of cuprous chloride in 100 grams of water.

The system: cuprous chloride–sodium chloride–water at 26·5° behaves similarly to the system: ferrous chloride–cuprous chloride–water. At the point where it is simultaneously saturated with respect to the individual salts, it contains 57·21 and 44·14 grams of cuprous chloride and sodium chloride respectively per 100 grams of water.

The transformation point of the system $FeCl_2,2H_2O + 2H_2O \rightleftharpoons FeCl_2,4H_2O$, as determined by cooling curves, was found to be 65·2°.

T. S. P.

Ammoniacal Sodium Cuprous Trithionate. KSHITIBHUSHAN BHADURI (*Zeitsch. anorg. Chem.*, 1912, **78**, 327).—Copper sulphate is precipitated with ammonia, and the precipitate is washed and dissolved in ammonia. Sodium thiosulphate is added, and after remaining overnight, blue crystals are obtained, the solution becoming colourless.

The product, after washing with water and alcohol and drying, forms sky-blue crystals, soluble in water or more readily in ammonia, and giving the reactions of a trithionate. The salt has the composition $3Cu_2S_3O_6,2Na_2S_3O_6,9NH_3$. C. H. D.

The System $HgCl_2$–$CuCl_2$–H_2O. FRANS A. H. SCHREINEMAKERS and J. C. THONUS (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 472—474).—In order to ascertain whether mercuric chloride and cupric chloride form a double salt, the form of the solubility isotherm has been determined by a series of solubility measurements at 35°. The composition of the residual "solid phase" as well as that of the solution was determined, and the numbers so obtained show that no double salt is formed at this temperature. A solution containing 21·5% of cupric chloride and 50·5% of mercuric chloride is saturated both with respect to cupric chloride ($CuCl_2,2H_2O$), and to mercuric chloride. The middle portion of the isotherm, where two solid phases coexist, is of very limited dimensions.

The data show that the solubility of mercuric chloride is greatly increased by the addition of cupric chloride. Whereas, in pure water, the solubility amounts to 8·5%, it increases to 52·8% in presence of 18·06% of cupric chloride. When the quantity of cupric chloride present is further increased, a slight diminution occurs in the percentage amount of dissolved mercuric chloride. H. M. D.

The Acid Dissociation Constant of Aluminium and Zinc Hydroxides. ROLAND EDGAR SLADE (*Zeitsch. anorg. Chem.*, 1912, **77**, 457—460. Compare P., 1910, **26**, 236; Klein, A., 1912, ii, 351; Hantzsch, *ibid.*, 644).—An approximate calculation shows that aluminium hydroxide must have an acid dissociation constant of at least 10^{-10}, and probably higher, and that zinc hydroxide, in its most stable form, must have a corresponding constant of not less than $0{\cdot}5 \times 10^{-12}$. C. H. D.

Ultramarine Compounds. L. WUNDER (*Zeitsch. anorg. Chem.*, 1912, **77**, 209—238).—The replacement of sodium in blue ultramarine by other metals has been studied by Heumann (A., 1877, ii, 572; 1878, 113; 1879, 437, 692; 1880, 217—367), and has now been further developed. The material is heated with the reacting solution to 120—180° in a closed glass tube, enclosed in sand in a steel cylinder.

Mercurous nitrate yields a greyish-blue mercuro-ultramarine, which loses mercury on heating and leaves a pure blue residue, which becomes yellow on heating and again blue on cooling, this change being capable of being repeated indefinitely. The product is very stable towards acids. Mercuric salts are reduced by ultramarine. Cadmium yields an olive-green product, whilst lead replaces the sodium completely. Lithium, ammonium, and calcium ultramarines have also been prepared.

The decomposition of ultramarine by alum solutions is not due to the acidity of the latter, but to the intermediate formation of an aluminium derivative. Chromium has the same effect. Ferrous ultramarine is dark greyish-blue, and is readily decomposed by acids.

Yellow phosphorus reduces ultramarine to a leuco-compound, which again becomes blue if heated in air. Red ultramarine is decomposed by acids without evolution of hydrogen sulphide, and is not changed by alum solution. Red ultramarine is best prepared by the action of nitric oxide on the blue compound, sulphur being removed in the process. Violet ultramarine is decomposed by alum, and also by acids, sulphur dioxide being evolved. Dry hydrogen reduces it, sulphur being removed as hydrogen sulphide.

Formulæ are proposed for all these compounds. Red ultramarine is regarded as an acid, the sodium salt of which is the violet compound. The blue compound contains the group Al—S—Na, which is absent from the red. C. H. D.

The Heusler Ferromagnetic Alloys of Manganese. EDGAR WEDEKIND (*Zeitsch. angew. Chem.*, 1912, **25**, 2524—2526).—A claim for priority against Heusler (*ibid.*, 2253) in respect to manganese borides, and the magnetic properties of binary compounds of manganese. C. H. D.

Ternary Alloys of Iron–Manganese–Copper. NICOLA PARRAVANO (*Gazzetta*, 1912, **42**, ii, 513—531).—Of the three binary systems comprised in the ternary system Fe–Mn–Cu, the system Fe–Cu has been studied by Sahmen (A., 1908, ii, 186), and the others by the author (A., 1912, ii, 1175, and this vol., ii, 58). The system Fe–Mn–Cu belongs to type I of the cases of solubility gaps in ternary systems discussed by Parravano and Sirovich (A., 1911, ii, 705), and in a theoretical discussion the author applies the conclusions there set forth to the construction of diagrams from the experimental results in the present instance. In addition to the diagrams, photographs are given of a number of the ternary alloys, which are thus shown to have the structure to be expected from their position in the space diagram. R. V. S.

Revision of the Atomic Weight of Iron. V. Analysis of Ferric Oxide. GREGORY P. BAXTER and CHARLES RUGLAS HOOVER (*J. Amer. Chem. Soc.*, 1912, **34**, 1657—1669).—From analyses of ferric oxide by reduction with hydrogen at 900°, Richards and Baxter (A., 1900, ii, 407) obtained the value 55·88 for the atomic weight of iron. Baxter (A., 1904, ii, 177) analysed ferrous bromide and found the value 55·845; on repeating this work with purer material, Baxter Thorvaldson, and Cobb (A., 1911, ii, 287) obtained the result 55·838. Baxter and Thorvaldson (A., 1911, ii, 288) further proved that meteoric and terrestrial iron give identical values.

In the present investigation, ferric oxide was prepared by igniting carefully purified ferric nitrate in a current of air. A weighed quantity of the oxide was reduced to the metal by heating it in a current of hydrogen at 1050—1100° for several hours. Two specimens of ferric nitrate were employed, one containing iron of terrestrial origin, and the other, meteoric iron.

The average of twelve analyses yielded 55·847 as the atomic weight of iron (O = 16·000). This when combined with the result obtained

from the analysis of ferrous bromide (Baxter, Thorvaldson, and Cobb, *loc. cit.*) gives the value 55·84. The identity of terrestrial and meteoric iron was confirmed. E. G.

The System Iron-Carbon. III. ANDREAS SMITS (*Zeitsch. Elektrochem.*, 1912, **18**, 1081—1086. Compare A., 1912, ii, 165, 769).—An answer to Ruff (A., 1912, ii, 917; compare also A., 1911, ii, 897). The remainder of the paper is a theoretical consideration of the results of Wittorf (A., 1912, ii, 259), who shows that the system iron–carbon undergoes two inverse separations by raising the temperature, namely, $C \longrightarrow Fe_4C \longrightarrow FeC \longrightarrow Fe_3C \longrightarrow C$. In this connexion the author discusses the relations of the separations of the substances C, FeC, FeC_2, C, which he shows are successively deposited on raising the temperature. *PT* curves of the system are given in which two quadruple points are indicated, at both of which graphite, FeC, solution and vapour are in equilibrium. On raising the temperature at the lower point, FeC is formed at the expense of the graphite, whilst at the higher point, graphite is produced at the expense of the FeC. The thermal relationships of the various changes are considered.

J. F. S.

The System Iron-Iron Sulphide. RICHARD LOEBE and E. BECKER (*Zeitsch. anorg. Chem.*, 1912, **77**, 301—319. Compare Treitschke and Tammann, A., 1906, ii, 547).—Ordinary ferrous sulphide always contains free iron and also oxide. A product containing 98·72% FeS is obtained by repeatedly melting natural pyrites. The mixtures are made by fusing this product with Swedish iron in porcelain tubes, using a kryptol furnace.

The equilibrium diagram shows a freezing-point curve of simple form, the two branches meeting in a eutectic point at 985° and 85% FeS. The solid components are practically immiscible on the iron side, whilst solid ferrous sulphide retains about 1%Fe in solution. The formation of two liquid layers and the occurrence of a crystallisation interval are not observed.

The transformations in the solid state have been examined by the differential method, and it is found that the sulphide is without influence on the transformation points of iron. A polymorphic transformation of ferrous sulphide occurs at 298°, and has been studied by the dilatometric method, using mercury as the filling liquid. The transformation at 138° is also observed in all mixtures containing more than 7% Fe (compare Rinne and Boeke, A., 1907, ii, 471). The brittleness of iron containing sulphide is due to this transformation.

Photo-micrographs of the alloys are given. The eutectic tends to become segregated in mixtures rich in sulphide. Alloys which have been in contact with oxygen contain a new eutectic. Fusion of iron sulphide with iron oxide, however, leads to the elimination of sulphur and formation of ferrite, and the structure is better developed by fusing the sulphide in contact with air. The composition of the eutectic is uncertain. The brittleness of iron containing sulphur at a red heat is due to the absorption of oxygen in this form.

C. H. D.

Stability of the Oxides of Cobalt in the Interval from Co_2O_3 to CoO. SIEGFRIED BURGSTALLER (*Chem. Zentr.*, 1912, ii, 1525—1526; from *Abhandl. Deut. naturwiss.-med. Ver. Böhmen*, 1912, **3**, 83—143).—The stability of the oxide of cobalt has been followed dynamically, in view of the numerous oxides mentioned in the literature and of the statical measurements of the dissociation pressures made by Richards and Baxter (A., 1900, ii, 78) and by Smith and Foote (A., 1908, ii, 847).

By means of baths of diphenylamine, b. p. 301·9°/760 mm., anthracene, b. p. 339·8°/760 mm., and anthraquinone, b. p. 377·2°/760 mm. the dissociation temperature of cobaltic oxide has been narrowed down to 372—373°/760 mm. Above this temperature the reduction of the oxide has been followed in a sulphur bath and in an electric oven, and after allowing for the possible sources of error (such as the time taken in warming up and in cooling down), the alteration of the oxygen concentration of the oxide with time, by rising or falling temperature, has been graphically portrayed.

From the dissociation temperature of cobalic oxide to a point between 705·5° and 869°, cobalto-cobaltic oxide is stable, above which the region for cobaltous oxide occurs. The transition points cannot be determined, however, because regions of solid solution of one oxide in the other must be passed through. From the reactions curve of the oxidation of cobalt in air it is also seen that between 300° and 431°, cobalto-cobaltic oxide is formed, and that at 869° the region of solid, solution between Co_3O_4 and CoO is entered.

The existence of solid solutions, and the fact that the speed of the dissociation becomes very slow after a short time, explain the numerous references to improbable oxides of cobalt. J. C. W.

The Replacement of Metals from Aqueous Solutions of their Salts by Hydrogen at High Temperatures and Pressures. IV. VLADIMIR IPATIEV and B. ZRJAGIN (*Ber.*, 1912, **45**, 3226—3229. Compare A., 1912, ii, 50).—In solutions of $2N$- and $0·2N$-cobalt sulphate and initial pressures of 100 atmos. of hydrogen, no formation of a precipitate takes place within twenty-four hours at 103°. At 145—150° a rosy-violet coloured, crystalline precipitate is formed, having the composition $CoSO_4,H_2O$; metallic cobalt also separates. If nitrogen or air is used instead of hydrogen, the $2N$-solution gives only the salt $CoSO_4,H_2O$.

When a quartz tube is used instead of a glass one, the reaction is not complete at 150° within four days, cobalt sulphate still remaining in solution. A glass tube could not be used for so long a time without being attacked.

At 150°, $2N$- and $0·2N$-cobalt nitrate solutions behave similarly to the sulphate solutions at 103°. At 205—210° a crystalline, brownish-black precipitate of cobaltic oxide, which is contaminated with silicic acid from the glass tube, is formed within a day (compare nickel nitrate, A., 1912, ii, 51). A similar result is obtained with N-solutions, both in glass and quartz tubes, whereas N-solutions of nickel nitrate give a small quantity only of a green, crystalline precipitate, containing 52·90—53·36% of nickel.

Solutions of cobalt chloride behave similarly to those of nickel chloride (*loc. cit.*), the reaction being reversible, namely, $CoCl_2 + H_2 \rightleftarrows Co + 2HCl$. T. S. P.

The Origin of the Colour Produced by Cobalt Solutions in Certain Mineral Colours. SIEGFRIED BURGSTALLER (*Chem. Zentr.*, 1912, ii, 1523—1525; from *Abhandl. Deut. naturwiss.-med. Ver. Böhmen.*, 1912, **3**, 57—80).—The coloured residues obtained by moistening certain inorganic oxides with cobalt solutions and then igniting are shown to be solid solutions in which a white substratum, such as alumina, does not modify the blue or red colour of the cobalt ion, whereas a yellow oxide, such as hot zinc oxide, produces a mixed colour.

Rinmann's green, prepared at 750—760° from zinc oxide moistened with cobalt nitrate, was extracted with ammonium carbonate, in which a solid solution of 7·05 mol. CoO to 100 mol. ZnO dissolved, whereas free cobaltous oxide was insoluble. Thénard's blue, obtained by evaporating aluminium nitrate with cobalt nitrate solution, and igniting the residue, also contained cobaltous oxide. No solvents could be found which would separate the solid solution from the free oxide, and other methods for investigating its constitution are being pursued. J. C. W.

Ternary Alloys of Nickel–Manganese–Copper. NICOLA PARRAVANO (*Gazzetta*, 1912, **42**, ii, 385—394).—The paper contains an account of this ternary system derived from the results of its thermal analysis and from the thermal analysis of the three constituent binary systems. Of these, the system Ni–Mn has been previously described by the author (A., 1912, ii, 1175), and the remaining two by other writers. The results of some new experiments with the system Cu–Mn are also given. The nature of the ternary system is exhibited in diagrams, and photographs are reproduced of a number of the ternary alloys prepared. R. V. S.

The Constitution of the Halogen Compounds of Bivalent Molybdenum. IVAN KOPPEL (*Zeitsch. anorg. Chem.*, 1912, **77**, 289—300).—The compounds having the empirical composition $MoCl_2$ and $MoBr_2$ are known to react in a manner which indicates a more complex constitution. The properties are now reviewed, and constitutional formulæ are proposed. The most important properties are the existence and stability of the radicles $(Mo_3R_4)''$, the formation of a crystalline hydroxide, the resistance to oxidation, the difference in solubility between the anhydrides and the hydrates, and the amphoteric character of the radicles.

The formulæ given assume a co-ordination number 4, the insoluble hydrates, for example, being $[Mo_3Cl_4R_2,2H_2O]H_2O$, where R is a halogen. The amphoteric hydroxy-compound is represented as $[Mo_3Cl_4(OH)_2,2H_2O]$, and the formation of salts from it is necessarily accompanied by isomeric change. C. H. D.

Molybdates. GEORG WEMPE (*Zeitsch. anorg. Chem.*, 1912, **78**, 298—326).—Ammonium tetramolybdate is best obtained by the

action of warm hydrochloric acid on the ordinary molybdate, and forms transparent, triclinic crystals, $(NH_4)_2O,4MoO_3,2H_2O$, of which 3·67 grams dissolve in 100 c.c. of water at 18°. Further decomposition gives the trimolybdate, $(NH_4)_2O,3MoO_3,H_2O$. Sodium tetramolybdate, $Na_2O,4MoO_3,6H_2O$, obtained by the action of nitric acid on the ordinary salt, is much more soluble than the ammonium salt. The trimolybdate is obtained with 6 or 9 H_2O from the mother liquor. Potassium tetramolybdate has not been obtained, the corresponding solutions yielding instead the trimolybdate, $K_2O,3MoO_3,3H_2O$. The potassium hydrogen tetramolybdate has the composition

$$K_2O,H_2O,8MoO_3,12H_2O.$$

Lithium tetramolybdate, obtained from Rammelsberg's salt and hydrochloric acid, forms triclinic crystals, $Li_2O,3H_2O,16MoO_3,6{\cdot}5H_2O$, from which a trimolybdate is obtained with 2 or 4 H_2O. A second tetramolybdate is $Li_2O,H_2O,8MoO_3,10H_2O$. The *rubidium* tetramolybates obtained are $Rb_2O,4MoO_3$; $Rb_2O,H_2O,8MoO_3,3H_2O$; $Rb_2O,MoO_3,Rb_2O,3MoO_3,5H_2O$; and $Rb_2O,4MoO_3,4H_2O$, whilst the trimolybdate has been obtained with $3H_2O$. The *caesium* salts are $Cs_2O,4MoO_3,3H_2O$; $5Cs_2O,12MoO_3,11H_2O$; and

$$Cs_2O,MoO_3,Cs_2O,3MoO_3,4{\cdot}5H_2O.$$

The *calcium*, $CaO,2H_2O,12MoO_3,21H_2O$ and $CaO,H_2O,8MoO_3,16H_2O$; *barium*, $BaO,H_2O,8MoO_3,14H_2O$ and $2(BaO,4MoO_3),7H_2O$; *strontium*, $2SrO,3H_2O,20MoO_3,21H_2O$; *thallous*, $Tl_2O,4MoO_3,H_2O$; *silver*, $Ag_2O,4MoO_3,6H_2O$; *cadmium*, $CdO,H_2O,8MoO_3,6H_2O$; *magnesium*, $MgO,H_2O,8MoO_3,20H_2O$; and *zinc*, $ZnO,H_2O,8MoO_3,14H_2O$, salts have also been obtained. C. H. D.

Iso- and Hetero-poly-acids. VI. Hydrates of Some Hetero-poly-acids. ARTHUR ROSENHEIM and JOHANNES JAENICKE (*Zeitsch. anorg. Chem.*, 1912, **77**, 239—251. Compare A., 1911, i, 109, 265; ii, 116, 612).—The following new hydrates of 12-phosphotungstic acid have been prepared: $H_7[P(W_2O_7)_6],28H_2O$, which is metastable at the ordinary temperature, and passes into the stable 22-hydrate. The transformation point must be below 0°. The addition of concentrated nitric acid to the solutions of precipitates the 19-hydrate.

12-Silicotungstic acid also yields two new hydrates,

$$H_8[Si(W_2O_7)_6],28H_2O,$$

which is stable below 29°, and the 22-hydrate, which is stable between 29° and 53°. 12-Borotungstic acid forms $H_9[B(W_2O_7)_6],28H_2O$, which does not pass into a 22-hydrate when heated. Nitric acid precipitates a 10-hydrate. The 22-hydrate previously described is hexagonal, and is derived from an acid isomeric with that of the 28-hydrate, the two hydrates crystallising simultaneously from solution.

Metatungstic acid, which is also a 12-hetero-poly-acid, yields only a single hydrate, $H_{10}[H_2(W_2O_7)_6],22H_2O$. 12-Phosphomolybdic acid yields a 28-hydrate, $H_7[P(Mo_2O_7)_6],28H_2O$, which apparently yields a 12-hydrate on dehydration, but the individual character of this hydrate is uncertain. A 22-hydrate is obtained by precipitation with nitric acid.

12-Silicomolybdic acid also forms a $H_8[Si(Mo_2O_7)_6],28H_2O$, from

which nitric acid precipitates a 12-hydrate, but a 22-hydrate has not been obtained. C. H. D.

Action of Acids on Uranous Oxide. A. COLANI (*Compt. rend.*, 1912, **155**, 1249—1251).—Using uranous oxide prepared by reduction of the green oxide with hydrogen, the author has obtained results widely different from those of Raynaud (A., 1912, ii, 166, 948). Whilst but a small amount of the uranous oxide goes into solution with sulphuric acid, a considerable amount is converted into the sulphate, and as such remains in the insoluble portion. Uranous oxide only dissolves slowly in hydrochloric acid, the amount dissolved in a given time varying widely with the mode of preparation of the oxide. Solution is continuous over a very long period of time. W. G.

Asserted Explosibility of Uranyl Nitrate. LAUNCELOT W. ANDREWS (*J. Amer. Chem. Soc.*, 1912, **34**, 1686—1687; *Chem. Zeit.*, 1912, **36**, 1463).—With reference to the statement of Ivanov (A., 1912, ii, 455) on the explosibility of uranyl nitrate, the author records the explosion of a quantity of uranyl nitrate, in the preparation of which ether had been employed. On adding strong solution of potassium hydroxide to some of the salt which had escaped decomposition, a marked odour of ether was produced, whilst another specimen when dissolved in water gave a deep blue colour to Congo-red paper, indicating the presence of nitric acid. It is considered that in this case the explosion was due to the water of crystallisation of the uranyl nitrate, $UrO_2(NO_3)_2,6H_2O$, having been replaced by ether and nitric acid, and it is regarded as probable that Ivanov's explosion was due to the same cause. E. G.

The System Tin–Iodine. WILLEM REINDERS and S. DE LANGE (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 474—481*).—The freezing-point curve for mixtures of iodine and stannic iodide consists of two branches meeting at a point corresponding with 79·6° and 60% by weight of stannic iodide. The corresponding boiling-point curve, which has been determined for atmospheric pressure, shows neither maximum nor minimum.

When stannic and stannous iodide are heated together at 350°, two liquid layers are formed, one of which consists of almost pure stannic iodide, whilst the other layer represents stannous iodide together with at most 6% of stannic iodide. When iodine is melted in contact with a small excess of tin, the product first formed is almost exclusively stannic iodide. The reaction $SnI_4 + Sn = 2SnI_2$ takes place extremely slowly, and even at 350° the velocity of this change is comparatively small.

Pure stannic iodide melts at 143·5° and boils at 340°, the corresponding temperatures for the stannous salt being 320° and 720°. H. M. D.

The Volatisation of Vanadic Acid by Halogens. ERNST B. AUERBACH and K. LANGE (*Zeitsch. angew. Chem.*, 1912, **25**, 2522—2523). —The observation of Ephraim (A., 1903, ii, 487) that vanadic acid

* and *Zeitsch. anorg. Chem.*, 1912, **79**, 230—238.

volatilises with hydrochloric acid, is confirmed. The loss when vanadic acid is heated with sodium chloride is also appreciable. When barium chloride is used, it is found that the greater part of the chlorine may be driven off with very little loss of vanadium, the chloride first formed being decomposed by the atmospheric moisture. If heated in a stream of dry carbon dioxide, red vapours are obtained, which condense to an oily liquid of unknown composition, containing vanadium. It is necessary, in the estimation of vanadium by means of mercurous nitrate, that chlorides should be absent. C. H. D.

Hetero-poly-acids Containing Vanadic Acid. WILHELM PRANDTL (*Zeitsch. anorg. Chem.*, 1912, **79**, 97—124. Compare A., 1912, ii, 167).—The author's view that compounds of this kind are derived from a hexa-vanadic acid is contrasted with the formulation due to Miolati (A., 1908, ii, 595) and Rosenheim (A., 1911, i, 109, 265; ii, 116, 612; this vol., ii, 59). Most of the well-defined compounds of this class may be represented as additive compounds of 4 or 6 mols. of molybdate and 1 mol. of hexavanadate.

Ammonium paramolybdate, $3(NH_4)_2O,7MoO_3,4H_2O$, is regarded as a compound of 1 mol. of diammonium trimolybdate with 4 mols. of ammonium hydrogen molybdate, $(NH_4)_2H_4Mo_3O_{12},4NH_4HMoO_4$. Acids remove ammonia from the monomolybdate molecule, which then polymerises to the trimolybdate, from which the hexamolybdate is obtained by elimination of water.

[With SIGMUND PERKOWSKI.]—The following new salts have been obtained: $KVO_3,K_2MoO_4,4H_2O$, or $K_3V_3O_9,3K_2MoO_4,12H_2O$, the normal salt of the series, which is pale yellow and very sensitive to acids. $Na_4V_6O_{17},6NaHMoO_4,12H_2O$, also yellow.

$$Na_6V_6O_{18},6Na_2H_4Mo_3O_{12},36H_2O,$$

pale yellow. $Ba_3V_6O_{18},6Na_2H_4Mo_3O_{12},20H_2O$ or $74H_2O$, according to the conditions of precipitation.

$$Na_2H_2V_6O_{17},Na_2H_4Mo_3O_{12},4NaHMoO_4,16H_2O;$$

$K_3HV_6O_{17},2KHMoO_4,2K_2H_4Mo_3O_{12},6H_2O$, which are more deeply coloured. $(NH_4)_4V_6O_{17},2NH_4HMoO_4,2(NH_4)_2H_4Mo_3O_{12},8H_2O$;

$$(NH_4)_3HV_6O_{17},2(NH_4)_2H_4Mo_3O_{12},4NH_4HMoO_4,6H_2O.$$

These salts are tabulated and correlated with others of the same series described in the literature. C. H. D.

Chemical Reactions of β-Gold and Crystallised Gold. MAURICE HANRIOT and FRANÇOIS RAOULT (*Compt. rend.*, 1912, **155**, 1085—1088. Compare A., 1911, ii, 791).—Contrary to general belief, ordinary gold as well as the brown (β) modification is attacked by nitric acid, the amount dissolved, whilst small, varying with the concentration of the acid, the β-modification being readily acted on. Fuming hydrochloric acid in the presence of oxygen also has a marked solvent effect. The best solvent for β-gold is a hot solution of auric chloride containing hydrochloric acid. On cooling the solution the dissolved gold crystallises out in the metallic state, and a determination of its magnetisation coefficient shows that, in this form, it consists almost entirely of the β-variety. This solvent has a much more marked action on the brown than the yellow gold, and it is the β-variety which passes into solution, thus leaving the insoluble residue

enriched with the α-variety. This fact is borne out by comparison of the magnetisation coefficients of the original brown gold, the crystallised gold, and the insoluble residue. W. G.

The Preparation and Application of Colloidal Platinum Metals. ALADAR SKITA and W. A. MEYER (*Ber.*, 1912, **45**, 3579—3589).—See this vol., i, 53.

Osmium Tetroxide as an Oxygen-carrier and the Activation of Chlorate Solutions. KARL A. HOFMANN (*Ber.*, 1912, **45**, 3329—3336).—In the presence of about 1 mg. of osmium tetroxide per 500 c.c., 1% solutions of *p*-leucaniline and leucomalachite-green become strongly coloured after a few hours on shaking in the presence of air.

Under an oxygen pressure of 10 atmospheres and temperatures of 50—100°, the following oxidations take place in the presence of 0·01 gram of osmium tetroxide per 200 c.c. of liquid: 40% alcohol is oxidised in three to four hours to acetic acid and aldehyde or acetal, traces of crotonaldehyde also being formed; 50% methyl alcohol gives formaldehyde and formic acid. The action on the aldehydes takes place very slowly, or not at all; for example, paracetaldehyde and acetal shows no signs of oxidation within eight days at 20°; vanillin only after twenty-four hours.

The acids, formic, acetic and oxalic, are very stable towards osmium tetroxide. Aniline sulphate is readily oxidised, and anthracene gives anthraquinone in acetic acid solution.

The following oxidising actions of potassium chlorate, in neutral or slightly acid solutions, take place very readily in the presence of osmium tetroxide, but not at all, or only extremely slowly, in its absence: arsenic to arsenic acid, hypophosphorous acid to phosphoric acid; hydrazine sulphate quantitatively to nitrogen, indigo-carmin to indigo-white, quinol to quinhydrone, aniline to emeraldin; mono- and di-methylaniline are oxidised; benzidine to diphenoquinone-di-imide, *p*-leucaniline and leucomalachite-green to the dyes; catechol, resorcinol, and tannin are oxidised, anthracene to anthraquinone, ethyl alcohol to acetal, no chlorination taking place; slightly acid potassium formate to carbon dioxide. Substances containing the ethylene linking, such as ethylene, propylene, amylene, indene, *r*-pinene, and dichloroethylene, $CHCl{:}CHCl$, are readily oxidised; trichloroethylene, $CHCl{:}CCl_2$, is only slowly oxidised, and perchloroethylene not at all. Allyl alcohol is much more readily oxidised than ethyl alcohol; *iso*eugenol is readily oxidised, whilst vanillin is not. Benzene containing thiophen gives a reaction due to the presence of the thiophen. Acetylene is oxidised.

Benzoic acid, bromobenzoic acid, naphthalene, and saturated ketones are not affected, and benzaldehyde only very slowly. T. S. P.

Mineralogical Chemistry.

Origin of Native Sulphur. A. W. KRUEMMER and R. EWALD (*Centr. Min.*, 1912, 638—640).—A large cavity in gypsum met with in the Barsinghausen mines was lined with bitumen, resting on which were large crystals of sulphur. Between the gypsum and the bitumen was a zone of calcium carbonate; and the gases in the cavity contained hydrogen sulphide and hydrocarbons. The sulphur had no doubt been formed by the reducing action of the hydrocarbons on the gypsum, for example:

I. $CaSO_4 + CH_4 = CaS + CO_2 + 2H_2O = CaCO_3 + H_2S + H_2O$.

II. $H_2S + H_2O + O = 2H_2O + S$.

The deposits of sulphur in Sicily, which are associated with gypsum and outbursts of gas containing hydrocarbons and carbon dioxide, have probably been formed in a similar manner. L. J. S.

Asphalt Theory of the Formation of Naphtha. K. W. CHARITSCHKOV (*Chem. Zeit.*, 1912, **36**, 1402).—The author finds that the decomposition products of Russian asphalt exhibit similarity to many Russian mineral oils. Specimens of the former yield, when distilled, paraffins, oils, and residues analogous to, and in approximately the same amounts as, the mineral oils, as shown in the appended table:

B. p.	Decomposition product.	Mineral oil (Grosny).
to 110°	5·72% (D 0·720)	4·78% (D 0·705)
110—150°	10·63% (D 0·765)	10·45% (D 0·7443)
150—220°	26·5 % (D 0·8108)	16·2 % (D 0·7219)

The author is led to the conclusion that naphtha is a product of the decomposition of asphalt. H. W.

Vrbaite, a New Thallium Mineral from Allchar, Macedonia. B. JEŽEK (*Zeitsch. Kryst. Min.*, 1912, **51**, 364—378). **Chemical Examination of Vrbaite.** FR. KŘEHLÍK (*Ibid.*, 379—383).—The new mineral was found as small (about 1 mm.) crystals embedded in realgar and orpiment. The crystals are orthorhombic, $a:b:c = 0·5659:1:0·4836$, with a tabular or pyramidal habit and a good brachypinacoidal cleavage. The mineral is opaque with a metallic to semi-metallic lustre and a greyish-black colour, but in thin splinters it is dark red and translucent; the streak is bright red with a tinge of yellow. $H = 3\frac{1}{2}$, D 5·30. It is readily fusible before the blowpipe, and is easily soluble in nitric acid. Analysis gives the formula $TlAs_2SbS_5$, representing a thallous salt of the acid HAs_3S_5, in which one atom of arsenic is replaced by antimony:

Tl.	Sb.	As.	S.	Fe.	Total.
29·52	18·34	24·06	25·20	1·85	98·97

L. J. S.

Iron Sulphide in the Miocene Clays of Govt. Samara, Russia. BRUNO DOSS (*Jahrb. Min.*, 1912, *Beil.-Bd.* 33, 662—713). —In boring for artesian water on the estates of the Brothers Melnikov, in the Novo-Usensk district, outbreaks of natural gas, containing 67·65% CH_4, 20·70% N, were encountered. The clays in these borings are impregnated with a black, very finely divided iron sulphide, which differs from the hydrated iron sulphide met with in the black mud of lakes and ponds. The material is magnetic: D 3·57—4·16 (the true value being probably 4·2—4·3). Analysis gave: Fe, 46·24; S, 51·92; insoluble, 3·95%, corresponding with the formula FeS_2. In another analysis the figures correspond with Fe_5S_7. The material is soluble in cold dilute hydrochloric acid with evolution of hydrogen sulphide, and it is much more readily attacked by various reagents (potassium cyanide, potassium hydroxide, iodine solution, etc., and even by boiling water) than is iron-pyrites. The material is regarded as a labile phase of iron disulphide, and is named *melnikovite*. Its mode of origin is discussed; it is regarded as having been derived from a colloidal form of iron sulphide. L. J. S.

Bauxite of the Croatian Karst and its Origin. MIJAT KIŠPATIC (*Jahrb. Min.*, 1912, *Beil.-Bd.* 34, 513—552).—Twenty analyses are given of bauxite from various localities in Croatia and also in Dalamatia and Bosnia; the extreme values shown are quoted under I and II. Analysis III is of the bauxite ("wochenite") from Wochein, Carniola:

	SiO_2.	TiO_2.	ZrO_2.	Al_2O_3.	Fe_2O_3.	MnO.	CaO.	Ign.	Total.
I.	0·87	nil.	nil.	24·54	1·80	nil.	nil.	8·11	—
II.	33·00	8·51	2·71	66·68	26·89	1·21	6·79	19·97	—
III.	61·31	trace	trace	16·95	12·46	trace	—	6·40	99·75

At these localities the bauxite occurs as beds in limestone and dolomite; it is dull red in colour, and usually oolitic in structure. Microscopical examination shows that the main constituent has the form of minute isotropic granules; this material is named *sporogelite* (compare Tućan, this vol., ii, 69), and to it is assigned the composition Al_2O_3,H_2O, corresponding with the crystalline diaspore. This colloidal material is sometimes white, but usually it is coloured by intermixture with colloidal iron oxide and hydroxide. Other minerals present, although usually only in small amounts, include diaspore, hydrargillite, quartz, felspar, amphiboles, felspars, micas, epidote, rutile, zircon, etc. The same materials were obtained when the limestones and dolomites were dissolved in acid; and it is considered that these bauxites, as well as those from some other localities (France, Italy, Georgia, etc.), represent the insoluble residues resulting from the weathering of these rocks. On the other hand, certain other bauxites (from the Vogelsberg) and laterite are the products of decomposition of basalt and other silicate rocks. L. J. S.

A New Deposit of Chrome-iron-ore in Northern Caucasus. N. BESBORODKO (*Jahrb. Min.*, 1912; *Beil.-Bd.*, 34, 783).—Veins of compact to granular chrome-iron-ore have been discovered in serpentine

about 12 km. south of the village Psemjonowka in prov. Kuban. Analysis I of an ore sample corresponds with about 85% of chromite. Secondary minerals occurring in the serpentine (an altered olivine-rock) include chrysotile, antigorite, chrome-chlorites (kaemmererite and kotschubeite), revdinskite, carbonates, and quartz. The revdinskite (anal. II) is apple-green with brownish patches, and occurs sparingly as a thin coating on the serpentine.

	SiO_2.	Cr_2O_3.	Al_2O_3.	FeO.	NiO.	MnO.	MgO.	CaO.	H_2O.	Total.
I.	1·66	59·09	8·08	18·43	—	0·20	12·47	0·91	0·20	101·04
II.	20·5	—	22·0		6·2	—	29·9	—	23·4	102·0

In the same district chromium and nickel minerals, respectively fuchsite and millerite, were detected in a contact-metamorphic rock (silicate hornfels). L. J. S.

Carboniferous Limestones of the Avon Gorge, Bristol. MILDRED B. CHAPMAN (*Geol. Mag.*, 1912, [v], 9, 498—503).—Twenty-one analyses are given of limestones from the various fossiliferous zones. The extreme values are: CaO, 29·38—55·63%; MgO, 0—16·76%; CO_2, 24·62—44·72%; $Fe_2O_3 + Al_2O_3$, 0·08—5·87%; insoluble in hydrochloric acid, 0·02—43·29%; P_2O_5, 0—0·14%. The insoluble residue consists of quartz, black carbonaceous matter, chalcedony, weathered felspar, zircon, and tourmaline. Those limestones which have been formed under coral-reef conditions contain very variable amounts of insoluble residue, whilst those which were rapidly deposited near a coastline are more pure. L. J. S.

Tsumebite, a New Lead Copper Phosphate. KARL BUSZ (*Festschrift Deut. Naturf. Aertze, Münster*, 1912, 182—185).—The new mineral occurs as small, emerald-green crystals with cerussite and chessylite on snow-white calamine ($ZnCO_3$), the latter cementing fragments of reddish-brown dolomite in the mines at Tsumeb, Otavi, German South-West Africa. The crystals are monoclinic with $a:b:c = 0·9974:1:0·8215$; $\beta = 81°44'$. Analysis agrees with the formula $P_2O_5,5(Pb,Cu)O,8H_2O$:

PbO.	CuO.	P_2O_5.	H_2O.	Total.	Sp. gr.
63·77	11·79	12·01	·12·33	99·90	6·133

L. J. S.

Ludlamite from Ashio, Japan. NOBUYO FUKUCHI (*Beitr. Min. Japan*, 1912, No. 4, 192—194).—This iron phosphate is found in the Ashio copper mines, prov. Shimotsuke, as druses of light green, transparent crystals, with a bright vitreous lustre. It is associated with crystals of vivianite, and it sometimes forms pseudomorphs after vivianite. The crystals are monoclinic and have the form of thick six-sided tablets with a perfect basal cleavage. $H = 3\frac{1}{2}$; streak, white. Analyses give the formula $Fe_7(OH)_2(PO_4)_4,7H_2O$:

FeO.	P_2O_5.	H_2O.	Insol. (in HCl).	MnO, Al_2O_3, CaO, MgO.
53·21	32·03	14·60	trace	traces
50·54	31·38	13·79	3·67	—

L. J. S.

The Constitution of Some "Salic" Silicates. HENRY S. WASHINGTON (*Amer. J. Sci.*, 1912, [iv], **34**, 555—571).—Accepting Streng's and Groth's suggestion that the quinquevalent groups $(R'Si)^v$ and $(R''Al)^v$, and in some cases the decivalent group $(CaSi_2)^x$, are present in certain silicates, the author shows that the constitution of all the members of the felspar, leucite, nephelite, and scapolite groups, and nearly all the zeolites, can be interpreted in such a way as to explain readily their composition, mutual relations, poly- and iso-morphism, resistance to acids, and their relation to the mutually common end alteration product, kaolinite.

The felspars, lenads (felspathoids, including leucite, nephelite, and their congeners), and most zeolites are regarded as salts, or isomorphous mixtures of salts, of an alumino-silicic acid, $H_5AlSi_2O_8$, or most probably of a polymeride of this, the five hydrogen atoms being isomorphously replaced by the groups $(R'Si)^v$, $(R''Al)^v$, and $(R''Si_2)^x$, R′ being K, Na and Li, and R″ being Na_2, K_2, Ca, and rarely Ba and Sr.

The scapolites are interpreted as salts of a different alumino-silicic acid, $H_{10}AlSi_3O_{12}$, the hydrogens being entirely replaced by the radicles $(NaSi)_2$ and $(CaAl)_2$. T. S. P.

Sinter from the Geyser of Obama, Japan. DENZŌ SATŌ (*Beitr. Min. Japan*, 1912, No. 4, 139—141).—The water issuing from the hot springs of Obama, prov. Hizen, is clear and odourless, with a slightly alkaline reaction, and a temperature of 100°. Three analyses of water from different springs are given: that from the Funtō-yu contains per litre: $CaCO_3$, 0·32150; $FeCO_3$, 0·01626; Na_2SO_4, 0·63577; NaCl, 5·66341; KCl, 1·63388; $MgCl_2$, 0·53581; $CaCl_2$, 0·27539; SiO_2, 0·21800; total solids 9·20390. $D^{15·5}$ 1·006. Analysis of a snow-white incoherent sinter forming a small cone around the orifice of this spring gave:

SiO_2.	Fe_2O_3.	Al_2O_3.	MnO.	CaO.	MgO.	K_2O.	Na_2O.	CO_2.	Cl.	Ign.	Total.
16·59	0·41	0·18	1·80	38·28	7·28	0·20	0·89	23·28	1·03	10·46	100·40

L. J. S.

A Felspar of Porto-Scuso (Sardaigne). GIUSEPPE CESARO (*Bull. Acad. roy. Belg.*, 1912, 553—569).—A detailed account of the crystallographic examination of a felspar from Porto-Scuso, which analysis shows to be a sodium orthose, with two molecules of sodium oxide and one of potassium oxide. The numerical data are tabulated. The author discusses the effect of the replacement of potassium by sodium on the values of the fundamental angles, and from his results calculates the values of these angles for a purely sodium orthose. At the end of the paper he gives an account of a method for measuring, under the microscope, the angle of the optical axes in a section passing through the obtuse bisectrix, and inclined to the acute bisectrix. The error for the method is calculated, that for 2ψ being 30′, that relative to α being 2′; for $2V$ 22′ to 24′. W. G.

Sericite from North Wales: Penninite and Labradorite from Ireland. ARTHUR HUTCHINSON and WALTER CAMPBELL SMITH (*Min. Mag.*, 1912, **16**, 264—271).—Sericite (anal. I) occurs as talc-like

aggregates of pale-green flakes in quartz veins intersecting dolerite and slate at Tan-y-Bwlch, Merionethshire. Refractive indices, $\beta = 1{\cdot}589$, $\gamma = 1{\cdot}594$, $2E = 68°50'$. In composition it conforms with type I of Clarke's formula, $Al(SiO_4)_3Al_2R_3'$. Penninite (anal. II) forms colourless to pale brown, hexagonal plates in the ophicalcite ("Connemara marble") which is quarried at Recess, Co. Galway. In composition, $H_{23}Mg_{12}Al_5Si_9O_{49}$, it approximates to pseudophite. Labradorite (anal. III) occurs as large, porphyritic crystals in dolerite dykes at St. John's Point near Ardglass, Co. Down. The optical constants are: $\alpha = 1{\cdot}5630$, $\beta = 1{\cdot}5665$, $\gamma = 1{\cdot}5712$, $2V = 81°48'$, extinction on (001) $-11°$, on (010) $-23°$; angle (001) : (010) $= 85°57'$. Formula, $33NaAlSi_3O_8,5KAlSi_3O_8,62CaAl_2Si_2O_8$.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O. (>105°).	H_2O. (105°).	Total.	Sp. gr.
I.	46·51	36·58	0·51	0·48	0·44	0·46	7·84	1·77	5·03	0·11	99·73	2·798
II.	34·81	16·21	1·09	0·36	0·75	30·05	1·85	—	12·71	1·89	99·72	2·619
III.	52·33	30·22	0·40	—	12·52	—	0·85	3·62	0·36		100·30	2·706

L. J. S.

Laumontite from Ashio, Japan. NOBUYO FUKUCHI (*Beitr. Min. Japan*, 1912, No. 4, 190—192).—A vein of laumonite occurs in liparite, the country-rock of the Ashio copper mines, prov. Shimotsuke. Crystals are perfectly colourless and long-prismatic in habit. Analysis of the fresh crystals gave the following results, corresponding with the formula $H_4CaAl_2Si_4O_{14},2\frac{1}{2}H_2O$; other determinations of water varied from 16·02 to 16·43%.

SiO_2.	Al_2O_3.	CaO.	H_2O.	Na_2O,K_2O,MgO, etc.
50·79	18·49	10·69	16·20	3·83

On exposure to the air, the crystals soon fall to a white powder, in which was found only 14·44% water, corresponding with the formula $H_4CaAl_2Si_4O_{14},2H_2O$. The latter formula is the one usually given for laumontite. L. J. S

Minerals of Taiwan (= Formosa). YŌHACHIRŌ OKAMOTO (*Beitr. Min. Japan*, 1912, No. 4, 157—188).—Fifty-one species of minerals (including petroleum and coal) are described; analyses are given of the following. Hornblende, as black crystals in the hornblende-pyroxene-andesite of the Daiton volcanic group (anal. I and II). Fuller's earth (?), white, greyish-blue or yellow, and more or less greasy, from Hōko-tō (anal. III); hygroscopic water 10·50%; portion soluble in hydrochloric acid 64·96%.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	Na_2O.	K_2O.	Ign.
I.	43·99	15·04	13·75	—	0·52	10·55	11·35	0·34	0·19	3·44
II.	41·67	14·14	—	16·18	0·69	11·10	14·16	1·98		nil.
III.	56·06	19·72	11·35	—	—	—	2·25	not det.		—

Alunite occurring as crystals (up to 2 cm. across) with auriferous enargite and native sulphur in the Kinkwaseki gold mines; IV. of pale violet and V of white alunite.

	SO_3.	Al_2O_3.	Fe_2O_3.	MgO.	K_2O.	H_2O.	Insol.	Total.	Sp. gr.
IV.	34·90	37·40	trace	nil.	6·18	13·24	7·42	99·14	2·787
V.	38·65	35·88	,,	0·69	6·09	11·60	6·42	99·33	—

A radioactive mineral consisting of barium and lead sulphate is deposited, together with native sulphur, etc., by the Hokuto hot springs, in the Daiton volcanic group. The water has a strong acid taste (containing free hydrochloric acid), an odour of hydrogen sulphide, and a temperature of 80—90°; it contains in 1000 parts: Na_2SO_4, 1·9055; NaCl, 0·9990; $Al_2(SO_4)_3$, 0·6588; KCl, 0·7130; NH_4Cl, 0·6073; $CaSO_4$, 0·4787; $FeSO_4$, trace; $Fe_2(SO_4)_3$, 0·5420; $MgSO_4$, 0·2024; $Al_2(HPO_4)_3$, 0·0012; $BaSO_4$, 0·0007; $PbSO_4$, trace; H_2SiO_3, 0·2174; HBO_2, 0·0710; HCl, 1·9596. D_{20}^{26} 1·0150. The radioactive material forms a coarsely fibrous crust (anal. VI) or clusters of brown, rhombic plates (anal. VII). These crystals are zoned and have angles agreeing approximately with those of barytes and anglesite; D 6·1; the α-ray activity is 0·0366 that of uranium oxide. Analysis VIII is of an accompanying dirty-grey crust of siliceous sinter.

	PbO.	BaO.	SrO.	CaO.	SO_3.	Fe_2O_3.	Al_2O_3.	MgO.	K_2O.	Na_2O.	H_2O.	Ign.	P_2O_5.	SiO_2.	Total.
VI.	21·96	32·04	0·93	0·51	30·81	3·93	0·88	1·04	nil.	0·53	2·53	—	0·01	1·27	96·44
VII.	19·38	42·27	trace	0·17	31·70	0·43	0·48	0·28	0·14	1·53	—	2·74	nil.	0·97	100·09
VIII*.	—	—	—	0·13	2·48	2·11	2·27	0·30	0·14	0·73	—	14·94	trace	77·10	100·20

* TiO_2 trace.

L. J. S.

The Tourmaline Group. WALDEMAR T. SCHALLER (*Zeitsch. Kryst. Min.*, 1912, 51, 321—343).—The following determinations of the physical constants and analyses were made on crystals of tourmaline:

	Locality.	Colour.	Sp. gr.	Axis *c*.	ω.	ε.	ω—ε (Na).
I.	Elba	Pale red	3·05	0·4448	1·651	1·630	0·021
II.	Mesa Grande, California	Red	3·04	0·4479	1·647	1·628	0·019
III.	,, ,, ,,	Pale green	3·04	0·4489	1·646	1·628	0·018
IV.	Ramona, California......	Black	3·22	0·4534	—	—	—
V.	Lost Valley, California	Black	3·16	—	—	—	—

	SiO_2.	B_2O_3.	Al_2O_3.	Ti_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.	Na_2O.	Li_2O.	H_2O.	F.	Total less O for F.
I.	37·89	10·28	43·85	0·04	0·11	0·11	0·07	—	—	2·43	1·66	3·47	0·10	99·97
II.	37·57	10·65	42·18	trace	0·19	0·24	1·20	—	—	2·05	1·92	3·38	0·39	99·60
III.	36·72	10·60	41·27	0·06	1·13	1·48	0·87	—	—	2·23	1·76	3·33	0·31	99·63
IV.	35·21	10·43	36·07	0·23	11·11	0·98	0·25	0·19	—	1·92	trace	3·51	—	99·90
V.	35·96	10·6	33·28	0·36	11·04	0·13	0·42	3·48	—	2·16	—	3·31	—	100·75

These new analyses conform very closely with Penfield and Foote's general formula $H_{20}B_2Si_4O_{21}$ (A., 1899, ii, 304). Together with some earlier analyses, they are discussed in detail. The ratio of $(H_2O+\frac{1}{2}F):SiO_2$ ranges from 3·72 : 12 to 4·17 : 12, and in the special formulæ proposed water is given as $3H_2O$. Further, the alumina varies inversely in amount with the other bases (R = Fe″, Mn″, Ca, Mg, K_2, Na_2, Li_2, and H_2 in excess of the $3H_2O$). The end components as plotted on a curve are:

$$12SiO_2,3B_2O_3,8Al_2O_3,3RO,3H_2O,$$

$$\text{and } 12SiO_2,3B_2O_3,5Al_2O_3,12RO,3H_2O.$$

In analysis I of Elba tourmaline still more alumina is present, and the component $12SiO_2,3B_2O_3,9Al_2O_3,3H_2O$ is assumed. There may also be several other members of the series, for example,

$$12SiO_3,3B_2O_3,7Al_2O_3,6RO,3H_2O.$$

Other special types are introduced by replacing RO by MgO, Li_2O, etc.

The composition of Ramona tourmaline (anal. IV) is, for example, expressed by the mixing of the following three components:

$$12SiO_2,3B_2O_3,8Al_2O_3,3H_2O,3H_2O,$$
$$12SiO_2,3B_2O_3,7Al_2O_3,6FeO,3H_2O,$$
$$12SiO_2,3B_2O_3,5Al_2O_3,12Na_2O,3H_2O.$$

Comparing the chemical composition and the physical constants, it is noticed that the specific gravity, crystallographic axis *c*, refractive indices, and double refraction reach a maximum with Al_2O_3 35—36%, and that this point separates two series of tourmalines. Magnesia-free-tourmalines contain more, and magnesia-tourmalines less, than this amount of alumina. The former occur in pegmatites, whilst the latter are usually found in metamorphic rocks and are brown or black in colour. L. J. S.

Minerals from the Pegmatite of Ampangabé, Madagascar. ALFRED LACROIX (*Bull. Soc. franç. Min.*, 1912, **35**, 180—199. Compare A., 1912, ii, 1182).—The pegmatite of Ampangabé, near Miandrarivo, consists of microcline, quartz and muscovite, and is exploited for beryl of gem-quality. This beryl is of the prismatic type very poor in alkalis, D 2·713—2·721. The gem material is of a fine blue colour, but delicate pink, colourless, yellow, and green stones are also found. Other minerals present in the pegmatite include monazite in crystals, columbite crystals, D 5·52 (anal. I by Pisani), ampangabeite (A., 1912, ii, 567), strüverite, etc. The strüverite is found as large, tetragonal crystals (up to 6 kilos.), which are usually elongated in the direction of a pyramid-edge (111 : 111), and sometimes twinned on (101), giving them an orthorhombic aspect. These crystals are optically uniaxial and positive, and have angles very close to the angles of rutile. The material is iron-black with a conchoidal to uneven fracture, D 4·91 ; anal. II by Pisani.

	TiO_2.	Ta_2O_5.	Cb_2O_5.	SnO_2.	FeO.	MnO.	Al_2O_3.	Total.
I.	—	12·60	64·60	0·40	15·00	7·30	—	99·90
II.	71·15	10·14	—	0·05	15·84	—	1·80	98·98

In a beryl-bearing pegmatite from the west of Miandrarivo is a fresh monazite, which in thin flakes is transparent and clear yellow, D 5·11, anal. III by Pisani.

P_2O_5.	Ce_2O_3.	$(La,Di)_2O_3$.	$(Y,Er)_2O_3$.	ThO_2.	Al_2O_3.	Fe_2O_3.	Loss on ignition.	Total.
27·45	31·85	27·90	2·93	9·15	0·21	0·42	0·74	100·65

L. J. S.

Nature and Origin of "Terra rossa." FRAN. TUČAN (*Jahrb. Min.*, 1912, *Beil.-Bd.* **34**, 401—430).—Terra rossa occurs in the crevices and cavities of the bare corroded limestones and dolomites of the Karst district, and it represents the insoluble residue left by the denudation of these rocks. It consists mainly of minute amorphous particles of aluminium hydroxide, Al_2O_3,H_2O; and for this colloidal mineral (corresponding with the crystalloid diaspore) the name *sporogelite* is proposed. The red colour is due to colloidal ferric hydroxide ($2Fe_2O_3,3H_2O$); and various accessory minerals are present as minute grains, namely, quartz, mica, epidote, hydrargillite, diaspore, amphibole, felspar, garnet, rutile, etc. The residues (averaging 0·32%)

obtained by dissolving the limestones in dilute acetic acid, or the dolomites in dilute hydrochloric acid, have the same reddish colour and are identical in mineralogical composition with the terra rossa. Analysis of terra rossa from various localities gave:

	SiO_2.	TiO_2.	ZrO_2.	Al_2O_3.	Fe_2O_3.	MnO.	CaO.	MgO.	K_2O,Na_2O,Li_2O.	H_2O.	CO_2.	Total.
I.	0·37	8·51	0·45	55·37	21·76	trace	trace	trace	trace	13·45	—	99·91
II.	26·20	0·51	0·81	39·14	14·03	1·45	,,	—	,,	18·14*	—	100·28
III.	35·42	0·30	0·10	32·89	15·03	0·93	0·43	trace	,,	15·32	0·23	100·55
IV.	43·61	trace	trace	27·80	11·75	trace	1·64	,,	,,	15·43*	—	100·23
V.	47·89	0·96	,,	24·38	12·63	1·18	0·68	,,	0·32	11·86	0·39	100·29
VI.	46·27	0·80	,,	26·61	12·64	0·12	1·13	,,	trace	13·32*	—	100·89
VII.	26·47	trace	,,	20·19	18·03	1·32	13·19	,,	,,	11·24	9·12	99·56
VIII.	32·11	,,	,,	25·69	6·20	—	14·44	0·48	,,	11·33	10·77	100·97
IX.	66·57	0·12	0·09	21·87	5·72	—	—	—	,,	5·58*	—	99·95

* Loss on ignition.

Analysis I of the purest material, from Županjac, Bosnia, is interpreted as: sporogelite, 70·38%; colloidal ferric hydroxide, 22·025%; rutile, 6·88%; zircon, 0·48%. In the other analyses the silica is present partly as quartz and partly as colloidal silicic acid, the latter being soluble in dilute hydrochloric and nitric acids. In anal. II, for example, 8·99% of the silica is soluble, and represents 43·89% colloidal silicic acid intermixed with 39·54% of sporogelite.

The sporogelite is regarded as an original constituent of the limestones, and to have been precipitated as such from the sea-water at the time that the limestones were deposited. The bauxites of the same region are identical chemically and mineralogically with the terra rossa, but they are of earlier date (compare Kišpatić, this vol., ii, 64).

L. J. S.

Analysis of Red Earth from the Floor of an Ancient Hut. JOHN O. HUGHES (*Chem. News*, 1912, **106**, 247).—A reddish-brown earth obtained from the floor of one of the ancient huts forming the stone fortress on the top of Penmaenmawr, Carnarvonshire, was found to have the following composition: substances insoluble in hydrochloric acid, silica, etc., 83·82%; alumina, 2·47%; iron oxide, 4·71%; magnesia, 1·45%; sodium and potassium oxides, 0·52%; phosphoric anhydride, 1·22%; sulphur trioxide, 0·13%; water (at 110°), 1·86%; loss on ignition, 3·70%; manganese oxide, calcium oxide, carbon dioxide, and chlorine, traces. Embedded in the earth were a few small pieces of charcoal. The author is of the opinion that the earth is the ash of some combustible substance (possibly peat) mixed with a portion of the surrounding soil.

W. P. S.

A New Fall of Meteoric Iron in Japan. MASUMI CHIKASHIGÉ and TADASU HIKI (*Zeitsch. anorg. Chem.*, 1912, **77**, 197—199).—A meteorite which fell in 1904 at Okano, in the province of Tamba, Japan, has been examined. The meteorite, which weighs 4742 grams, contains Fe, 94·85%; Ni, 4·44%; Co, 0·48%; P, 0·23%; Cu, trace, and has D 7·98. The ground-mass consists of nickeliferous iron, showing Neumann's lines on etching. The phosphide occurs as distinct rhabdite crystals.

Heating at 1300° for thirty minutes causes granulation of the mass, and the Neumann's lines disappear.

C. H. D.

Meteoric Fall near Holbrook, Arizona. GEORGE P. MERRILL (*Smithsonian Miscell. Collections*, 1912, **60**, No. 9, 1—4. Compare Foote, A., 1912, ii, 1183).—The stones of this recent and remarkable fall resemble in lithological character those of the Pultusk (Poland) shower of 1868, and in Brezina's classification belong to "spherulitic chondrite, crystalline, Cck." The material consists of orthorhombic with occasional monoclinic pyroxenes and of olivine with small scattered masses of metallic iron and iron sulphide; numerous chondrules are set in a loose aggregate of particles. The iron sulphide forms granules up to 8 mm. across, and resembles pyrrhotite in its bronzy lustre; it is, however, non-magnetic, $D^{22\cdot6} = 4\cdot61$, and analysis II gives the formula FeS, proving the material to be troilite. The stone has $D^{22\cdot6} = 3\cdot48$, and contains: silicates, 87·48; metal, 4·85; troilite, 7·56; schreibersite, 0·11%. Analysis by J. E. Whitfield of the metallic portion gave I, the sulphide II, and of the silicate portion the results under III.

	Fe.	Ni.	Co.	Cu.	S.	Total.
I.	90·50	8·68	0·64	0·29	—	100·11
II.	63·62		nil.		36·50	100·12

	SiO_2.	Al_2O_3.	FeO.	CaO.	MgO.	MnO.	NiO.	Na_2O.	Total.
III.	41·93	4·30	21·85	2·40	29·11	0·25	0·08	trace	99·92

L. J. S.

Meteoric Stones of El Nakhla El Baharia (Egypt). GEORGE T. PRIOR (*Min. Mag.*, 1912, **16**, 274—281. Compare A., 1911, ii, 1106; 1912, ii, 361).—One of the stones, weighing 274 grams, of this recent fall was examined. Thin sections show a holocrystalline aggregate of green diopside and brown olivine (there being no hypersthene as stated in previous accounts), with a little interstitial matter consisting of felspar laths. The diopside shows "herring-bone" structure, and its optical constants are $\alpha = 1\cdot685$, $\beta = 1\cdot69$, $\gamma = 1\cdot72$, $2V = 44—48°$, $c:\mathfrak{c} = 40—44°$; its composition II (calculated from I and III) corresponds with $3MgSiO_3,3CaSiO_3,2FeSiO_3$. The olivine is characterised by the presence of dark brown to black enclosures with a definite crystallographic orientation; $\alpha = 1\cdot75$, $\beta = 1\cdot785$, $\gamma = 1\cdot80$, $2V = 67°$; analysis III is of selected grains, and IV of the portion of the stone soluble in hydrochloric acid, corresponding with $2Fe_2SiO_4,Mg_2SiO_4$. This olivine is near to hortonolite, and is much more ferriferous than any meteoric olivine previously described. The bulk analysis of the meteorite is given under I, corresponding with the following mineral composition: diopside, 76·70; olivine, 13·25; felspar, 6·76; magnetite, 1·87; ilmenite, 0·73; chromite, 0·49; troilite (?), 0·17; water, 0·24%.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	Total.	Sp. gr.
I.*	48·96	1·74	1·29	19·63	15·17	12·01	100·45	3·47
II.	52·73	—	—	14·93	19·22	13·12	100·00	3·42
III.	32·59	—	—	51·80	1·11	15·60	101·10	3·98
IV.	33·06	—	—	51·67	1·86	13·03	99·62	—

* Also: TiO_2, 0·38; Cr_2O_3, 0·33; MnO, 0·09; Na_2O, 0·41; K_2O, 0·14; S, 0·06, H_2O, 0·24.

Consisting mainly of monoclinic pyroxene and olivine with no metallic iron, this meteorite approaches most closely to the angrite group. L. J. S.

Meteorite Fall in Central Japan. TETSUGORO WAKIMIZU (*Beitr. Min. Japan*, 1912, No. 4, 145—150).—A fall of stones was observed on July 24, 1909, near the town of Gifu, prov. Mino. Twenty-four stones, the largest weighing 4039 grams, were picked up over an area of 12 × 5 km. The material, D 3·57, is classed as a white chondrite with very little nickel-iron and iron sulphide. Under the microscope it is seen to be holocrystalline, and to consist essentially of olivine and bronzite. Analysis gave:

SiO_2.	P_2O_5.	TiO_2.	Fe_2O_3	Fe.	Ni.	Mn.	CaO.	MgO.	S.	SO_3.	C.	H_2O.	Total.
41·012	0·458	0·416	5·470	20·583	0·183	0·910	2·768	24·707	2·185	0·201	trace	0·334	99·227

L. J. S.

Analytical Chemistry.

The Estimation of Water and of Carbon Dioxide in Minerals and Rocks. MAX DITTRICH and W. EITEL (*Zeitsch. anorg. Chem.*, 1912, 77, 365—376. Compare A., 1912, ii, 804).—It has not been found practicable to estimate water and carbon dioxide in minerals and rocks by fusion with sodium metaphosphate or borax, as a constant weight is not obtained in blank experiments. On the other hand, heating the material in a stream of dry air in a silica tube is found to be satisfactory. The air supply tube is also of silica, and is ground in and held by springs. A spiral of silver gauze is used to retain sulphur. In the case of minerals which lose water with difficulty, the final heating is performed by means of the blow-pipe. Rocks containing epidote, mica or hornblende often do not lose the whole of their water through these minerals becoming enclosed. Much better results are obtained by the use of a platinum electric furnace surrounding the silica tube. The water is then driven off completely, except in the case of materials containing much fluorine. Calcite does not lose its carbon dioxide completely, unless first mixed with powdered quartz, with a blowpipe, but is completely decomposed in the electric furnace at 1100°. The silica tubes last well at 1000°, but devitrify at higher temperatures. By the use of a platinum-iridium tube and a boat of the same material, the most refractory rocks lose their water and carbon dioxide completely at 1250—1300°.

C. H. D.

New Reagent for Chlorine and Bromine, Free and Combined. GEORGES DENIGÈS and L. CHELLE (*Compt. rend.*, 1912, 155, 1010—1012. Compare A., 1912, ii, 1208; Guareschi, *ibid.*, 989).—The reagent is prepared by the addition of 10 c.c. of a solution of magenta

(1 in 1000) to 100 c.c. of sulphuric acid (5% by volume). This is then mixed with an equal volume of acetic acid, and 4 c.c. of strong sulphuric acid are added. This solution is coloured yellow by chlorine and reddish-violet by bromine, the colour being best shown by shaking with chloroform. If the halogens are combined as metallic salts, the solution is acidified, the iodine removed by a ferric salt, the bromine liberated by the addition of potassium chromate and tested for, and the chlorine then liberated by potassium permanganate and separately tested for. The vapours are absorbed in dilute alkali before applying the test. The method can be applied quantitatively for dealing with small quantities of bromine as in natural waters, and is more delicate than the methods at present in use. W. G.

The Iodic Acid Process for the Estimation of Bromine in Halogen Salts. FRANK A. GOOCH and P. L. BLUMENTHAL (*Amer. J. Sci.*, 1912, [iv], 469—474).—A criticism of Bugarszky's process (boiling the solution containing bromides and chlorides with potassium iodate and dilute sulphuric acid and determining the loss in iodine: A., 1896, ii, 216).

The authors find that although the process was thought to be an ideal one, it is vitiated by secondary effects. The latter may be reasonably attributed to the action of small amounts of iodine monochloride or monobromide formed in the interaction of iodic acid and free iodine with hydrochloric acid and hydrobromic acid.

Substitution of chloric acid for iodic acid cannot be recommended. L. DE K.

Oxidisable Substances in the Air. L. SCHWARZ and GEORG MÜNCHMEYER (*Chem. Zentr.*, 1912, ii, 1695; from *Zeitsch. Hyg. Infekt.-Krankh.*, 1912, **72**, 371—384).—Henriet and Bouyssy's method (A., 1911, ii, 532) whereby the titration of condensed water is taken as a measure of the degree of vitiation of an atmosphere, is criticised. Such condensed water gives different readings at different temperatures, and would only give a correct value if all the moisture in the atmosphere could be condensed, or if it contained oxidisable substances to the same extent as the collected water, which is not the case. J. C. W.

An Apparatus for Microanalysis of Blood Gases and Micro-respirometry. HANS WINTERSTEIN (*Biochem. Zeitsch.*, 1912, **46**, 440—449).—The apparatus (which is figured) is a combination of the Barcroft-Haldane and Petterson systems. It consists essentially of two pear-shaped flasks, one of which is a compensation flask, and the other serves for the actual analysis. They communicate by means of three-way stopcocks either with the outer air or with one another. The latter communication is through an etched capillary tube containing an oil drop. The analysis flask communicates, furthermore, with a manometer, of which the narrower limb which is nearer the flask is a capillary, graduated in millimetres. The outer limb is broader, and is closed by a piece of indiarubber with a screw-clamp, and a piece of solid glass rod. The flasks communicate; the meniscus of the oil drop in the capillary connecting the two

flasks is brought to a certain point by turning the screw-clamp on the indiarubber, and the height of the mercury in the graduated limb of the manometer is then read. This takes place with the same materials in each flask, and the whole apparatus is kept in a water-bath. If the measurement to be carried out consists in the determination of the oxygen content, Haldane's ferricyanide method is employed, the reagent being kept in spoons fused on to the stoppers. The apparatus, after the first reading and adjustment, is then removed from the water-bath and shaken, so as to bring the ferricyanide into the blood and ammonia mixtures, whilst the two flasks are kept closed and out of communication with one another. They are then brought back to the water-bath, brought into communication, the position of the oil drop in the communicating flask is readjusted, and the height of the manometer is read. The difference between this and the original reading gives the amount of oxygen evolved.

S. B. S.

Estimation of Tellurium by means of Hydrazine Hydrate. J. B. MENKE (*Zeitsch. anorg. Chem.*, 1912, 77, 282—288).—See this vol., ii, 41.

Detection of Nitrogen in Organic Substances. H. ZELLNER (*Pharm. Zeit.*, 1912, 57, 979—980).—For the detection of small quantities of nitrogen, or when the amount of the substance to be tested is not large, the following modification of the usual test may be employed. The substance is fused with potassium, the fused mass is dissolved in water, and the solution is warmed after the addition of ferrous sulphate. The solution is then filtered, and the filtrate is poured on the surface of ferric chloride solution acidified with hydrochloric acid. If nitrogen is present in the substance, a blue zone appears at the junction of the two liquids. W. P. S.

A New Gas-analytical Method for the Estimation of Nitric Oxide. I. OSKAR BAUDISCH and GABRIEL KLINGER (*Ber.*, 1912, 45, 3231—3236).—The method depends on the fact that when air is passed into nitric oxide standing in contact with solid potassium hydroxide, nitrogen trioxide (N_2O_3) is formed, and immediately converted by the hydroxide into potassium nitrite, there being no formation of nitrogen dioxide. Four-fifths of the contraction thereby caused is due to nitric oxide, as expressed by the equation: $4NO + O_2 + 4KOH = 4KNO_2 + 2H_2O$.

The analysis is carried out in Fuller's gas-analysis apparatus; the pipette contains slightly moistened stick potassium hydroxide, with which the nitric oxide is in contact before air is passed in, and all measurements are carried over mercury. Before passing the nitric oxide into the pipette the latter is completely filled with mercury.

The method gives accurate results, even in the presence of nitrous oxide or hydrogen. The reverse method of passing the nitric oxide into air standing over potassium hydroxide cannot be used, since a mixture of N_2O_3 and NO_2 is formed. T. S. P.

Detection of Nitrous Acid in Water. PRIMOT (*Chem. Zentr.*, 1912, ii, 1846—1847; from *Bull. Sci. Pharmacol.*, 1912, **19**, 546—547). —To 10 c.c. of the water 4 or 5 drops of a 1—1·5% solution of benzidine, *o*-tolidine, or dianisidine in 30—40% alcohol are added. The mixture is then acidified with 5 or 6 drops of acetic acid and shaken, when the development of a yellow colour, which deepens in time, shows the presence of a nitrite. Benzidine is the least sensitive reagent. The limit of sensitiveness is below 0·01 mg. of nitrous acid per litre. J. C. W.

Estimation of Nitrates with Indigo. LUIGI ERMANNO CAVAZZA (*Chem. Zentr.*, 1912, **11**, 1061—1062; from *Atti II. Congr. Naz. Chim. applic.*, 1912).—Ten grams of powdered pure indigo are introduced (with cooling) in small quantities into 50 c.c. of fuming sulphuric acid, and after forty-eight hours the solution is diluted to a litre. Fifty c.c. of the liquid are then diluted so that 10 c.c. correspond with 0·001 gram of nitrogen pentoxide. When dealing with nitrates, a stronger solution may be employed. Organic matters if present should be removed by adding to 25 c.c. of the solution the requisite amount of potassium permanganate (previously determined); 30 c.c. of sulphuric acid are added, and the whole heated over a small flame and titrated. When the liquid turns bright yellow, the heating is discontinued and the titration rapidly brought to an end. In testing ordinary water, concentration by evaporation is not necessary as the end reaction is so very sensitive. L. DE K.

The Marsh Arsenic Test. GEORG LOCKEMANN (*Chem. Zeit.*, 1912, **36**, 1465—1466).—Historical. The original Marsh apparatus and modifications of it are described. L. DE K.

Estimation of Small Quantities of Carbon Monoxide. OTTO BRUNCK (*Zeitsch. angew. Chem.*, 1912, **25**, 2479—2481).—A suitable flask of known capacity (say, a litre flask) is fitted with a doubly perforated rubber cork closed by means of rods. After filling the flask with the air to be examined, 50 c.c. of sodium palladium chloride (1 c.c. = 0·004762 gram of palladium) are introduced from a pipette (while gently loosening the second rod), followed by 25 c.c. of 5% solution of sodium acetate; the volume of liquid is, of course, deducted from the volume of the gas tested.

After an hour's action with frequent shaking, the palladium which has deposited owing to the reducing action of the carbon monoxide is collected and ignited with the usual precautions; 1 gram of metallic palladium = 0·2624 gram, or 210 c.c. of carbon monoxide.

Hydrogen and the unsaturated hydrocarbons should be absent, as they also exert a reducing action. L. DE K.

Simple Apparatus for the Estimation of Carbon Dioxide. W. R. FORBES (*Chem. News*, 1912, **106**, 284).—The apparatus consists essentially of an inverted V-tube closed at either end and provided in the middle with a ground stopper carrying a delivery tube and tap. In use, the acid is placed in one limb and the carbonate in the other. Reaction is started by suitably inclining the apparatus. H. W.

Cobaltinitrite Method of Estimating Potassium. F. H. MacDougall (*J. Amer. Chem. Soc.*, 1912, **34**, 1684—1686).—In the estimation of potassium by the cobaltinitrite method, it is usual to boil the yellow precipitate with excess of *N*/10-potassium permanganate, then add dilute sulphuric and oxalic acids, and finally to titrate with *N*/10-permanganate. The oxidation of the nitrite thus takes place in alkaline solution, and the permanganate is reduced to manganese dioxide. The latter reacts but slowly with the oxalic acid added subsequently, since the mixture is so dilute. The author has therefore studied the effect of adding dilute sulphuric acid to the yellow precipitate before oxidising it with permanganate.

It has been found that accurate results can be obtained in this way, but that a different factor must be employed in the calculation; according to the usual method, 1 c.c. of *N*/10-permanganate is equivalent to 0·0007111 gram K or 0·0008564 gram K_2O, whilst with the modified method, 1 c.c. of *N*/10-permanganate corresponds with 0·0006518 gram K or 0·0007850 gram K_2O. E. G.

Determination of the Sensitiveness of the Hydroxide Reactions for the Common Metals. Louis J. Curtman and A. D. St. John (*J. Amer. Chem. Soc.*, 1912, **34**, 1679—1684).—A study has been made of the sensitiveness of the hydroxide test for metals. The experiments consisted in treating a solution of a salt of the metal with 10% ammonia or sodinm hydroxide, the final volume being 5 c.c. In the following cases, ammonia was used as the precipitant and the limiting concentrations of the metals at which a precipitate was visible were: lead, 1—6500; mercury (in the mercuric state), 1—13,000; bismuth, 1—10,000; iron, 1—80,000; aluminium, 1—100,000; chromium, 1—170,000; zinc, 1—80,000. For the following metals, sodium hydroxide was employed as the reagent and the limits found were: silver, 1—40,000; mercury (in the mercurous state), 1—200,000; copper, 1—10,000; cadmium, 1—40,000; nickel, 1—80,000; cobalt, 1—80,000; magnesium, 1—10,000. In the case of manganese, either ammonia or sodium hydroxide can be used, the limiting concentration in each case being 1—170,000. E. G.

Estimation of Lead in Lead Paints. Franz Utz (*Chem. Zentr.*, 1912, ii, 1788; from *Farbenzeit.*, **18**, 18—20).—The nitric acid solution of the lead compound is electrolysed at 60—65° by a current of 0·05—1·5 amperes, using gauze electrodes, and the lead dioxide is washed without breaking the current and then dried at 200°. J. C. W.

Cuprous Iodide. Moritz Kohn and Arthur Klein (*Zeitsch. anorg. Chem.*, 1912, **77**, 252—254).—Cuprous iodide may be analysed by the method of Baubigny and Chavanne for iodine in organic substances (A., 1903, ii, 510; 1904, ii, 203). One to 1·5 gram of silver nitrate is dissolved in 40 c.c. of concentrated sulphuric acid in a flask, and, after cooling, 5 grams of pure potassium dichromate are added. This is then dissolved by warming, and the whole is again cooled. After adding 0·3 gram of the substance, the flask is warmed

and shaken until the evolution of oxygen begins. The silver iodide formed at first dissolves as iodate. After cooling, the contents of the flask are poured into 80 c.c. of water, reduced by sodium sulphite, and allowed to remain until the silver iodide has settled. This is collected on a Gooch filter after the addition of nitric acid, dried at 130°, and weighed.

Copper is estimated by heating 0·5 gram of the substance with 15—20 c.c. of nitric acid (1 : 1), converting into sulphate, and precipitating as sulphide.

Like potassium bromide (Kohn, A., 1909, ii, 891), ammonium bromide solutions dissolve cuprous iodide, the solubility increasing rapidly with the concentration. C. H. D.

Sensitiveness of the Bead and Lead Dioxide Tests for Manganese with Special Reference to the Interference of Iron. LOUIS J. CURTMAN and A. D. ST. JOHN (*J. Amer. Chem. Soc.*, 1912, **34**, 1675—1679).—A study has been made of the sensitiveness of the bead and lead dioxide tests for manganese and the influence of iron on these tests. The results show that the lead dioxide test is not trustworthy in presence of 300 or 400 parts of iron to 1 part of manganese unless as much as 0·2 mg. of manganese is present, but that the bead test is efficient with larger quantities of iron provided that as much as 0·005 mg. of manganese is introduced into the bead and certain specified precautions are observed. E. G.

Estimation of Iron in Water. F. KÖNIG (*Chem. Zentr.*, 1912, ii, 1064; from *Apoth. Zeit.*, **27**, 536—537).—Klut's nitric acid process (*ibid.*, 1909, ii, 1076) for the colorimetric estimation of iron in waters gives good results with samples absorbing not more than 80 mg. of potassium permanganate per litre. When this amount is exceeded, the iron should be estimated, colorimetrically, in the residue after ignition. L. DE K.

Reagent for Detecting Small Quantities of Nickel. V. FORTINI (*Chem. Zeit.*, 1912, **36**, 1461).—The following solution is recommended for the detection of nickel in plated wares and nickel alloys. 0·5 Gram of dimethylglyoxime is dissolved in 5 c.c. of 98% alcohol, and 5 c.c. of ammonia are added. After rinsing the surface with ether, a drop of the reagent is applied, when a rose-coloured spot will form should nickel be present. Previous heating in the oxidation flame will render the test still more delicate. The presence of other metals usually present does not interfere. The spot formed may be easily removed with a towel. L. DE K.

Test for Methane. I. OTTO HAUSER and H. HERZFELD (*Ber.*, 1912, **45**, 3515—3516).—Methane and ozonised oxygen react with each other with the formation of formaldehyde, which reaction may be used as a very delicate test for methane. The gas to be tested is mixed with ozonised oxygen and the mixture passed through a tube containing moistened glass wool, which is afterwards extracted with water and the solution tested for formaldehyde with morphine and sulphuric acid.

Methane is the only hydrocarbon which gives formaldehyde. Ethane gives acetaldehyde or acetic acid, but the reaction is much slower than with methane, whilst acetylene is oxidised explosively to carbon dioxide. The reaction with acetylene takes place also in acetone solution, and is accompanied by a beautiful green luminescence. Toluene is oxidised by ozone with formation of formic acid.

T. S. P.

Analysis of Hydrocarbon Mixtures. Oscar Routala (*Chem. Zentr.*, 1912, ii, 638; from *Ann. Acad. Sci. Fennicae, A.*, **2**, No. 13, 19 pp.).—The iodine absorption process for the testing of petroleums is too much affected by the personal equation, and reports founded on it should be accompanied by a careful description of details of analysis, including time of action, temperature, exposure to light, and volume of iodine solution added. Frank's bromine process (*Chem. Ind.*, 1901, **24**, 263) may be successfully applied when small quantities of the substance are to be tested, also when the refining degree of colourless or pale petroleum products has to be determined, or when the degree of purity of olefines has to be ascertained. From the bromine number the percentage of the olefine is calculated directly by the formula $A = [K + (n - 5)c].G$, in which $A = \%$ of the olefine, $K =$ a constant, n the mean number of carbon atoms for the olefine boiling at between the limits of temperature (at least 5), $c =$ a constant ($= 0{\cdot}875°$), and G the bromine number. For amylene, $K = 0{\cdot}4375$; for hexylene, $0{\cdot}5950$; for heptylene, $0{\cdot}6075$; for each additional CH_2-group, the constant increases on the average by $0{\cdot}0875$. To show the accuracy of the formula a bromine number was taken of a mixture of amylene and *iso*pentane, and the result agreed with the sulphuric acid process and the density.

L. de K.

Methoxyl Estimation with Hydriodic Acid and Phenol. Fritz Weishut (*Monatsh.*, 1912, **33**, 1165—1172).—It is found that many substances which fail to give satisfactory results for the estimation of the methoxyl group, even in the presence of acetic anhydride, can be made to do so by using a mixture of hydriodic acid with approximately one-quarter its volume of phenol. In most cases the reduction is complete in about one and a-half hours, but methyl nitroanisate required five and a-half hours.

D. F. T.

Estimation of Higher Alcohols in Wine. Theodore von Fellenberg (*Chem. Zentr.*, 1912, ii, 1851; from *Mitt. Lebensmitt. Hyg.*, **3**, 231—235).—The colour reaction which higher alcohols give with salicylaldehyde and concentrated sulphuric acid (A., 1911, ii, 667) has been applied to wine. Natural wines are found to contain about three parts per 1000 of higher alcohols, which suggests that the accepted value for cognac (1 per 1000) is very low.

J. C. W.

A Colour Reaction of Wine. Theodore von Fellenberg (*Chem. Zentr.*, 1912, ii, 1850—1851; from *Mitt. Lebensmitt. Hyg.*, **3**, 228—231).—A colour reaction which phloroglucinol gives with vanillin and hydrochloric acid is also obtained with wine, which

probably contains, therefore, an unsaturated alcohol. The red colour may be matched against a standard solution of acid magenta.

J. C. W.

Examination of Lead Precipitates in Wine; Pentose and Methylpentose Estimations in Grapes and Wine. THEODORE VON FELLENBERG (*Chem. Zentr.*, 1912, ii, 1850; from *Mitt. Lebensmitt. Hyg.*, **3**, 213—217).—After precipitation with just the required amount of lead acetate (found by a series of preliminary tests) there are still some substances in natural wines, although scarcely at all in sophisticated wines, which may be precipitated by basic lead nitrate. The precipitate contains succinic acid, inositol, pectin, pentosan, and methylpentosan. The pectin of grapes contains pentose and methylpentose, but does not account for the whole of these sugars, which are present both in the free state, unprecipitable by basic lead nitrate, as well as in the form of pentosans. J. C. W.

A Simple Method of Characterising Acraldehyde. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1912, 524).—The acraldehyde vapour is condensed in distilled water, through which a slow stream of oxygen is then passed until the solution is strongly acid. On dissolving freshly precipitated silver oxide in this liquid and concentrating the clear solution, silver acrylate crystallises out in the pure state. W. G.

A Bromometric Estimation of Formic Acid. H. MÄDER (*Chem. Zentr.*, 1912, ii, 1401; from *Apoth. Zeit.*, 1912, **27**, 746—747). —A method for the estimation of formic acid is given; it depends on the oxidation of the acid by bromine. The solution is left for twelve to fifteen hours with bromide and bromate of potassium and phosphoric acid in a stoppered bottle, when the unused bromate is decomposed by potassium iodide and estimated with thiosulphate.

J. C. W.

The Detection of Acetoacetic Acid by Sodium Nitroprusside and Ammonia. VICTOR JOHN HARDING and ROBERT FULFORD RUTTAN (*Bio-Chem. J.*, 1912, **6**, 445—450).—Le Nobel's test for acetone in the urine, in which the urine is treated with acetic acid, sodium nitroprusside and ammonia, was found to give a less distinct reaction with urine to which acetone had been added than in natural acetonuric urines; furthermore, in the latter cases the reaction was less distinct in distillates containing relatively large amounts of acetone than in the original urine. The authors show now, that the Le Nobel test is really a reaction for acetoacetic acid and not for acetone, and as such it is capable of detecting 1 part of this acid in 30,000, whereas the ordinary ferric chloride test fails when the dilution is only 1 in 7000.

S. B. S.

Detection of Benzoic Compounds. OTTO SCHMATOLLA (*Pharm. Zeit.*, 1912, **57**, 947).—Twenty c.c. of a solution to be tested for the presence of benzoic acid are mixed with 5 c.c. of hydrogen peroxide

and a solution, prepared by dissolving 5 grams each of ferrous sulphate and boric acid in 100 c.c. of water, is added until the mixture no longer becomes darker in colour. Should benzoic acid be present, a dark bluish-green coloration develops with a few seconds. The test will detect the presence of 1 part of benzoic acid in 15,000 parts of solution. A similar reaction is given by all benzoic compounds, hippuric acid, etc. Benzoic acid, however, may be separated from hippuric acid in mixtures of the same by extracting the former acid with light petroleum. By means of suitable solvents, benzoic acid may be separated from salicylic acid, and then identified by the above reaction. W. P. S.

Nature of the Reactions of Naphthenic Acids. K. W. CHARITSCHKOV (*Chem. Zeit.*, 1912, **36**, 1378. Compare A., 1910, ii, 549; 1911, ii, 543).—The reactions of naphthenic acid described previously with copper sulphate, ferrous salts, cobalt nitrate, and hydrogen peroxide are characteristic of *cyclo*pentanemonocarboxylic acids, and are not shown by acids which contain the *cyclo*hexane ring, such as *cyclo*hexylacetic acid. H. W.

A New Method for the Colorimetric Estimation of Uric Acid in Urine. OTTO FOLIN and A. B. MACALLUM, jun. (*J. Biol. Chem.*, 1912, **13**, 363—370).—The method is based on the colour produced by the action of phosphotungstic acid. W. D. H.

Detection and Estimation of Arachis Oil. NORMAN EVERS (*Analyst*, 1912, **37**, 487—492).—After trying various methods already proposed, the author gives the following process: 5 grams of the sample (say, olive oil) are saponified with 25 c.c. of alcoholic potassium hydroxide (80 grams in 80 c.c. of water and diluted to a litre with 90% alcohol) in a reflux apparatus. To the hot soap solution are added 7·5 c.c. of dilute glacial acetic acid (1:2) and 100 c.c. of 70% alcohol containing 1 vol.% of hydrochloric acid, and the liquid is then cooled to 12—14° for an hour. The deposit is collected and washed with the acid alcohol (temp. 17—19°) until the filtrate gives no turbidity with water, the washings being measured. The precipitate, according to its bulk, is dissolved in 25 to 70 c.c. of hot 90% alcohol and cooled to 15—20°. If abundant crystals appear, then after one to three hours they are collected and washed, first with 90% alcohol (about half the volume used for crystallisation), and finally with 50 c.c. of 70% alcohol. The crystals are now dissolved in hot ether, and this is then distilled off in a weighed flask; the residue is dried at 100° and weighed. Should the m. p. be lower than 71°, the acid should be recrystallised from 80% alcohol. A correction for solubility should be made, for which a table is given. If no, or but few, crystals are obtained from the 90% alcohol, a sufficient quantity of water is added to reduce this to 70% strength. Any deposit then formed within an hour at 17—19° is collected, washed with 70% alcohol, and weighed as before, applying the correction for solubility. It must be recrystallised if the m. p. is below 71°.

4·54 Grams of crystals = 100 grams of arachis oil. The following

oils gave no crystals: olive oils, including three superfine Maloga and eight of unknown origin, almond, poppy, and rape oils. L. DE K.

Estimation of Cyanogen Compounds in Gas-Liquors. FRANZ WEISSER (*Chem. Zeit.*, 1912, **36**, 1285—1287).—*Estimation of ammonium cyanide.*—This is found by difference from the total cyanogen and that present as ferrocyanide. *Total cyanogen.*—500 c.c. of the liquor are mixed with 50 c.c. aqueous potassium hydroxide (1 : 1) and 50 c.c. 10% ferrous sulphate, and heated for one to two hours on the water-bath. After cooling and diluting to a litre, 100 c.c. of the filtrate are acidified with hydrochloric acid, and 5 c.c. of 10% ferric chloride are added. The Prussian-blue formed is collected and then again decomposed with dilute aqueous potassium hydroxide. The filtrate, which contains all the cyanogen as ferrocyanide, is evaporated with excess of sulphuric acid, and the residue is gently ignited. The residual iron oxide is then estimated as usual by titration with permanganate. One c.c. of $N/100$-permanganate = 0·00156 gram of cyanogen.

Ammonium ferrocyanide.—100—500 c.c. of the liquor are evaporated, and the residue is gently ignited. The iron is then titrated as usual; 1 c.c. of $N/100$ permanganate = 0·00284 gram of the ferrocyanide.

Ammonium thiocyanate.—The author has slightly modified Pfeiffer's colorimetric process. Fifty c.c. of the sample are diluted with 50 c.c. of water, and evaporated on the water-bath to 30 c.c. so as to expel the free ammonia. After diluting to 100 c.c., 20 c.c. of the solution (= 10 c.c. of sample) are mixed with 10 c.c. of ferric chloride solution (5 parts of the salt made up to 100 parts with 10% hydrochloric acid) and diluted to 500 c.c. An aliquot part of the liquid is then matched as usual with a solution of ammonium thiocyanate of known strength. L. DE K.

Estimation of Scatole and Indole in Fæces. CURT MOEWES (*Chem. Zentr.*, 1912, ii, 1702; from *Zeitsch. expt. Path. Ther.*, **11**, 555). —The scatole and indole obtained by extracting the steam distillate with light petroleum are precipitated by dimethylaminobenzaldehyde, and the dye is dissolved in water and compared in a Plesch chromophotometer with a test solution of 1 : 100,000 made from equal parts of indole and scatole. Values of 0·008—0·024 gram per 100 grams of fæcal matter were obtained. J. C. W.

Action of Activated Aluminium on Alkaloidal Extracts Its Use in Toxicology. EMILE KOHN-ABREST (*Compt. rend.*, 1912, **155**, 1179—1181. Compare A., 1912, ii, 648—768).—A study of the behaviour of the more common vegetable alkaloids, pure, or mixed with viscera, in the presence of activated aluminium. The hydrated oxide formed from the activated aluminium only fixes a certain small proportion of alkaloids, such as strychnine, quinine, and cocaine in alcoholic solution acidified with tartaric acid, whilst on the other hand it retains almost all the nicotine. Data are given for some fourteen alkaloids. Alcoholic extracts of viscera containing morphine

and strychnine, after treatment with activated aluminium, are obtained in a state of great purity, wherein the alkaloids can be readily detected and estimated. W. G.

Distinction between Cocaine and its Substitutes. D. SCHERBATSCHEV (*Chem. Zentr.*, 1912, [ii], 386; from *Apoth. Zeit.*, 1912, **27**, 441. Compare Hankin, A., 1911, ii, 162).—The appearance under the microscope of solutions of β-eucaine, nirvanine, alypine, holocaine, and novocaine, when solutions of ammonia (10%), potassium hydroxide (10%), or sodium hydrogen carbonate (saturated) are added to them, is described. T. A. H.

Gravimetric Estimation of Quinine as Nitroprusside. P. J. KRUYSSE (*Pharm. Weekblad*, 1912, **49**, 1117—1120).—Quinine nitroprusside is obtained as a crystalline precipitate when a neutral solution of a quinine salt is treated with sodium nitroprusside; its solubility is less than that of the tartrate or oxalate, 100,000 parts of water dissolving 39 parts of the salt. For the estimation of quinine in powdered cinchona bark, 5 grams of the latter are mixed with 3·5 c.c. of water, 1 c.c. of ammonia and 2·5 grams of slaked lime, and the mixture is extracted in a Soxhlet apparatus for two hours with acetone. After the acetone has been evaporated from the extract, the residue is dissolved in 25 c.c. of 2% hydrochloric acid, the solution is filtered, rendered alkaline, and shaken with ether. The ethereal solution is then shaken with dilute hydrochloric acid, the separated acid solution is neutralised, diluted to 50 c.c., heated to 90°, and treated with 0·5 gram of ammonium oxalate. After cooling, the precipitate is collected on a filter, washed with a small quantity of water, and then dissolved in 5 c.c. of 2% hydrochloric acid. This solution is nearly neutralised, and the excess of oxalate is removed as calcium oxalate. The solution is now neutralised with ammonia, diluted to 70 c.c., heated to boiling, and treated with 0·5 gram of sodium nitroprusside. After cooling, the precipitate is collected, washed with water, dried at 100°, and weighed. The treatment with ammonium oxalate is for the purpose of separating cinchonine from the quinine. W. P. S.

Estimation of Quinine Sulphate in Cinchona Bark. P. J. KRUYSSE (*Pharm. Weekblad*, 1912, **49**, 1135—1136).—The author (preceding abstract) regrets he was not acquainted with the work of Kramers (A., 1897, ii, 83), who, however, did not succeed in applying the nitroprusside reaction quantitatively. L. DE K.

Hyposulphite in Volumetric Analysis. I. WILHELM SIEGMUND (*Monatsh.*, 1912, **33**, 1431—1445).—The hyposulphites give stable compounds with the ketones, which, in contradistinction to the formaldehyde-hyposulphites, act as reducing agents in the cold. Solutions of these compounds may therefore be used as standard reducing agents in volumetric analysis. The author finds that a convenient solution has the following composition: 10 grams of sodium hyposulphite, 15 c.c. of acetone, and 35 c.c. of ammonia (D = 0·91) to one litre of

water. The solution is kept, under a layer of paraffin oil, in a stock bottle from which a burette can be filled automatically; the top of the liquid in the burette is covered with toluene to prevent contact with the air. The tip of the burette is connected with the titration flask by means of a piece of glass tubing, which is bent twice at right angles, and passes through the rubber stopper of the flask. The stopper also contains inlet and exit tubes for a current of oxygen-free carbon dioxide, and a thermometer.

The solution of the hyposulphite is standardised by means of iron alum, or an oxidised solution of ferrous ammonium sulphate, using ammonium thiocyanate as indicator, and in the presence of sulphuric acid. The titration is carried out in the cold, with vigorous shaking; the sulphite formed has no action on the ferric salt. The solution is fairly stable, but should be standardised daily.

Experiments with a large number of azo-dyes, dyes which form leuco-compounds and nitro-colouring matters, show that they are reduced quantitatively by the above hyposulphite solution.

T. S. P.

Methods of Estimating Saponins. (Mlle.) MARIE KORSAKOV (*Compt. rend.*, 1912, **155**, 844—846).—A critical study of the methods at present employed for estimating saponins. Christophson's method based on the precipitation of the saponin as a barium compound is inaccurate, since the whole of the saponin does not separate, and further the barium hydroxide precipitates, from plant extracts, other substances than saponins, which on hydrolysis yield dextrose. A modification of Kruskul's method gives good results. The plant is dried, finely powdered, and extracted with boiling alcohol (60%). The extract is filtered, the alcohol distilled off, and the residue evaporated on the water-bath with calcined magnesia. The resulting paste is extracted with boiling alcohol (80%), the extract filtered, and precipitated with ether. The precipitate is dissolved in 3% sulphuric acid, and hydrolysed in an autoclave at 105° for one hour, the sapogenin liberated being washed with water, dissolved in absolute alcohol, and weighed after distilling off the alcohol. W. G.

A Delicate Test for the Detection of Albumin in Urine. ADOLF JOLLES (*Zeitsch. physiol. Chem.*, 1912, **81**, 205—206. Compare A., 1896, ii, 344).—The reagent is composed of mercuric chloride, 10 parts, citric acid 20 parts, sodium chlorate 20 parts, water 500 parts. Five c.c. of the filtered urine are added to each of three test-tubes. To (1) and (2) 1 c.c. of 30% acetic acid is added, 5 c.c. of the reagent are put in (1), and the other tubes are filled with water to the same level. The tubes are observed against a black background, (3) being placed in the middle. The reaction is sensitive to 1 part of albumin in 120,000. E. F. A.

Chemistry and Estimation of Gelatin. M. BERRÁR (*Biochem. Zeitsch.*, 1912, **47**, 189—214).—Gelatin forms saturated solutions in water in the following strengths: 0·62% at 21°, 0·60% at 18°, and 0·56% at 17°. If the concentrations only slightly exceed these pro-

portions, a gel is formed. Gelatin cannot be precipitated quantitatively by alcohol, or by metaphosphoric acid, as it completely dissolves in excess of the latter reagent, the proteins being only partly soluble in excess. At room temperature it is not precipitated quantitatively by picric acid, but at 8° precipitation is complete when a gelatin solution is mixed with a saturated aqueous solution of the acid. The acid combining power of gelatin was estimated by precipitation with potassium-mercuric iodide and picric acid solutions. Hydrochloric acid could not be used for this purpose, as the precipitate dissolves in excess of the acid. By this means it was found that 1 gram of gelatin combines with the equivalent of 11·3 c.c. *N*/10-acid, which corresponds with a molecular weight of 823. The picric acid precipitate of gelatin dissolves in alcohol and in 2% urea solution containing sodium chloride. If a mixture of 1 part of saturated aqueous solution of picric acid and 4 parts of alcohol are added to a gelatin solution, the gelatin is not precipitated, whereas other proteins are. The gelatin is, however, precipitated quantitatively from this gelatin-picric acid solution in alcohol by the addition of excess of aqueous picric acid solution in the cold. The precipitate again dissolves on warming to 40°, or treating again with absolute alcohol. On these reactions a method is based for estimating quantitatively gelatin in the presence of other proteins. It was incidentally observed that the nitrogen in picric acid can be quantitatively estimated by Kjeldahl's process, if it is first reduced by iron and glacial acetic acid. S. B. S.

The Rideal-Walker Phenol Control. A Possible Discordant Factor in the Standardisation of Disinfectants. J. T. Ainslie Walker and John M. Weiss (*J. Franklin Inst.*, 1912, 101—112).—The accuracy of the Rideal-Walker process depends on the purity of the phenol which is employed as the standard. Ordinary crystallised phenol is usually contaminated by cresols to such an extent as to render it unsuitable for the purposes of bactericidal control; four specimens of phenol examined by the authors were found to contain from 1·1 to 12·8% of cresols. As cresol has approximately three times the bactericidal efficiency of phenol, the error from this cause may be very considerable. The purity of the phenol should be ascertained by a determination of its solidifying point, and phenol having a lower solidifying point than 40° should be rejected. Synthetic phenol prepared by the authors showed a solidifying point of 40·5°. The bromine titration method does not yield trustworthy results as regards the purity of the phenol, but it may be employed for checking the strength of the 5% stock solution prepared from pure phenol. W. P. S.

General and Physical Chemistry.

New Observations Relative to the Zeeman Effect in the Hydrogen Spectrum. F. CROZE (*Compt. rend.*, 1912, 155, 1607—1610. Compare A., 1912, ii, 613).—The author has extended his study of the Zeeman effect in the case of hydrogen to the δ-line, and has made new measurements, for this line and the α-, β-, and γ-lines, of the value of $\Delta\lambda$ in a field of 24,122 gauss. He maintains his previous view that these three rays furnish a pure triplet with normal deviation, and replies to Paschen and Back (*Ann. Physik.*, 1912, [iv], **39**, 897), putting forward an explanation as to why their results differ from his. W. G.

The Dispersion of Certain Metals in the Visible Spectrum. CONSTANTIN ZAKRZEWSKI (*Bull. Acad. Sci. Cracow*, 1912, 842—849).—A formula is deduced, by means of which the optical constants of a metal can be calculated from the phase differences of the components, parallel and perpendicular to the plane of incidence, measured for two different angles of incidence. This method of obtaining the constants does not, like the usual method, involve the preparation of highly polished metallic mirrors. The formula is applied to data obtained by the author for nickel and zinc, and to Drude's measurements for silver. H. M. D.

Electric Behaviour of Certain Vapours which Exhibit Absorption Bands. F. BURGER and JOHANNES KOENIGSBERGER (*Physikal. Zeitsch.*, 1912, **13**, 1198—1199).—The nature of the process which gives rise to banded emission and absorption is further discussed (compare A., 1912, ii, 405). Bromine and nitrogen peroxide exhibit banded spectra, and experiments with these substances are described which show that the carriers responsible for the banded spectra in these two cases cannot be due either to electrons or free ions so far as the visible spectrum is concerned. An upper limiting value for the proportion of ionised molecules is calculated, which also indicates that the banded absorption cannot be attributed to the occurrence of ionised molecules. H. M. D.

The Absorption Curve of Colloidal Silver Solutions. R. GANS (*Physikal. Zeitsch.*, 1912, **13**, 1185—1186).—On the assumption that the colloidal particles have the form of ellipsoids of rotation, the author has calculated the form of the absorption curve for the region $\lambda = 4200$ to $\lambda = 7500$ for varying values of the axial ratios. As in the case of gold solutions (A., 1912, ii, 508) the curve thus obtained may be utilised in the investigation of the geometrical form of the particles present in colloidal solutions of silver. H. M. D.

The Influence of Acid Radicles on the Colour Intensity of Copper Salts. CHARLES SCOTT GARRETT (*Zeitsch. Elektrochem.*, 1913, **19**, 1—7).—The molecular extinction of a number of soluble

copper salts was determined by means of a Hüfner spectrophotometer. The salts $CuCl_2$, $CuBr_2$, $Cu(NO_3)_2$, $Cu(ClO_3)_2$, $CuCr_2O_7$, $CuSO_4$, and $Cu(ClO_4)_2$ were examined at concentrations from $1n$—$0·01n$. The experimental results are discussed and interpreted on the basis of Baly's theory of the action of a solvent on a dissolved substance. It is shown (1) that when a concentrated solution is diluted, a penetration of the salt molecule system by the solvent molecule system occurs; (2) the mean number of solvent molecules, the fields of force of which penetrate the field of force of the dissolved molecule, conditions the process of solution at a given concentration; (3) every vibration of the copper atom in the undissociated molecule, which is active in the absorption of light, is influenced by the free electric field of the typical atoms of the acid radicle; (4) the light absorption due to the copper is not specifically influenced by the presence of a coloured acid radicle, as is frequently the case with organic substances, and (5) there is a strengthening of the light absorption when the free electric field of the acid radicle is negative. J. F. S.

Absorption Spectra of Solutions as Affected by Temperature and by Dilution. Quantitative Study of Absorption Spectra by means of the Radiomicrometer. HARRY C. JONES and J. SAM GUY (*Amer. Chem. J.*, 1913, **49**, 1—46).—In an earlier paper (A., 1912, ii, 70) an account was given of a study of the effect of heat and of dilution on the absorption spectra of certain neodymium salts. The work on these salts has now been continued and the investigation has been extended to praseodymium nitrate and chloride, and to uranyl nitrate and sulphate. The radiomicrometer employed was a slightly modified form of that described previously. E. G.

Quantitative Investigation of the Absorption of Ultraviolet Rays by the Fatty Acids and their Isomeric Esters. JEAN BIELECKI and VICTOR HENRI (*Compt. rend.*, 1912, **155**, 1617—1620. Compare A., 1912, ii, 882).—The authors have made a more detailed comparison of the absorptive power in the case of three fatty acids and the esters isomeric with them, and in the case of a number of groups of isomeric esters, the absorption being measured in aqueous and alcoholic solutions and with rays of varying wavelengths. Curves and tables are given, and the results show that (1) the absorption spectrum of the various acids is different from that of the esters isomeric with them, this difference being independent of the solvent; (2) the absorption of the ultraviolet rays is controlled by the molecular complexity and augments with increasing complexity. There is also a considerable variation in the absorption spectra of the isomeric esters, dependent on the molecular arrangement, as is shown by a study of the four esters, butyl acetate, propyl propionate, ethyl *n*-butyrate, and methyl valerate. W. G.

The Absorption Phenomena of Oxyhæmoglobin in the Grating Spectrum. OTTO SCHUMM (*Zeitsch. physiol. Chem.*, 1913, **83**, 1—24).—The spectrum obtained by a diffraction grating is

spoken of as the natural spectrum, in contradistinction to that obtained by a prism. Careful measurements of the three bands (two in the visible, one in the ultra-violet region) are given, and the results figured in plates. Some variations occur even in the blood of the same species, and it is not possible to distinguish the oxyhæmoglobin of different animals by any such spectrum differences.

W. D. H.

Long- and Short-waved Absorption and Fluorescence Bands of the Carbonyl Group. M. GELBKE (*Jahrb. Radioaktiv. Elektronik*, 1913, 10, 1—34).—The ultra-violet absorption of a number of ketones has been examined, the substances being dissolved for the most part in ethyl alcohol, although in a few cases the substances were investigated in the form of saturated vapour or dissolved in water or *n*-hexane. From a comparison of the short-waved absorption bands of acetone and its substituted derivatives, it is found that the acetone band, which has its maximum at $\lambda = 268\mu\mu$, is displaced in the direction of greater wave-lengths when one or more hydrogen atoms are substituted by alkyl, halogen, phenyl, nitroso- or carbonyl groups. In the case of alkyl substitution, the displacement of the maximum amounts to 5—$10\mu\mu$, whilst the effect of halogens, the phenyl, nitroso- and carbonyl groups is greater. The displacement of the band is accompanied by an increase in the absorption and also by a broadening of the band. From a comparison of acetone and *cyclo*hexanone it appears that the influence of ring formation is comparatively small.

In addition to the above-mentioned short-waved band, acetone shows a band with a maximum at about $\lambda = 365\mu\mu$, which extends from about $\lambda = 327\mu\mu$ into the visible spectrum. A similar band is also found in the substituted derivatives of acetone, and this it is which gives rise to the yellow colour exhibited by many such substances which contain the carbonyl group.

From a comparison of the absorption spectra of dimethyl diketone and methyl ethyl diketone with that of acetone, it is found that the short-waved band in the α-diketones is shifted about 5—$10\mu\mu$ in the direction of longer wave-lengths, and that the absorption is considerably intensified. In regard to the long-waved band, the shift exhibited by the two α-diketones amounts to about $30\mu\mu$ and the intensity is increased about forty times. In the case of β-diketones the intensification of the long-waved absorption band is not nearly so great as that observed for the α-diketones.

From a comparison of the spectra of methylheptenone, mesityl oxide, and phorone with that of acetone, it is found that both the short and long-waved bands are not appreciably shifted by a conjugated ethylene linking, although the intensity of the absorption increases very considerably in both cases. If the ethylene linking is not conjugated, but separated from the carbonyl group by two methylene groups, the absorption intensity of the short-waved band appears to be increased to a much smaller extent that when conjugation occurs.

The results of the spectrographic examination of the fluorescence bands

of acetone, dimethyl diketone, and oxalosuccinonitrile have been published previously (A., 1912, ii, 713), but a large number of other substances have now been examined in regard to the emission of fluorescent light when subjected to the action of intense ultra-violet radiation These observations show that the activity of the carbonyl group in this direction is quite general, fluorescence being exhibited by both mono- and di-ketones, and by both cyclic and acyclic compounds in which it occurs. It is thus proved that the faculty of fluorescence is by no means confined to ring compounds. H. M. D.

Rotation Dispersion. ERNST DEUSSEN (*J. pr. Chem.*, 1913, [ii], **87**, 96).—A correction. In reply to Tschugaev (this vol., ii, 3), the author admits that the rotations for mercury light recorded in previous papers (A., 1912, ii, 510, 1020) refer to light of wave-length $546\mu\mu$, and not 491 $\mu\mu$. F. B.

The Rotation Dispersion of Some Coloured Lactates. H. VOLK (*Ber.*, 1912, **45**, 3744—3748).—Abnormal rotation dispersion of coloured asymmetric organic compounds, which has, hitherto, only been studied in the case of somewhat complicated substances (Grossmann, A., 1900, ii, 372, and Tschugaev, A., 1909, ii, 631), has now been observed with the copper, nickel, and cobalt salts of *l*-lactic acid. A maximum rotation is found in each case, in the region of selective absorption. Increase of temperature diminishes the rotation, but does not affect the character of the dispersion.

For the preparation of these salts, zinc ammonium *l*-lactate (Purdie, T., 1893, **63**, 1143), which has a normal but comparatively high rotation-dispersion, is boiled with baryta water to expel ammonia and precipitate the zinc, and after removing the excess of barium hydroxide by means of carbon dioxide the filtrate is treated with the equivalent amount of the metallic sulphate and allowed to crystallise.

Copper l-*lactate*, $Cu(C_3H_5O_3)_2,1H_2O$, a light blue, crystalline powder, has a maximum rotation and absorption in yellow light; [M], calculated for lactic acid, falls from 18·5 in the green to 15·6 in the dark blue. *Nickel* l-*lactate*, $Ni(C_3H_5O_3)_2,4H_2O$, a light green powder, is remarkable in that it is *laevo*-rotatory in all parts of the spectrum; the maximum rotation, [M] = −0·8, and strongest absorption are in the yellow.

Cobalt l-*lactate*, $Co(C_3H_5O_3)_2,2H_2O$, a light red powder, has maximum absorption for green light, in which [M] = 30; the rotation falls towards either end of the spectrum, and changes sign between light blue and dark blue. J. C. W.

Sunlight. PAUL C. FREER and HARRY D. GIBBS (*J. Physical Chem.*, 1912, **16**, 709—738).—The influence of sunlight on chemical and physiological processes is supposed by some to be greater in the tropics than in temperate climates. On the assumption that the difference lies in the intensity of the ultra-violet radiation, an investigation of the photochemical action of tropical sunlight should yield some information as to its probable physiological action.

The effect of sunlight in Manila in promoting the coloration of

a number of benzene derivatives, such as cresol and aniline, has been described from time to time by Gibbs. Since these reactions have large temperature-coefficients, and the temperatures of solutions exposed to the sun in Manila may attain 50°, Gibbs' experiments gave no certain indication that sunlight is abnormally active in the tropics.

Measurements of the total insolation in heat units made with the Ångström pyroheliometer at various latitudes indicate that the heat intensity varies but little from place to place. The intensity of violet and ultra-violet radiation is conveniently measured by the rate of decomposition of oxalic acid in presence of uranyl acetate. This reaction has a very small temperature-coefficient, and when used under standard conditions gives useful comparative results.

In Manila the average amount of oxalic acid decomposed in one hour during one year was 12·45%, the maximum being 17·8% and the minimum 1·15%. The average values obtained by other observers were as follows: Baguio (Philippine Is.) 14·2%; Honolulu, 13·9%; Kuala Lumpur (Malay States), 15·29%; Khartoum, 17·8% (using quartz flask); Washington, 11·96%; Tucson (Arizona), 13·0%; Munich, 8·39%. When the sky is clear, the activity is almost the same everywhere, and the lower averages in the higher latitudes may be ascribed to the higher percentage of dull days.

Oxyhæmoglobin is converted by ultra-violet light into methæmoglobin which can be detected in the blood of rabbits which have died by exposure to the sun. Nevertheless, experiments in which rabbits, monkeys, and men of different shade were exposed to the sun seem to lead to the conclusion that the ill-effects are wholly due to the rise in blood-temperature and that the resistance of an individual depends largely on his opportunity for cooling by radiation, etc., and the perfection of his heat-regulating system of sweat glands; thus black, grey, and white rabbits, monkeys, and men, showed an increasing resistivity. Monkeys exposed to the sun in Manila died in less than two hours, the blood temperature rising almost 10°, but when the animals were kept cool by a fan, although exposed to the full radiation, including the ultra-violet, no ill-effects followed. The brain in these experiments was to some extent protected by the hair on the head.

R. J. C.

Photochemical Reduction of Copper Sulphate. CHARLES W. BENNETT (*J. Physical Chem.*, 1912, **16**, 782—785).—The author propounds the theory that the light which is absorbed by cupric sulphate solution tends to decompose it, so that a reducing agent might be found which, although without action in the dark, would precipitate copper when assisted by radiations of appropriate wavelength.

Experiments are cited to show that light reduces ammoniacal copper sulphate to cuprous oxide in presence of hydrazine hydrate, and that the precipitation of copper phosphide from 5% cupric sulphate solution by an ethereal solution of phosphorus (Mrs. Fulhame, 1794) is accelerated by the light from a carbon arc. In the latter case a quartz vessel was used. R. J. C.

The First Stages in the Photolysis of Ethyl Alcohol, Acetaldehyde, and Acetic Acid. DANIEL BERTHELOT and HENRY GAUDECHON (*Compt. rend.*, 1913, **156**, 68—71).—Of the three substances studied. acetaldehyde is the only one which is acted on by sunlight ($\lambda > 0\cdot3\mu$), the alcohol and acid requiring radiations of shorter wave-length. There are four stages in the photolysis of acetaldehyde, namely: (1) gaseous decomposition into carbon monoxide and methane (compare A., 1910, i, 543). (2) Polymerisation and subsequent evolution of hydrocarbons, such as ethane, etc. (compare A., 1910, ii, 814). (3) Formation of resinous products. (4) Conversion of the aldehyde into acetic acid. Only the first reaction is produced by initial ultra-violet rays, the three others requiring the mean or extreme rays.

The photolysis of ethyl alcohol consists fundamentally of the evolution of hydrogen and formation of acetaldehyde, which is then further decomposed (compare A., 1911, ii, 835). Acetic acid, on decomposition by the rays from an Heraeus lamp, gives a gaseous product containing carbon dioxide (44%), carbon monoxide (17%), and combustible gases (39%) (compare A., 1910, ii, 814). Water has no effect on the products of photolysis, but lessens the rate of the reaction. W. G.

Photolysis of Different Complex Sugars (Bioses and Trioses) by Ultra-violet Rays. DANIEL BERTHELOT and HENRY GAUDECHON (*Compt. rend.*, 1912, **155**, 1506—1509. Compare A., 1912, ii, 1120).—A study of the decomposition of the bioses, maltose, lactose, trehalose and gentiobiose, and the trioses, raffinose, melezitose and gentianose, by ultra-violet rays of varying wave-length. In the case of the trioses no first stage of formation of a monose and a biose could be detected. After the first stage in the decomposition, the action was the same as in the case of the monoses (*loc. cit.*). W. G.

The Radio-elements, the Periodic System, and the Constitution of the Atom. A. VAN DEN BROCK (*Physikal. Zeitsch.*, 1913, **14**, 32—41).—This paper deals with recent work in the radioactive disintegration series and in the rare earth group, with the intra-atomic charge and theories of the constitution of the atom and their connexion with the periodic law in a manner unsuitable for abstraction. F. S.

Evidence of Spontaneous Alterations of Concentration in Solutions and Gases. THEODOR SVEDBERG (*Physikal. Zeitsch.*, 1913, **14**, 22—26. Compare A., 1912, ii, 905, 906).—The question is discussed as to whether the relative deviation of the number of α-particles produced in a volume element of a solution of a radio-active substance from the mean value should be theoretically greater than the corresponding relative deviation from the mean value in the case of the solid substance. It has been shown previously that the ratio of the mean deviations should be $\sqrt{2}:1$, and experimental observations indicate that this is approximately the case. Further arguments are

now put forward in support of the correctness of the above theoretical conclusion.

The question of the detection of spontaneous alterations in the concentration of solutions of other than radioactive substances is also examined with reference to the negative results which have been obtained up to the present. The author draws the conclusion that such changes cannot be detected by the methods of examination which are at present available. H. M. D.

Excitation of γ-Rays by α-Rays. JAMES CHADWICK (*Phil. Mag.*, 1913, [vi], 25, 193—197. Compare A., 1912, ii, 1025).—Further evidence is given that the impact of α-rays on metals of high atomic weight excites γ-rays. A tube, of such thin glass that the α-rays escape, containing radium emanation was surrounded with two concentric tubes of metals of widely different atomic weights, of thickness just sufficient to stop all the α-rays. The position of the two metals was transposed, and the ionisation with the two arrangements accurately compared by a balance method. Always when the metal of high atomic weight was next the emanation tube and bombarded by α-rays, the ionisation current was slightly greater than when the metal bombarded was of low atomic weight. The effect was much increased by filling the ionisation chamber with vapour, such as carbon disulphide or methyl iodide. The ratio of the ionisation in these vapours to that in air by *X*-rays of low penetrating power is much greater than for *X*-rays of high penetrating power, and it was to be expected that the γ-rays generated by α-rays would have a much lower penetrating power than the primary γ-rays, and that the part of the effect due to them would be greater in a heavy vapour than in air. If a thickness of light material was placed round the tube, sufficient to absorb the α-rays, the effect disappeared. That it was not due to very soft β-rays was proved by experimenting in a powerful magnetic field sufficient to coil up the β-rays and prevent them from reaching the metal. This did not cause any change in the effect. With outer tube of aluminium, the inner tube being of the following materials: gold, silver, copper, aluminium, paper; the relative ionisations in carbon disulphide vapour were respectively, 104·8, 102·5, 101·2, 100, and 99·7. This shows that the excitation of γ-rays by α-rays increases with the atomic weight of the material bombarded. A rough estimate of the coefficient of absorption of the excited γ-rays was 8 (cm.$^{-1}$ of aluminium).

In confirmation it has been shown, with A. S. Russell, that ionium and polonium, which give α-rays without β-rays, give-γ-rays in amount sufficient to be studied in detail. F. S.

Retardation of α-Particles by Metals. E. MARSDEN and H. RICHARDSON (*Phil. Mag.*, 1913, [vi], 25, 184—193. Compare Taylor, A., 1908, ii, 783; 1909, ii, 850).—The "air-equivalent" of a metal foil is the distance in cm. by which the range of an α-particle at 76 cm. and 15° is reduced in passage through the foil, and is, for materials of atomic weight greater than that of air, the less the less the velocity of the α-particle, or the nearer it is to the end of its range. This variation has been studied for the α-rays of radium-*C*

by a scintillation method, which offers advantages, only the fastest α-particles, that is, those which have not been scattered, being observed. A zinc sulphide screen is rigidly attached in the focus of the microscope, and is carried by the rack and pinion to any required distance from the source of α-rays. Between on a separate rack and pinion the foil is mounted, and the air-equivalent of the foil studied at various parts of the range of the α-particles. Tables are given for the variation of the air-equivalent, which is considerable, especially near the end of the path, with the range, and also a curve from which the air-equivalent of any thickness of foil (Au, Ag, and Al) at any part of the range can be deduced. A brightening of the screen, just outside the extreme range of the α-particles themselves, which is unaffected by a transverse magnetic field, was observed and is ascribed possibly to γ-rays excited by α-rays (see preceding abstract).

F. S.

Absorption of β-Rays. J. A. GRAY (*Proc. Roy. Soc.*, 1912, *A*, **87**, 487—489).—Two experiments on the absorption of the β-rays of radium-*E* by paper show that the rays become more and more absorbable, practically none passing 56 sheets, weighing 8·77 mg. per cm.^{2}, the percentage transmitted by 5 sheets decreasing from 50 to 10.

These results are explained on the view that β-rays are both retarded and stopped by matter, and when the velocity of the surviving rays falls below the previous mean velocity, the exponential law can no longer hold.

F. S.

Similarity in Nature of *X*- and Primary γ-Rays. J. A. GRAY (*Proc. Roy. Soc.*, 1912, *A*, **87**, 489—501).—The absorption of the primary γ-rays of radium-*E* and of the γ-rays excited in lead by the β-rays of radium-*E* is compared with the absorption of *X*-rays. The γ-rays of radium-*E* are absorbed somewhat similarly to characteristic secondary *X*-rays excited in silver. There is no discontinuity, with respect to absorption, between *X*- and γ-rays. Tin absorbs the γ-rays of radium-*E* to an abnormal extent, but for iron and gold compared with aluminium, the absorption is similar to that of the silver *X*-rays.

An investigation of the radiation reflected from radiators of various materials showed that the γ-rays of radium-*E* excite the characteristic *X*-radiation in silver, tin, barium, neodymium, and praseodymium. This furnishes the most definite proof possible that *X*-rays and γ-rays are of the same nature.

Lastly, the scattering of γ-rays of radium-*E* and of *X*-rays has been compared, and it is shown that the phenomena is similar both in magnitude and character for both radiations.

F. S.

Expansion Apparatus for Making Visible the Paths of Ionising Particles in Gases, and the Results Obtained with this Apparatus. CHARLES T. R. WILSON (*Jahrb. Radioaktiv. Elektronik*, 1913, **10**, 34—35. Compare A., 1911, ii, 565).—The expansion apparatus and method of illuminating the condensed water droplets, described in the previous paper, have been improved in several

respects with the result that it has been possible to obtain photographs of the most rapidly moving β-rays, which show the droplets due to the individual ions. The greatly increased size of the cloud chamber in the new apparatus, not only enables the entire course of the longest-ranged α-particles to be registered, but its depth is such that horizontal beams of X-rays may be examined without any danger of interference from the proximity of the roof or base of the chamber. The photographic records obtained under the new conditions are, moreover, much more distinct than those given by the earlier form of apparatus.

In regard to the α-particles, the photographs show that these move along paths which are approximately rectilinear, except for the last 2 mm., where there is a very marked change in direction. Apart from this sudden and pronounced change at the end of the range, there is, however, in many cases a small and gradual change in direction over the greater part of the course, and the photographs thus afford evidence of both single and compound scattering.

The photographs of the β-rays indicate that the ions are formed in pairs over a considerable portion of the path, but that at certain points closely packed groups of twenty or thirty ions are produced. The occurrence of these groups of ions is regarded as evidence of the emission by the atoms of secondary corpuscles which possess sufficient energy to produce ionisation over a small range. In opposition to the α-rays, the β-rays never exhibit sudden changes in direction, although the slow change due to compound scattering is clearly shown, provided the velocity of the rays is not too large.

The X-ray photographs show that β-rays proceed from points in the paths of the X-rays beam. Apart from this production of β-rays, the X-rays appear to give rise to no effect which is photographically registered on the plates. Corresponding with the heterogeneity of the X-rays, it is found that the paths of the individual β-particles vary considerably in length. The rays appear to show both simple and compound scattering, although the latter effect appears to be the much more frequent and characteristic type. The emission of the β-rays appears to be uniformly distributed in all directions, and no evidence of any dependence on the direction in which the X-ray beam is propagated has been obtained.

In the case of both the β-ray and X-ray photographs, it has been possible to ascertain approximately, by counting the droplets, the number of ions which are produced per centimetre of path.

H. M. D.

Ionisation Produced by β- and γ-Rays at High Pressures. D. C. H. FLORANCE (*Phil. Mag.*, 1913, [vi], 25, 172—183).—The absorption and ionisation produced in air at high pressure with the β-rays of uranium-X and with the secondary β-rays generated by the γ-rays of radium-C have been studied by means of a special cylindrical ionisation vessel with pressures of air up to 80 atmospheres. Complete saturation could not be obtained, even with a field of 1800 volts per cm., the shape of the curves being similar to those obtained with α-rays. There is for constant voltage a constant ratio for the ionisa-

tion currents at any two pressures, and although saturation is not attained, the ionisation currents are proportional to the intensity of the radiation at different pressures. The experimental value found for μ(cm.$^{-1}$ of air at atmospheric pressure) for the β-rays of uranium-X was, for plates 7 cm. diameter and 1 cm. apart, 0·04, but the true value for a parallel beam of β-rays was deduced to be 0·007, in agreement with the value of μ in solids. The values for the emergent and incident β-rays produced by γ-rays of radium-C were 0·046 and 0·056, and they appear to be independent of the nature of the material in which they originate. With plates 1 cm. apart the part of the ionisation due to β-rays originating in the gas is negligible at atmospheric pressure and 25% of the total ionisation at 80 atmospheres.

F. S.

Recombination of Ions Produced by Röntgen Rays. S. J. PLIMPTON (*Phil. Mag.*, 1913, [vi], **25**, 65—81; *Amer. J. Sci.*, 1913, [iv], **35**, 39—53).—The value of a, the coefficient of recombination of the ions in the equation $dn/dt = -an^2$, was determined by ionising the gas between two parallel plate electrodes by a single flash of X-rays, restricted so as not to fall upon the plates, allowing the ions produced to recombine in absence of any external field for small intervals of time, regulated and determined mechanically, and then by sudden application of a field driving the residual ions to the electrodes and so evaluating their numbers. In this way the effect of ionic diffusion can be greatly reduced, corpuscular radiation from the metal plates eliminated, uniformity of X-rays secured, and the initial stages of recombination studied. The results revealed, especially for carbon dioxide, an initial value of a relatively large, but decreasing and becoming constant after intervals usually of about one-third of a second. This is explained by initial recombination of the pair of ions formed before they have moved by diffusion out of their range of mutual influence, and the high value in carbon dioxide and the slower rate at which the normal value is attained are ascribed to the slower diffusion in this gas than in air. If a field acts during the flash, ceasing to act simultaneously with the cessation of the flash, the final value of a is not affected, but the initial value is decreased. A table is given of the absolute values of a at various time-intervals from the cessation of ionisation for air, carbon dioxide, sulphur dioxide, methyl iodide, ethyl chloride, ethyl bromide, and ethyl ether at various pressures. For air, the initial value of a/e, when e is the atomic charge, is 11,540, and the final value, 3960.

F. S.

Further Experiments on the Mobility of the Positive Ions at Low Pressures. GEORGE W. TODD (*Phil. Mag.*, 1913, [vi], **25**, 163—171. Compare A., 1912, ii, 245, 1050).—The experiments have been repeated with a larger apparatus in order to obtain information at lower pressures, at which it was formerly suggested sub-molecular particles might constitute the positive ions. The new experiments show nothing like the enormous increases in the mobilities previously observed, but indicate that below the

pressure of 1 mm. the mobilities vary with the period of alternation of the field when the period is high (above 150 ~). F. S.

Combination of Hydrogen and Oxygen in the Presence of Heated Platinum and Carbon. J. R. Thompson (*Physikal. Zeitsch.*, 1913, **14**, 11—15).—Experiments have been made with the object of ascertaining whether there is any connexion between the temperature at which hydrogen and oxygen begin to combine in contact with heated platinum or carbon, and that at which these begin to emit negatively charged particles.

The platinum spiral or carbon filament was contained in a cylindrical glass tube which could either be exhausted or connected with a supply of the gas mixture. The temperature of the spiral could be gradually raised by means of a regulated current from an accumulator battery and a voltmeter placed across the ends of the wire enabled the resistance to be measured. An aluminium cylinder surrounding the heated wire was connected with one pair of quadrants of a Dolezalek electrometer, and permitted the measurement of the electrical effect at gradually increasing temperatures.

From observations made when the tube was highly exhausted and when hydrogen and oxygen were admitted at different pressures measured by the manometer, it has been found that in the case of platinum and of carbon, the temperature at which the emission of negative particles is first observed is within the limits of experimental error identical with the temperature at which combination occurs between the hydrogen and oxygen. In all cases the explosive combination of the gases was found to be accompanied by large ionisation currents, but these could not be measured. The actual temperatures at which the two effects occur were not measured, the temperature being measured in terms of the resistance of the wire as ascertained from the readings of the voltmeter and ammeter. The influence of the gas on the observed resistance was allowed for by means of a series of readings with the apparatus when the heated wire was in contact with air at different pressures.

Preliminary observations show also that combination of hydrogen and oxygen occurs if the platinum wire is subjected to the action of a beam of *X*-rays. The combination occurs more readily if the percentage of hydrogen is less than 10. H. M. D.

Investigation of the Spectrum of Ionium. Alexander S. Russell and R. Rossi (*Proc. Roy. Soc.*, 1912, *A*, **87**, 478—484).—The ionium preparation employed (Boltwood, A., 1911, ii, 359), from measurements of the number of α-particles emitted, should contain 16% of ionium, if the period of that substance is 100,000 years, the remainder being thorium oxide. After chemical purification of the ionium-thorium preparation by various methods, its arc spectrum between the wave-lengths 3800 to 5000 was photographed in juxtaposition with that of a pure thorium oxide preparation, in the first order by a Rowland's grating of 21·5 feet radius giving a dispersion of 2·6 Ångström units per mm. The spectrum was identical with that of pure thorium save for the presence of five of the stronger lines of

scandium, the amount of which in the purified preparation was estimated as three or four parts per thousand. It was found that an admixture in thorium oxide of 1% of cerium oxide could easily, and 1% of uranium oxide could just, be detected spectroscopically. The obvious conclusion is that ionium cannot be present in the preparation to the extent of more than 1 or 2%, and that its period of average life cannot be more than 12,000 years.

This result is consistent with the estimate given by Soddy of at least 100,000 years, only if at least one unknown product of long life intervenes between uranium and radium. On the other hand, the period deduced from the range of the α-rays, 200,000 years, is not consistent with the result obtained unless the α-rays of ionium are exceptional. It is possible that ionium has no arc spectrum in the region investigated, although this is improbable, or that ionium and thorium have identical spectra, as they have identical chemical properties.

In a note, the paper on the same subject by Exner and Haschek (*Sitzungsber. K. Akad. Wiss Wien*, 1912, **121**, *iia*, 1075) with the same result is referred to, the ionium in the Austrian preparation being estimated as two-thirds of that in the one employed. F. S.

The Solid Radioactive Disintegration Products Suspended in the Atmosphere. K. W. FRITZ KOHLRAUSCH (*Physikal. Zeitsch.*, 1912, **13**, 1193).—Certain corrections are discussed in the methods employed in the measurement of the solid radioactive products in the atmosphere, and new expressions more in accord with recent work are deduced. For the determination of the amount of radium-A in the air by passing the air at a suitable velocity for a known time through a tubular condenser with inner electrode negative, and measuring the ionisation current at the end due to the active deposit on the inner electrode, tables are given showing the ratio of the effect for any time of aspiration to that for an indefinitely long time. In the second place the effect of the thorium products in the air is taken into consideration. F. S.

Electro-chemistry of Extremely Dilute Solutions, in Particular of Radioactive Substances. KARL F. HERZFELD (*Physikal. Zeitsch.*, 1913, **14**, 29—32).—If a metal plate is immersed in a solution of one of its salts which contains a mixture of two radioactive substances in a definite ratio, then, according to the experiments of Hevesy (A., 1912, ii, 414), the ratio in which the radioactive metals separate on the metal plate is dependent solely on the potential difference at the contact surface of the metal and its salt solution. This observation is contrary to what would be expected on the basis of Nernst's formula for the equilibrium at the surface. The discrepancy may be explained if it is assumed that the quantity of deposited radioactive metal in the equilibrium condition is not sufficient to form a complete molecular layer. If P' denotes the solution pressure of the radioactive metal, p_0 the osmotic pressure of the amount initially present in the solution, and π the pressure corresponding with the metal deposited in the equilibrium condition then the cathode potential E, will be related to these quantities by the equation

$E = RT\log P'\pi/(p_0 - \pi)$. The application of this equilibrium equation to two radioactive substances present in the solution leads to results in agreement with the observed facts. In regard to the variation of the ratio of the deposited metals with the magnitude of the potential at the metal surface, the formula gives a curve which is also of the same type as that representing the experimental data. H. M. D.

Electrical Excitation in the Splashing of Liquids (Ballo-Electricity). CHRISTIAN CHRISTIANSEN (*Ann. Physik*, 1913, [iv], 40, 107—137).—An account is given of experiments in which the electrical phenomena associated with the incidence of liquid spray on a solid surface have been investigated. By means of a current of air under constant pressure, the liquid under examination is made to issue from a small aperture in the form of a fine spray which impinges on a plate or on the walls of a tube of the solid substance to be investigated. In most of the experiments a platinum disk or tube was employed, and this was connected by a wire with the liquid in the supply reservoir, and also with one pair of quadrants of an electrometer, the opposite pair being earthed.

The magnitude of the electrical effect obtained when distilled water is sprayed was found to vary very considerably with the sample of water employed. In searching for the cause of these irregularities, it has been found that contact of the water with any substance, such as glass, paper, wool, silk, oils, etc., which has been exposed to the air for a considerable time, gives rise to a greatly increased electrometer deflection. The influence of electrolytes on the ballo-electric effect is relatively very small, and the much greater influence of contact with the above-mentioned substances is supposed to be due to the condensation of radioactive substances on the air-exposed surfaces.

The deflections obtained with aqueous solutions of acids, bases, and salts, and the influence of dilution have been examined, with the result that the chemical nature of the electrolyte appears to be of little importance in connexion with the phenomenon. According to the magnitude of the electrical effect it is possible to divide aqueous solutions into two groups. When solutions belonging to these different groups are mixed, it is found that the ballo-electric activity of the mixed solution is very much greater than that of the components. As an example, it may be mentioned that if equal volumes of molar solutions of ethyl alcohol and potassium chloride are mixed together, the effects obtained with the mixed solution was 7·0, whilst that given by the alcohol solution was 0·9, and by the potassium chloride 0·1. Several such mixtures have been investigated in such a way as to obtain comparative numbers for related substances belonging to the two above-mentioned ballo-electric groups.

Other experiments show that the effect varies with the nature of the solid surface on which the liquid spray impinges. With a distilled water spray, platinum glass and ivory become positively charged, whilst paraffin becomes negative. In the case of wax and shellac, the solid is at first negatively charged, but after prolonged action the sign of the charge becomes reversed. The most constant results are obtained with a platinum surface. H. M. D.

Dielectric Constants of Dissolved Salts. II. PAUL WALDEN (*Bull. Acad. St. Pétersbourg*, 1912, [vi], 1055—1086).—Investigations similar to those previously made with chloroform solutions (compare A., 1912, ii, 421) have been carried out with solutions in dichloromethane (dielectric constant, 8·3) and in ethyl formate (dielectric constant, 8·2), which differ from chloroform in giving measurable ionic dissociation of the salts employed (*loc. cit.*). Further, ethyl formate is a solvent of an entirely different type, so that its use opens up the possibility of studying the chemical rôle of the atoms constituting the solvent.

As with chloroform so also with dichloromethane, the dissolution of the salts is accompanied by a considerable increase in the dielectric constant of the solvent. Further, the dielectric constants of the salts, calculated by means of Philip's, Bouty's, and Silberstein's formula, are mostly very high, the greatest values being obtained with the first of these formulæ. In dichloromethane, the value of the dielectric constant of any salt is much higher than in chloroform. This constant also increases with the complexity of the salt and, according to Philip's formula, has the values: $NHEt_2,HCl$, 88; NEt_3,HCl, 390, and NEt_4Cl, 1980; the numbers for the corresponding nitrates are 71, 425, and 1365 respectively.

For one and the same salt at equal dilutions, the molecular conductivity is from ten to thirty times as great in dichloromethane as in chloroform, and whilst in the latter solvent it diminishes rapidly and continuously as the dilution increases, in the former a minimum is observed at a certain dilution. The conclusion is drawn that the ions formed from the salt are able to raise the dielectric constant of the solution and also the dissociating power of the solvent.

Ebullioscopic measurements show that the salts have different molecular magnitudes in these two solvents, these being, for NEt_4Cl, M_6 in chloroform and M_2 in dichloromethane, and for NEt_3,HCl, M_2 and $M_1 - M_2$ respectively. The increased values of the dielectric constants in dichloromethane may be due partly to this depolymerisation and partly to a specific catalytic influence of the solvent.

The chemical process of salt-formation by the conjunction of two neutral constituents ($NEt_3 + EtBr$, etc.) is expressed physically in a reconstruction of the dielectric properties of these constituents in such a way that the new product shows a dielectric constant which is about six, thirteen, or eighteen times that calculated additively for secondary amine, tertiary amine, and tetralkylammonium salts respectively.

Calculation by means of the Clausius-Mosotti equation, $x = (K-1)/(K+2)$, where x represents the fraction of the total volume actually occupied by the molecules, shows that these salts are the best electrolytes for which x approaches the value 1.

Not only is the general behaviour of ethyl formate as regards the alteration of the dielectric constants of dissolved alkylamino-salts similar to that of dichloromethane, but the actual values of these constants are very nearly equal with the two solvents. Sodium iodide and lithium bromide are characterised by extremely high dielectric

constants in ethyl formate, the values obtained being 5595—6820 and 4760—5300 respectively according to Philip's formula; calcium iodide shows a much smaller value (1540), and mercuric chloride one still smaller (490); thus, the dielectric constant of these salts diminishes with their capacity to dissociate.

The results obtained with solutions of salts in the strongly-ionising solvents acetone, acetylacetone, acetonitrile, and propionitrile confirm the conclusion that if the dielectric constant of the medium remains constant, the formation of ions increases the ionising tendency and the degree of electrolytic dissociation of the salt.

Certain anomalies exhibited by solutions are discussed in connexion with the increases produced in the dielectric constants, and hence in the ionising power of solvents by the dissolution of electrolytes. It is pointed out that this phenomenon must be taken into account in considering deviations from the law of mass action (Ostwald's dilution law), the rôle of neutral salts, the disagreement of salts dissolved in media having feeble ionising actions with the requirements of the theory of Arrhenius, etc., since by it, as well as by the other well-known factors, the degree of electrolytic dissociation is appreciably altered. T. H. P.

Behaviour of Carbon on Electrical Pulverisation. CARL THOMAE (*Zeitsch. Chem. Ind. Kolloide*, 1912, **11**, 268—269).—If a continuous current of 3—4 amperes at 220 volts is passed between retort-graphite electrodes immersed in pure water, the liquid remains quite transparent, but if a very small quantity of sodium hydroxide is added, a dark brown colloidal solution is obtained. The solution is stable, and may be boiled without change, but the addition of hydrochloric acid or sodium chloride gives rise to a black precipitate. Similar results were obtained with arc-lamp-carbon electrodes.

H. M. D.

Theory of the Electrical Synthesis of Colloids. CARL BENEDICKS (*Zeitsch. Chem. Ind. Kolloide*, 1912, **11**, 263—268).—A criticism of the views expressed by Kutscherov (A., 1912, ii, 1148) in connexion with the interpretation of the phenomena of electrical pulverisation. In opposition to the theory that the process is partly electrochemical in nature, the author maintains that the observations can be adequately explained on the assumption that the action is entirely thermal in character. H. M. D.

The Mobility of the Bromide Ion in Water. CARL DRUCKER, M. TARLE, and L. GOMEZ. (*Zeitsch. Elektrochem.*, 1913, **19**, 8—11).—The transport numbers of tribenzylmethylammonium bromide were determined at 20° by the usual method, employing a zinc anode and a platinum cathode. As a mean of many experiments, the value $n_a = 0{\cdot}775$ was obtained. To calculate the mobility of the bromine ion from this figure, the conductivity values at 18° were used (Drucker, A., 1912, ii, 732). The temperature-coefficient of the conductivity was determined, and found to be 0·022 between 18° and 25°, and from these data the mobility of the bromine ion is 65·5. This value is much

lower than that obtained by Kohlrausch (67·0), and affects the conductivity, at infinite dilution, of potassium bromide, making it 129·8 instead of 132·6, as extrapolated by Kohlrausch. Possible sources of error in the Kohlrausch value are discussed. It is shown, on calculating the degree of dissociation of potassium bromide from the new value, that it obeys the Ostwald dilution law up to 0·01*n*. The authors assert that, very probably, all strong electrolytes obey the dilution law up to this concentration. J. F. S.

Investigation of the Chemical Reactions Taking Place at the Cathode and Anode During the Electrolysis of Simple Salt Solutions. J. HAMILTON PATERSON (*Proc. Univ. Durham Phil. Soc.*, 1912, 4, 187—220).—The author describes a small electrolytic cell which allows of the microscopic examination of the deposits formed on the electrodes during electrolysis. Experiments made with simple salts (chlorides, nitrates, or sulphates) of a number of metals have shown that it is possible to obtain from cobalt, nickel iron, zinc, cadmium, manganese, and possibly lead salts, either the pure metal or the hydroxide, deposited on the cathode. In the case of cobalt, the film of hydroxide has a deep blue colour, but the moment the current stops it turns green; the composition of the green compound corresponds with the formula $Co(OH)_2,H_2O$.

The conditions of concentration and current density affecting the production of these substances has been noted, and it has been found that the dilution necessary to produce the hydroxide increases and the limit of current strength decreases as we proceed along the list of metals in the order given.

The hydroxide of the metal is not produced as a secondary reaction of the metal deposited on the cathode, but is a precipitate from the electrolyte in the cathode area. F. B.

The Constitution of Water and the Thermal Variation of its Magnetisation. AUGUSTE PICCARD (*Compt. rend.*, 1912, 155, 1497—1499. Compare this vol., ii, 17).—From a study of the change in the coefficient of magnetisation of water on solidification at 0°, and a comparison of the curves representing respectively the variation in density and magnetisation coefficient with respect to temperature, the author draws the conclusion that, in water at the ordinary temperature, there are two different substances in equilibrium. W. G.

New Thermo-regulator for Instantaneous Adjustment to any Given Temperature. R. FÄNDER (*Chem. Zeit.*, 1913, 37, 40).—The regulator bears much resemblance to that of Reichardt, but differs in having the adjusting screw on the lower half of the capillary tube, the upper half of the tube being graduated from 30° to 100°.

The regulator is set by immersing it in a water-bath at any temperature, and adjusting the mercury column so that the readings on the capillary tube correspond with those of a thermometer in the bath for about a minute. The mercury is then raised or lowered to the graduations corresponding with the desired temperature, and the regulator is ready for use. H. B. H.

The Expansion Coefficient of Graphite. ARTHUR L. DAY and ROBERT B. SOSMAN (*J. Ind. Eng. Chem.*, 1912, **4**, 490—492).—Contains sketches of the apparatus employed by the authors for measuring the expansion coefficient of graphites, whilst the results obtained are demonstrated in tables and curves. From the wide divergence in expansion coefficients obtained, the conclusion is drawn, contrary to the views of Le Chatelier and Wologdine (A., 1908, ii, 177) and in harmony with those of Arsem (A., 1912, ii, 250), that there must be some fundamental difference between the various forms of graphite. F. M. G. M.

Volume Changes of Amalgams. J. WÜRSCHMIDT (*Ber. Deut. physikal. Ges.*, 1912, **14**, 1065—1087).—The influence of temperature on the thermal expansion of a number of amalgams has been examined with the aid of a special type of dilatometer. The curves obtained by plotting the coefficient of expansion as a function of the temperature exhibit very sharp maxima at definite temperatures. In the case of the tin, lead, and cadmium amalgams, which according to Puschin (A., 1903, ii, 212) consist of solid solutions, these temperatures are identical with the melting points of the alloys. On the other hand, the zinc amalgams, which consist of mechanical mixtures of the components, exhibit the maximum expansion at temperatures between 50° and 70°, which are very much lower than the melting points of the alloys. In regard to the nature of the expansion temperature curve, sodium amalgam resembles the corresponding tin, lead, and cadmium alloys, but differs from these in that the volume changes with time when the temperature is kept constant. H. M. D.

Thermal Conductivity of the Metals and its Relation to Their Other Properties. STEFANO PAGLIANI (*Nuovo Cim.*, 1912, [vi], **4**, ii, 482—497).—The author gives a table showing the coefficients of thermal conductivity, the specific heats and the densities of a number of metals, the material being derived from published results of various workers. By a comparison of other published data, he shows that the metals can be arranged in a series, in which increased conductivity and reflecting power are associated with decrease of emissive power, and that these properties also fall within the regularity of the periodic law. R. V. S.

Theory of Specific Heats. MAX BORN and TH. VON KÁRMÁN (*Physikal. Zeitsch.*, 1913, **14**, 15—19).—Reference is made to a previous paper (*ibid.*, 1912, **13**, 297), in which the discrepancy between the observed specific heats of solid substances at low temperatures and the values calculated from Einstein's formula has been eliminated to a large extent by means of a modified specific heat formula. The theory on which this is based is compared with the theory advanced by Debye (A., 1912, ii, 1134), and it is shown that the approximation formula proposed by Debye for the calculation of the atomic heats of solid non-atomic substances can be deduced from the general formula given by the authors. In the case of anisotropic substances, the approxima-

tion formula is inapplicable, and the general formula referred to must be employed in the calculation of the specific heats. H. M. D.

Specific Heat of Certain Elements at Low Temperatures. TADEUSZ ESTREICHER and M. STANIEWSKI (*Bull. Acad. Sci. Cracow*, 1912, 834—841. Compare A., 1911, ii, 16).—The authors have determined the mean specific heats of bromine, iodine, sodium, potassium, and manganese over the temperature intervals $-190°$ to $18°$ and $-18°$ to $18°$. The mixture method was employed with water or toluene as calorimetric liquid. The specific heat of toluene at the ordinary temperature was found to be $0·4015 \pm 0·0003$ cal.

From the observations, the following average specific heat values are deduced: bromine 0·07016 ($-190°$ to $-18°$); iodine 0·0454 ($-191°$ to $-80°$), 0·04852 ($-80°$ to $17°$); sodium 0·2478 ($-191°$ to $-80°$), 0·2714 ($-80°$ to $17°$); potassium 0·1551 ($-191°$ to $-80°$), 0·1677 ($-80°$ to $18°$); manganese 0·08203 ($-188°$ to $-79·2°$), 0·10906 ($-79·2°$ to $15°$). These values agree in general very well with the numbers obtained by Koref (A., 1911, ii, 964). H. M. D.

Measurement of the Specific Heat of Solid Substances at High Temperatures. MARCELLO VON PIRANI (*Ber. Deut. physikal. Ges.*, 1912, **14**, 1037—1054).—Three methods are described by means of which the true specific heats of different metals have been determined at high temperatures.

In the first method, the apparatus consists of an insulated electrically heated tube furnace, the temperature of which is adjusted to that at which the specific heat measurement is to be made. Inside this is a much smaller tube furnace, the temperature of which is measured by means of a thermo-couple. If a quantity of electrical energy, measured by a watt-meter, is passed through the coils of the inner tube during time t, its temperature will be raised by a small amount, $\Delta\theta$, which is measured by the couple.

Under exactly similar conditions, the energy required to produce the same rise of temperature when the inner tube is filled with the substance under examination is determined. From the data thus obtained the specific heat of the substance may be calculated.

The two other methods are somewhat similar and depend on the fact that when a conducting substance is heated electrically to a high temperature in a vacuum, the electrical energy communicated is lost almost entirely in the form of radiant energy. If the supply of electrical energy is increased for a short interval of time, the temperature will increase to an extent determined by the specific heat of the substance and by the increased amount of radiation. Since the latter case can be determined by experiments in the stationary condition it is obvious that the measurement of the extra electrical energy and of the consequent rise in temperature will afford a means of obtaining the specific heats of the metals at very high temperatures. The specific heats of tantalum and tungsten have been measured in this way at temperatures between about 350° and 1400°. Data are also recorded for iron between 110° and 970°. The curve showing the relationship between the specific heat of iron and the temperature is

very irregular, showing a very decided maximum at about 7 0°, and a sharp minimum at about 790°. No evidence of this minimum has been obtained in previous high-temperature measurements.

H. M. D.

Measurement of Specific Heats of Solid Substances at High Temperatures. ALFRED MAGNUS (*Physikal. Zeitsch.*, 1913, **14**, 5—10).—The measurements were made with a form of calorimeter similar to that used by Nernst, Koref, and Lindemann (A., 1910, ii, 263), but in order to diminish the influence of the heat losses incurred in the introduction of the heated substances into the calorimeter, its capacity was increased about fifty times. The block of copper weighing 22 kilograms was provided with a conical shaped central cavity for the reception of the heated substance which was contained in a conical silver tube fitted with a stopper. The rise in temperature of the copper calorimeter was measured by means of a battery of 50 iron constantan thermocouples, half the junctions being situated in deep holes in the block of copper and the other half in the water-bath surrounding the Dewar vessel containing the copper block. Data representing the mean specific heats between the room temperature and 100°, 270°, 550°, and 750° have been obtained, the substances examined being quartz, amorphous silica, magnesium oxide, calcium oxide, zinc oxide, lead oxide, sodium and potassium chlorides, sodium and potassium bromides, and calcium carbonate.

The molecular heats appear to be in satisfactory agreement with those arrived at by recent workers at lower temperatures, continuous curves being obtained when the available molecular heats are plotted as a function of the temperature. The values for sodium chloride, potassium chloride, and potassium bromide are also in agreement with those calculated from the equation $C_p = C_v + ACp^2T$, in which $A = 2{\cdot}7$, 2·7, and $3{\cdot}3 \times 10^{-5}$ for the three salts respectively.

H. M. D.

Investigations on Specific Heat. VI. Calculation of Atomic Heats. WALTHER NERNST and F. A. LINDEMANN (*Sitzungsber. K. Akad. Wiss. Berlin*, 1912, 1160—1171. Compare A., 1911, ii, 464, 964, 1059).—On the assumption that a vibrating atom gives rise to a continuous spectrum corresponding with a continuous series of component vibrations, Debye (A., 1912, ii, 1134) has obtained a modified Einstein formula for the specific heat of a monatomic element. This has been applied in the calculation of the atomic heats of aluminium, copper, silver, diamond, potassium and sodium chloride at different temperatures, and the results are compared with the experimental data. This comparison shows that the new formula agrees better with experiment than either of the older formulæ of Einstein and of Nernst and Lindemann.

The available specific heat data indicate that two groups of elements may be distinguished. In the one group, the variation of the specific heat with the temperature can be satisfactorily represented by means of Debye's formula, whilst the substances in the other group are characterised by an appreciably less rapid fall in the specific heat with falling temperature than is required by the formula. Crystalline

elements belonging to the first group are probably monatomic, whilst those of the second group are probably polyatomic. The fact that potassium and sodium chloride behave like monatomic substances is attributed to the approximate equality of the vibration frequencies of the component atoms. H. M. D.

Investigations on Specific Heat. VII. Calculation of Chemical Affinities. WALTHER NERNST (*Sitzungsber. K. Akad. Wiss. Berlin*, 1912, 1172—1176).—The effect of the substitution of Debye's formula for the specific heat in place of that used by Nernst and Lindemann is considered in reference to the application of the author's heat theorem to the calculation of chemical affinities. Tables are given which indicate the magnitude of the correction factors for a series of vibration frequencies. H. M. D.

The Polymerisation of Substances at Low Temperatures. JACQUES DUCLAUX (*Compt. rend.*, 1912, **155**, 1509—1511. Compare this vol., ii, 18).—A mathematical paper in which the author shows that the value of $\int_{T_0}^{T_b} \frac{dQ}{T}$, where dQ is the quantity of heat necessary at each temperature, T, to produce the modification studied, T_0 the absolute zero, and T_b is the absolute boiling point of the substance, is a constant for all substances and equal to 42 or twice the value of the constant in the Pictet-Trouton law, obtained by dividing the molecular heat of vaporisation by the temperature of vaporisation. The values are given as calculated for ten substances, the specific heat of which has been completely studied. W. G.

The Liquid Condition (Correction). WILLIAM C. McC. LEWIS (*Zeitsch. physikal. Chem.*, 1913, **81**, 626—628. Compare A., 1911, ii, 855).—The author shows that the expression $L = -T\alpha/\rho\beta$ has only an empirical meaning, and he develops from thermodynamical principles the expression $l = -T\alpha/\beta$, in which l is the latent heat of expansion, that is, the amount of heat which must be added to a system to cause an increase in volume of one unit whilst the temperature is kept constant, α is the coefficient of expansion, and β the compressibility. The expression only holds for homogeneous systems, that is, either entirely liquid or entirely gaseous. The author has calculated the values of l for a number of liquids, and finds that its value is of the same order as the latent heat of vaporisation, from which he draws the conclusion that the region of molecular attraction must be of the same order as the mean distance of the molecules from one another, that is, about 10^{-8} cm. J. F. S.

Simple Method for Determining the Melting Point of the Less Fusible Substances. ERN. HAVAS (*Chem. Zeit.*, 1912, **36**, 1438).—The author recommends a modification of the mercury method, in which the substance, of which the melting point is to be determined, is placed in small quantity on the surface of mercury,

which is gradually heated. The mercury is replaced by an alloy of 2 parts of tin and 1 of lead (ordinary soft solder), and melting points up to 450° can readily be determined. T. S. P.

Melting Point of Fire Bricks. C. W. KANOLT (*Tech. Papers, Bur. Stands.*, 1912, No. 10, 1—17).—The melting point was taken as the lowest temperature at which a small piece of the brick could be distinctly seen to flow. An electric vacuum furnace was used, and the melting points of fifty-four samples of fire brick, including fire-clay, bauxite, silica, magnesia, and chromite bricks were determined, as well as the melting points of the following materials important in the manufacture of fire brick: kaolin, 1740°; pure alumina, 2010°; bauxite, 1820°; bauxite clay, 1795; chromite, 2180°. T. S. P.

Pressure-temperature Diagrams for *p*-Azoxyanisole and *a*-Naphthylamine. NICOLAI A. PUSCHIN and I. V. GREBENSCHTSCHIKOV (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1728—1736).—These diagrams have been investigated by the manometric method.

Up to pressures of 1088 kilograms per sq. cm., the melting point of *p*-azoxyanisole is a linear function of the pressure, and is expressed by the formula $t_p = 135{\cdot}9° + 0{\cdot}03949p$. Hulett, whose measurements were confined to the region 1—300 atmospheres, found the value 0·0486 for the pressure-coefficient of the melting point (A., 1899, ii, 468), this differing considerably from the authors' value, 0·0395. A possible bending of the melting-point curve at higher pressures, such as occurs with the great majority of other substances, has not been investigated. The transition point from the crystalline state to the liquid-crystalline condition varies linearly with the pressure as far as 2000 kilograms per sq. cm., and is expressed by $t_p = 117{\cdot}3° + 0{\cdot}02560p$ (Hulett, *loc. cit.*, found $dT_2/dp = 0{\cdot}0320$). Increase of the pressure from 2000 to 2645 kilograms per sq. cm. is accompanied by increasing divergence of the transition point from the rectilinear curve, this behaviour being similar to that of the melting points of substances crystallising with diminution of volume.

The considerable difference between the pressure-coefficients of the melting and transition points of *p*-azoxyanisole and the rectilinear character of the curve connecting melting point and pressure up to 1088 kilograms per sq. cm. are regarded as contradictory to Ostwald's assertion (*Lehrbuch der allgemeinen Chemie*, 2nd Edition, II, 2, 392) that, with liquid-crystalline substances, small values for the change of volume on melting and for the heat of crystallisation readily become zero at pressures slightly in excess of that of the atmosphere; or, in other words, that with liquid crystals, the critical point for liquid-to-crystals can be realised experimentally.

For pressures up to 3000 kilograms per sq. cm., the melting point of *a*-naphthylamine is nearly a linear function of the pressure, and is given by: $t_p = 48{\cdot}5° + 0{\cdot}01723p—0{\cdot}000000555p^2$. The value, 0·0168, for dT/dp from 1 to 500 kilograms per sq. cm. differs considerably from the value, 0·0200, found by Hulett (*loc. cit.*). The authors' results do not agree with those of Damien (*Compt. rend.*, 1891, **112**, 785), which would indicate a maximum for the temperature-pressure

curve of α-naphthylamine at a pressure of 83 atmospheres. The equation given above shows that a maximum may be expected at about 182° (15500 kilograms per sq. cm.), so that at higher temperatures and pressures crystalline α-naphthylamine would be incapable of existence. T. H. P.

Thermal Analysis. T. VAN DER LINDEN (*J. Chim. phys.*, 1912, 10, 454—466).—The paper gives an account of the theory of the method largely used by Holleman and his pupils, of estimating the composition of mixtures from freezing-point data alone.

In a homogeneous liquid with n components, which form no compounds or mixed crystals at atmospheric pressure, the total weight of the system being 100, the degrees of freedom $=n$, of which $(n-1)$ are variable concentrations and the remaining one is the temperature. On cooling the system, one of the n constituents crystallises out at the first freezing point, and as there are now two phases, the degrees of freedom are reduced to $(n-1)$. The first solidifying temperature is therefore fixed by the proportions of the $(n-1)$ constituents remaining in the melt. Similarly the second solidifying point is a function of the $(n-2)$ constituents remaining, and so on; thus the $(n-1)$th freezing point is independent of the proportions of the $(n-2)$ constituents already solidified, but dependent on the ratio a of the two constituents remaining in the melt, that is, the $(n-1)$th freezing point $=f(a)$. This function is represented by a curve similar to the ordinary binary freezing-point curve given by the two constituents in question. Hence the observation of the $(n-1)$th freezing point enables the ratio a of the remaining constituents to be estimated.

Any pair of constituents can be arranged to crystallise out last by the addition of suitable amounts of certain of them, and thus by the observation of the $(n-1)$th freezing points of $(n-1)$ solutions, the composition of the original mixture of n substances is arrived at.

Binary mixtures $(n=2)$ are therefore analysed by one freezing-point measurement. Ternary mixtures require two estimations of second freezing points, quaternary mixtures three estimations of third freezing points, and so on. The observation of third and higher freezing points is very difficult, owing to the large amount of solid matter already present. With ternary mixtures, it is necessary to obtain two complete second freezing-point curves with mixtures of known composition. Each of these curves represents the binary freezing-point diagram of two constituents saturated with the third.

In some cases simplified methods are possible. For instance, when the freezing-point diagram of a ternary mixture has the "ideal" form the three binary curves are superposable. The influence of a quantity of O on the solidifying point of P being the same as the influence of an equimolecular quantity of M, is also the same as that of an equivalent quantity of a mixture of O and M mixed. In this ideal case the first freezing points of two solutions depositing P and O respectively, say, are sufficient to establish the compositions of the two solutions. This is tantamount to reducing a ternary mixture to a binary one.

The method most used is to combine the two principles and establish

the composition of the solution by one first and one second freezing point measured successively. Similar simplifications are sometimes possible in the case of quaternary mixtures, particularly where some of the four constituents are isomeric substances. R. J. C.

Relations of Isomorphism in Organometallic Compounds. III. Derivatives of Bivalent Metalloids. PAUL PASCAL (*Bull. Soc. chim.*, 1912, [iv], 11, 1030—1037. Compare A., 1912, i, 739).—The author has determined the freezing-point curves of binary mixtures of phenyl ether, phenyl sulphide, phenyl selenide, and phenyl telluride. These substances were each purified by fractional crystallisation, and were found to have the following melting points: 26°, −21·5°, 2·5°, and 4·2° respectively.

Phenyl sulphide and phenyl selenide give a continuous series of mixed crystals, the freezing-point curve passing through a minimum at −26·7°, corresponding with the mixture containing 5% of the selenide. Similar results are obtained with mixtures of the selenide and the telluride, the minimum point being −4·2°, corresponding with the mixture containing 80·4% of the selenide, and with mixtures of the sulphide and telluride, the mixture containing 83·42% of the sulphide having the minimum freezing point, −30·7°.

Phenyl ether and phenyl sulphide do not form a continuous series of mixed crystals, the freezing-point curve exhibiting a eutectic point at −27·7°, corresponding with a mixture containing 13·3% of the ether. The two series of mixed crystals in equilibrium at the eutectic point contain respectively 4·5 and 53% of phenyl ether.

The above results agree with the classification of sulphur, selenium, and tellurium, apart from oxygen. T. S. P.

Internal Pressure and Latent Heat of Liquids. WILLIAM C. McC. LEWIS (*Phil. Mag.*, 1913, [vi], 25, 61—65. Compare A., 1912, ii, 136).—For the internal pressure of a liquid, the author has obtained previously the expression $K - l = TdK/dT$, where K is the internal pressure and l the latent heat of vaporisation of 1 c.c. According to Davies (A., 1912, ii, 902) the temperature-coefficient of the internal pressure dK/KdT is equal to the coefficient of expansion a, and by substituting in the above equation, it is found that $K = l/(1 + aT)$, which is identical with one of the results obtained by Davies.

If l is considered to represent the latent heat of expansion of the liquid (the heat absorption corresponding with isothermal expansion equal to 1 c.c.), it is deduced that $l = -Ta/\beta$, where a is the coefficient of thermal expansion and β the compressibility of the liquid. For non-associated liquids, the latent heat of expansion calculated from this equation is of the same order of magnitude as the latent heat of vaporisation. For associated liquids the differences are much greater.

Values representing the internal pressure are calculated for a number of liquids from the equation $K = l/(1 + aT)$ on the assumption that l is the latent heat of expansion. The numbers so obtained are approximately double those recorded previously. H. M. D.

Guldberg's Law and the Corresponding States. ANATOLE LEDUC (*Compt. rend.*, 1913. 156, 65—66).—A criticism of Boutaric's deductions (this vol., ii, 21), in which the author suggests a modification of Guldberg's law to read: the boiling points of substances under equally reduced pressures are corresponding temperatures. W. G.

Composition and Pressure of the Vapour of Solutions. M. S. VREVSKI (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1739—1747).—The results previously obtained (A., 1912, ii, 1139) with aqueous solutions of methyl, ethyl, and propyl alcohols containing from 20—30% to 100% of alcohol are in complete accord with the relation established by Duhem and Margules between the partial pressures of the vapours and the compositions of the solutions: $d\,ln\,p_1/d\,ln\,x = d\,ln\,p_2/d\,ln(1-x)$. The applicability of this relation to the solutions containing less than 20—30% of alcohol remains undecided, owing to the lack of detailed experimental data.

The author discusses the numerical results, from which he draws the following conclusions: (1) The displacement produced in the equilibrium between solutions of two liquids and their saturated vapours, with constant volume of the system, by change of temperature, is subject to Le Chatelier and van't Hoff's law, which may be formulated as follows: In all cases of equilibrium between phases of variable composition, heating of the system under constant volume leads, in the phase formed with absorption of heat, to increase of that component the transformation of which absorbs the greatest quantity of heat. (2) On the basis of Kirchhoff's theory, the change in the composition of the vapour under the influence of temperature may be regarded as the result of the combined action of two factors, the physico-mechanical and the physico-chemical. In every system formed with either development or absorption of heat, there exists a region of parallel, and one of opposed, action of the two factors. The limits of these regions are the solutions corresponding with the maximum or minimum heat of formation. (3) The direction in which the change in composition of the vapour proceeds under the influence of temperature remains the same for all concentrations of the solution, if, in the region where the actions of the two factors are opposed, the magnitude of the physico-mechanical factor always predominates. (4) On change of temperature of solutions formed without heat-effect, the variation in the composition of the vapour takes place under the influence of a single physico-mechanical factor and follows the same law as does change in the composition of the vapour of mechanical mixtures; (5) with change of temperature of a solution which possesses a vapour-pressure curve showing a maximum, the composition of the vapour and that of the mixture with constant boiling point change in one and the same direction. (6) If, however, the vapour-pressure curve shows a minimum, the compositions of the vapour and that of the mixture with constant boiling point change in opposite directions.

T. H. P.

Association of Ethyl Ether and Chloroform in the Gaseous State. FRIEDRICH DOLEZALEK and ALFRED SCHULZE (*Ber. Deut. physikal. Ges.*, 1912, 14, 1091—1096).—It is shown that the mixing of the

vapours of ethyl ether and chloroform at 80° and atmospheric pressure is accompanied by contraction. When the volumes of the two vapours are equal, the data obtained correspond with a reduction of pressure of 4·8 mm. of mercury when the volume is kept constant. It is shown that the observed contraction is not due to deviations of the vapours from the gas laws, and the change in volume is consequently attributed to the formation of a compound. The magnitude of the volume change indicates that an equimolar mixture of ethyl ether and chloroform at 80° and atmospheric pressure contains 0·64 mol. % of the compound. By applying the law of mass action it is seen that the molecular proportion of the compound in the vapour mixture will increase almost in the same ratio as the total pressure. Similarly it is shown that the saturated vapour in equilibrium with an equimolar liquid mixture of the two substances at 80° should contain 1·4 mol. % of the compound. Since the liquid phase contains 14·6 mols. % of the compound it follows from the vapour pressure law for binary mixtures that the vapour pressure of the compound at 80° should be about 0·26 atmosphere. H. M. D.

Isotherms of Diatomic Gases and of their Binary Mixtures. XI. Determinations with the Volumenometer of the Compressibility of Gases under Small Pressures and at Low Temperatures. W. J. DE HAAS (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 299—306. Compare A., 1912, ii, 1138).—The question of the distribution of pressure between the volumenometer and the piezometer used in the measurements of the compressibility of gases at low temperatures is discussed and a formula is deduced for calculating the change in the difference of pressure between the two communicating vessels as a function of the time. This formula involves the dimensions of the apparatus and the distribution of temperature along the connecting capillary. The curve corresponding with the formula is in satisfactory agreement with the actual observations of the change in the pressure difference with time. H. M. D.

The Critical Point. ETTORE CARDOSO (*J. Chim. phys.*, 1912, **10**, 470—496. Compare A., 1911, ii, 854).—In order to evaluate the compression coefficients of gases to 1 part in 10,000 for atomic-weight calculations, the critical temperatures and pressures must be known within the limits 0·1° and 0·1 atm. respectively. The temperature and pressure ought to be observed at the same time with the same specimen of gas, so that any error due to impurity may affect both values equally. Although various investigators have given critical pressures to within 0·01 atm., the author considers that they were not justified, since, in general, a variation of 0·001° in the temperature corresponds with 0·01 atm. in the pressure. At the same time it is admitted that observations of pressure or temperature made separately as by the Natterer tube may be more accurate than the author's as far as the actual specimen handled is concerned.

The paper describes the methods employed at Geneva in critical constant investigations. The gases were purified by fractional distillation under vacuum (compare Briner and Cardoso, A., 1909, ii,

124), alternating with passage through suitable absorbents maintained slightly above the boiling point of the gas. A sample of gas was not considered sufficiently purified until it could be liquefied at pressures constant to within 0·05 atm. at two different temperatures, one of which was near the critical point.

A manometer of the barometer type was used, consisting of a 1 mm. capillary tube with suitable bulbs in the upper and lower parts, surrounded with a glycerol-water jacket maintained at a constant temperature. It was filled with atmospheric nitrogen the compressibility of which is known from Amagat's accurate data. The manometer was read to 0·1 mm., corresponding with not more than 0·02 atm. pressure. Owing to the uncertainty of the capillary correction in a 1 mm. tube, closer reading would have been useless, and the use of a finer capillary would have introduced unknown errors due to diffraction and the retention of small gas bubbles below the meniscus. The different manometers agreed to within 0·1 atm. at least, and the accuracy of the methods was confirmed by the fact that concordant critical data were obtained with different manometers and different samples of gas, often at considerable intervals of time.

The working tube was provided with a small piece of soft iron wire constituting the armature of an electromagnetic agitator of the Kuenen type. On approaching the critical temperature, the meniscus disappears and the so-called "critical opalescence" is seen. The point of maximum opalescence is held by some to be the critical temperature (compare Nernst, "Theoretical Chemistry"). The opalescence usually extends over a range of 0·03°, but by means of the Kuenen agitator the range could be extended to 0·3° to 0·4°. The opalescence is therefore due to the formation of an emulsion of gas and liquid, which, being of nearly equal density, do not separate. The true critical point is taken as the point at which the opalescence disappears. This could be estimated to within $\pm 0{\cdot}05°$, and is about 0·15° higher than the point of maximum opalescence. It is possible that an invisible opalescence persists at an even higher temperature, since in experiments made without the stirrer a slight diffraction could still be observed at the spot where the meniscus had been.

Critical data to the nearest 0·05 atm. and 0·05° are tabulated for hydrogen chloride, ammonia, carbon dioxide, sulphur dioxide, nitrous oxide, hydrogen sulphide, acetylene, ethylene, ethane, and cyanogen.

R. J. C.

Critical Constants of Ethane, Carbon Dioxide, and Sulphur Dioxide. ETTORE CARDOSO and R. BELL (*J. Chim. phys.*, 1912, 10, 497—503).—Ethane prepared from ethyl iodide by the Grignard reaction contained air and ethyl iodide and ether vapours as well as other impurities which were removed by suitable absorbents followed by fractional distillation. Ethane prepared by Frankland and Kolbe's method, by cautious addition of propionitrile to metallic sodium in a vacuum, was readily purified by absorbents only. The purified ethane, having m. p. $-172{\cdot}5°$ and b. p. $-84{\cdot}1°$, possessed an agreeable

ethereal odour. Its critical constants were $t_c = +32{\cdot}10^\circ \pm 0{\cdot}10^\circ$ and $p_c = 48{\cdot}85 \pm 0{\cdot}10$ atm.

Carbon dioxide, prepared by heating sodium hydrogen carbonate, was washed and fractionated ten times. Its critical constants were $t_c = +31{\cdot}00^\circ \pm 0{\cdot}10^\circ$ and $p_c = 72{\cdot}85 \pm 0{\cdot}10$ atm. The critical opalescence was observed as low as $30{\cdot}60^\circ$, but the point of maximum opalescence could not be decided.

Commercial sulphur dioxide was washed and purified by ten distillations. Its critical constants were $t_c = +157{\cdot}15^\circ \pm 0{\cdot}10^\circ$ and $p_c = 77{\cdot}65 \pm 0{\cdot}10$ atm. The point of maximum opalescence could not be observed owing to an opalescent deposit on the glass tube. This appeared to result from the action of light and heat on the sulphur dioxide, but it was ascertained that even 300 hours' heating did not alter the critical constants of the gas. R. J. C.

Critical Constants of Ethylene, Nitrous Oxide, and Hydrogen Sulphide. ETTORE CARDOSO and E. ARNI (*J. Chim. phys.*, 1912, **10**, 504—508).—Ethylene prepared by the action of sulphuric acid on ethyl alcohol and purified by washing and fractional distillation had m. p. $-169{\cdot}00^\circ$ and b. p. $-104{\cdot}3^\circ$. The critical constants were found to be $t_c = +9{\cdot}50^\circ \pm 0{\cdot}10^\circ$ and $p_c = 50{\cdot}65 \pm 0{\cdot}10$ atm. The critical opalescence extended from $+9{\cdot}05^\circ$ to $9{\cdot}50^\circ$.

Nitrous oxide was prepared by the action of saturated aqueous sodium nitrite on hydroxylamine hydrochloride in a vacuum. When washed and fractionated ten times it gave a perfectly colourless solid. The critical constants were $t_c = +36{\cdot}50^\circ \pm 0{\cdot}10^\circ$ and $p_c = 71{\cdot}65 \pm 0{\cdot}10$ atm. The critical opalescence extended from $36{\cdot}0^\circ$ to $36{\cdot}5^\circ$, and had its maximum at about $36{\cdot}3^\circ$.

Hydrogen sulphide prepared by the action of hydrochloric acid on purified precipitated iron sulphide in a vacuum was washed in water containing iron sulphide in suspension, and then dried and fractionated fourteen times in a vacuum. The purified gas of f. p. -83° and b. p. $-60{\cdot}2^\circ$ was without action on clean mercury, and was perfectly stable at the critical point. The critical constants were $t_c = +100{\cdot}40^\circ \pm 0{\cdot}10^\circ$ and $p_c = 89{\cdot}05 \pm 0{\cdot}10$ atm. R. J. C.

Critical Constants of Ammonia. ETTORE CARDOSO and (Mlle.) A. GILTAY (*J. Chim. phys.*, 1912, **10**, 514—516).—Ammonia was prepared by heating purified ammonium chloride with excess of calcined marble. It was dried by barium oxide and sodium wire, and distilled four times through the same reagents. Four further fractional distillations served to remove traces of air and hydrogen. The critical constants were $t_c = +132{\cdot}90^\circ \pm 0{\cdot}10^\circ$ and $p_c = 112{\cdot}30 \pm 0{\cdot}10$ atm.

The critical opalescence was observed from $132{\cdot}6^\circ$ to $132{\cdot}9^\circ$ with a maximum at about $132{\cdot}75^\circ$. R. J. C.

Critical Constants of Hydrogen Chloride. ETTORE CARDOSO and A. F. O. GERMANN (*J. Chim. phys.*, 1912, **10**, 517—519).—Purified sodium chloride was decomposed with pure concentrated sulphuric acid in a vacuum, the apparatus being constructed with fused joints throughout. The hydrogen chloride was dried with sulphuric

acid and phosphoric oxide, and fractionally distilled twelve times in all, first through phosphoric oxide and afterwards without it. The solidified hydrogen chloride was absolutely free from the pink tint usually attributed to a compound of phosphorus or to nitric oxide. It had m. p. $-111{\cdot}4^{\circ}$, and b. p. $-83{\cdot}1^{\circ}$. The critical constants were $t_c = +51{\cdot}40^{\circ} \pm 0{\cdot}10^{\circ}$ and $p_c = 81{\cdot}55 \pm 0{\cdot}15$ atm. R. J. C.

Free Energy of Chemical Substances. Introduction. GILBERT N. LEWIS (*J. Amer. Chem. Soc.*, 1913, **35**, 1—30).—This paper is introductory to a series in which the free energy of chemical substances will be systematically studied. A detailed account is given of the general methods used in free energy calculations, including the consideration of the notation and fundamental units, the laws of energy, the change of energy with pressure, the relation between activity and fugacity and the free energy, free energy and the equilibrium constant, free energy and *E.M.F.*, and the influence of temperature on the free energy change. E. G.

Tempering [of Metals] without Deformation. MAURICE HANRIOT (*Compt. rend.*, 1912, **155**, 1502—1504. Compare A., 1912, ii, 1137).—Cubes of a number of metals and alloys were submitted to high pressure when immersed in vaselin, and it was found that, whilst the cubes were not deformed and the internal structure, as examined micrographically for brass, was unaltered, the substances had undergone considerable tempering, as was shown by measuring their hardness, elongation, and breaking strain before and after the compression.
W. G.

The Rectilinear Diameter for Argon. ÉMILE MATHIAS, H. KAMERLINGH ONNES, and C. A. CROMMELIN (*Proc. K. Akad. Wetensch.*, 1912, **15**, 667—673).—A preliminary account is given of the apparatus and mode of procedure adopted in the determination of the densities of liquid and saturated vapour at a series of different temperatures. The mode of calculating the requisite data from the experimental observations is described, but no results are communicated. H. M. D.

Specific Gravities of Saturated Aqueous Solutions of Various Salts at Different Temperatures. N. A. TSCHERNAJ (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1565—1576).—The author has determined the specific gravities (weights of 1 c.c.) of saturated solutions of a number of salts at intervals of 10° from 0° to 70° (or 90°). These salts may be divided into two groups: (1) those forming saturated solutions which increase in specific gravity with rise of temperature and with increase in the salt-content: potassium chloride, nitrate and sulphate, sodium and barium nitrates; (2) those with which the reverse takes place: sodium chloride.

These salts also show different behaviour with reference to the variation with temperature of the quotient dP/dV, where dP represents the increase per 10° of the amount of salt (grams) dissolved by 100 grams of water, and dV the corresponding increase in volume (c.c.) of

the solution. With rise of temperature from 0° to 70°, this quotient shows a continuous increase from 0·12 to 0·5 with sodium chloride, remains almost constant with potassium chloride (1·69), sodium nitrate (1·9), potassium nitrate (2·1), and potassium sulphate (2·2), and continually diminishes from about 5 to 1·6 with barium nitrate.

T. H. P.

Compressibility of Gases. GEORGES BAUME and E. WOURTZEL (*J. Chim. phys.*, 1912, **10**, 520—522).—The relation of pressure to volume in sulphur dioxide, methyl ether, and chloroform vapour has been represented by the equation $pv = 1 + a(1 - L/L_1)$, where L is the density at pressure p, and L_1 the weight of a normal litre of the gas considered (compare Baume, A., 1908, ii, 372). The deviation coefficient a is numerically the same as Berthelot's deviation coefficient $A^1{}_0$ in the case of permanent gases, but with easily liquefiable gases $A^1{}_0 = a/(1 + a)$. This equation may be reduced to $A^1{}_0 = a - a^2$ when a^3 is negligible.

R. J. C.

Adsorption and Saturated Surfaces. ROBERT MARC (*Zeitsch. physikal. Chem.*, 1913, **81**, 641—694 Compare Schmidt, A., 1910, ii, 1041; 1911, ii, 969).—The adsorption of a large number of substances on the crystal surfaces of barium sulphate, barium carbonate, rhombohedral calcium carbonate, strontium carbonate, lead carbonate, and lead sulphate was investigated by measuring the change in the refractive indices of the solution of many substances by means of an interferometer. It was shown that colloidal substances are easily adsorbed on crystal surfaces, whereas crystalline substances are only adsorbed to a very slight extent. Crystalline substances adsorb more if they are capable of forming isomorphous or mixed crystals with the adsorbing substances; thus potassium nitrate is adsorbed by barium carbonate, whilst sodium nitrate is not; on the other hand, sodium nitrate is adsorbed by rhombohedral calcium carbonate, whilst potassium nitrate is not. The adsorption isothermals can be divided into three types: (1) Those in which a stronger bend is present than is demanded by the exponential formula, and which reach the saturation value continuously. (2) Those which agree at all points with the exponential formula. In this case, even though the measurements were made very close together, it was impossible to determine whether there was a break in the curve or not. (3) Those curves of substances which at low concentrations have a great tendency to be adsorbed, and give a very steep curve and reach the saturation point at very low concentrations. The adsorbed substance is the factor which conditions the type of curve in any case. It is shown that when the saturation values for a series of substances with one given adsorbing medium have a given ratio, then the ratio of the saturation values for those substances with another adsorbing medium will be the same. The formulæ of Schmidt and Arrhenius are discussed, and it is shown that the Arrhenius formula holds well for substances giving curves of the first type, but for curves of the second type it holds only over a portion of the curve and ceases to hold some distance before the saturation value is reached, whilst for curves of the third type it

does not hold at all. It is, however, shown that the Arrhenius formula probably represents ideal conditions which are only existent when molecular compounds are not formed in the adsorption layer. J. F. S.

Adsorption. VII. Chemical Hysteresis of Starches. Adam V. Rakovski (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1722—1728).—The investigations here described are a continuation of those published in papers I. and II. (A., 1911, ii, 470), and deal with curves intermediate to those of hydration and dehydration of Bermuda arrowroot and rice starches. These intermediate curves are found to be virtually reversible, but not throughout their whole length. Detailed study of such curves would, however, be possible only with colloids showing a considerably greater separation of the curves of hydration and dehydration than is the case with starches.

The presence of about 1% of mercuric chloride in potato starch exerts no appreciable influence on the course of either hydration or dehydration. T. H. P.

Relation between the Conductivity of Acids and their Absorption by Hide. André Brochet (*Compt. rend.*, 1912, **155**, 1614—1617).—Measurements have been made of the amount of acid absorbed by shaking 10 grams of hide powder for four hours with 200 c.c. of an $N/10$-solution of the acid concerned, containing 100 grams of sodium chloride per litre. Measurements have been made with three classes of acids varying in conductivity, namely: (1) good conductors, (2) moderate conductors, (3) poor conductors. In class (1) inorganic acids and organic acids of the type of trichloroacetic acid were examined. The absorption of acids by the hide is a general phenomenon, and is the result of a chemical combination, the amount of acid absorbed being proportional to the chemical equivalent of the acid. The fraction of the gram-equivalent of acid absorbed by one kilo. of dry hide, whilst constant for each class, does show a slight diminution with diminution in conductivity; but while the absorption diminishes only in the ratio 3 : 2, the conductivity diminishes as 100 : 1. W. G.

Some Properties of the Thiocyanate Ion. Herbert Freundlich and A. N. Seal (*Zeitsch. Chem. Ind. Kolloide*, 1912, **11**, 257—263).—The lyotropic properties of solutions of potassium chloride and potassium thiocyanate have been compared in a quantitative manner with the object of determining the position of the thiocyanate ion in the lyotropic series. The properties examined were the following: the influence of the electrolyte on the solubility of benzoic acid, the effect on the surface tension, the absorbability by animal charcoal, the retarding influence on the rate of ester saponification, and the effect on the rate of increase of the viscosity of gelatin solutions. The observations show that the lyotropic influence of the thiocyanate ion is distinctly smaller than that of the chloride ion, and that its position in the series of anions is close to the iodide end in the

series: fluoride, sulphate, phosphate, chloride, nitrate, bromide, iodide. In this series the lyotropic influence diminishes from left to right.

H. M. D.

Surface Tension of Protein Solutions. II. FILIPPO BOTTAZZI and E. D'AGOSTINO (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 561—572. Compare Bottazzi, A., 1912, ii, 1042).—The paper records in tables and curves the results of further experiments with Traube's stalagmometer on solutions of serum-albumin to which various quantities of hydrochloric acid, sodium hydroxide, or sodium chloride were added. From the experiments it appears that the value n (number of drops) depends entirely on the undissociated molecules of the protein or of its salts, for an increase in the concentration of these molecules increases n (that is, the surface tension is lowered). In order to obtain the maximum dissociation of the albuminate, it is necessary to add more acid or alkali in weak solutions than in stronger ones. This indicates the presence of salts of a weak base (or acid), and for the same reason the maximum dissociation will be reached only when more than the equivalent amount of sodium hydroxide or of hydrochloric acid is added. From the amounts thus added it appears that the molecular weight of the albumin should be somewhat above 1000. From the curves it also appears that the albumin chloride is much less dissociated than the sodium albuminate at the same dilution. The addition of sodium chloride diminishes the dissociation of both the albumin salts, but its influence is much greater on the chloride than on the albuminate. The addition of sodium chloride also diminishes the dissociation of the free albumin, probably owing to the formation of undissociated secondary products.

R. V. S.

Molecular Complexity in the Liquid State. WILLIAM E. S. TURNER (*J. Chim. phys.*, 1912, **10**, 467—469. Compare Guye, A., 1911, ii, 1067).—The author agrees with Guye that liquids which give a high value of Ramsay and Shields' constant are not necessarily dissociated, since error may arise from abnormality in the surface film of the liquid, but cannot agree that in his experiments, criticised by Guye, the surface films of diphenylamine and phenylurethane were oxidised. The value obtained with diphenylamine was in accord with that obtained by Dutoit and Friedrich (A., 1900, ii, 194).

R. J. C.

Mode of Ionisation of Sulphuric Acid in Dilute Aqueous Solutions. JOSEPH A. MULLER (*Compt. rend.*, 1912, **155**, 1499—1502).—From a series of determinations of the coefficients of ionisation and heat of dilution of aqueous solutions of sulphuric acid, the author deduces that, in dilute aqueous solutions, sulphuric acid is ionised into the two ions SO_4H' and $H^{\cdot}$, and that this ionisation is accompanied by development of heat within the limits of the experimental temperatures (14—38°).

W. G.

Application of the Theory of Chemical Potential to the Thermodynamical Theory of Solutions. III. Action of Gravity on a Solution. The Solute Potential. Extension of the Theory. SYDNEY A. SHORTER (*Phil. Mag.*, 1913, [vi], **25**, 31—42. Compare A., 1912, ii, 24, 437).—From a general theorem

enunciated by Gibbs, the author deduces a formula for the influence of gravity on a binary mixture. This formula is found to be in accordance with the equation obtained directly by Duhem. Formulæ are also given for the practical calculation of the gravity effect from osmotic pressure, vapour pressure, and freezing-point data.

In the second part of the paper, the theory given in Parts I and II. (*loc. cit.*) is extended to solutions containing any number of non-volatile solutes. Exact formulæ are deduced connecting the osmotic pressure, vapour pressure, and freezing point with the lowering effect exerted by the solutes on the chemical potential of the solvent. Thermodynamically, the solutes may be regarded as a single substance, and hence the formulæ relating to a binary solution may be generalised in a very simple manner. H. M. D.

Studies of the Processes Operative in Solutions. XX. The Conversion of Ammonium Cyanate into Carbamide, Especially as Influenced by Alcohols. ERIC E. WALKER (*Proc. Roy. Soc.*, 1912, *A*, **87**, 539—554. Compare J. Walker and Kay, T., 1897, 489).—Experiments have been made to determine the influence of ethyl, propyl, and *iso*butyl alcohol on the rate of transformation of ammonium cyanate into carbamide when the ratio of cyanate to water in the solution is kept constant. The measurements were made at 40°, and the rate of change at any moment was obtained by determining the tangent to the smooth curve drawn through the points representing the cyanate concentrations after a series of time intervals.

In aqueous solution the rate of change varies approximately as the square of the concentration of the cyanate, as found by Walker and Hambly (T., 1895, **71**, 746), but the carbamide and ammonium carbonate which are formed have some influence on the velocity. Since the carbonate is formed very rapidly at the beginning of the experiment, the velocity coefficient is abnormally high at first, and during the later stages of the change the coefficient is again too large because of the accelerating effect of the ammonium carbonate. The addition of carbamide to the original solution has also the effect of increasing the mean velocity coefficient, a result which is probably due to its influence on the side-reaction by which ammonium carbonate is produced.

The data obtained in a series of experiments in which the molar ratio of ammonium cyanate to water was 0·15 : 100, and in which the number of mols. of ethyl alcohol was increased from 0 to 120 per 100 of water, show that the rate of change is increased in proportion to the amount of alcohol present. When the alcohol and water are present in equimolar proportions, the rate of change is, however, only about five times as large as the rate in the absence of alcohol (compare Walker and Kay, *loc. cit.*).

From comparative experiments in which ethyl, propyl, and *iso*butyl alcohols were added to the aqueous solution of the cyanate, it appears that the activity increases considerably with the molecular weight of the alcohol. The percentage increase in velocity per mol. of added alcohol was found to be 3·30%, 4·92%, and 7·3% respectively for a solu-

tion containing 0·15 mol. of cyanate per 100 mols. of water. The order in which the alcohols are arranged is the same as that obtained on contrasting their activities as precipitants of salts from aqueous solutions and their physiological activity as hormones. It is supposed that the action of the alcohols is largely mechanical, the larger molecules having the greater effect both on account of their size and their greater mobility by reason of their smaller affinity for water.

H. M. D.

Studies of the Processes Operative in Solutions. XXI. Hydrolysis of Sucrose by Dilute Acids. FREDERICK P. WORLEY (*Proc. Roy. Soc.*, 1912, *A*, 87, 555—563).—The conclusion drawn by Armstrong and Caldwell (A., 1904, i, 1070), that the hydrolytic action of dilute acids on sucrose is closely analogous to that of enzymes, has been subjected to examination in a further series of experiments with dilute sulphuric acid at 25°. In three comparative observations the solutions contained 0·01 mol. acid, 200 mols. of water, and 1, 2 and 4 mols. of sucrose respectively. From the measured time changes in the rotation of the solutions, it is evident, that the rate of hydrolysis diminishes as the reaction proceeds in accordance with the requirements of the mass law. The view that the hydrolysis in dilute acid solution is characterised by an initial period in which the sucrose is hydrolysed at a constant rate, finds no support from the data which have now been obtained. There is, therefore, a considerable difference between the sucroclastic action of dilute acids and small quantities of enzymes.

It is pointed out that this conclusion has already been drawn by Rosanoff, Clark and Sibley (A., 1912, ii, 34), but that the arguments put forward by these authors are unsound. H. M. D.

Studies of the Processes Operative in Solutions. XXII. Hydrolysis of Sucrose by Sulphuric Acid; Improvements in Polarimetric Apparatus. FREDERICK P. WORLEY (*Proc. Roy. Soc.*, 1912, *A*, 87, 563—581).—Similar experiments to those described in previous papers have been made with sulphuric acid as a catalyst in order to ascertain the influence of dilution on the hydrolytic activity in the case of a dibasic acid. The various substances were used in the proportion of 1 mol. of sulphuric acid, 30 to 200 mols. of water, and either 0·125 or 0·25 mol. of sucrose. From the velocity coefficients at the different dilutions, the value of the apparent molecular hydration has been calculated. This increases from 12·2 to 15·8 when the molar ratio of water to acid increases from 30 to 80, remaining practically constant on further dilution. By comparing the results with those obtained for hydrochloric, nitric, and *p*-dichloro- and *p*-di-iodobenzenesulphonic acids, it is found that the maximum apparent hydration is reached at an earlier stage in the case of sulphuric acid than when the monobasic acids are employed as catalysts.

From the final and initial rotations of the differently concentrated solutions it appears that the degree of optical inversion varies with the dilution. In the case of the most concentrated solution, the ratio of the rotations was found to be 0·342, whereas 0·298 was obtained for the most dilute solution. This variation is attributed to the influence

of the acid on the rotatory power of the sugars present, the lævulose being responsible in all probability for the major part of the effect. In view of this phenomenon and of the influence of the mutarotation of the dextrose and lævulose, it might be doubted whether the polarimetric method affords a satisfactory measure of the rate of hydrolysis of sucrose. A theoretical examination of the subject from this point of view shows, however, that the velocity coefficient is not affected either by an alteration in the rotatory power of the invert sugar as a consequence of the presence of the acid or by the mutarotation of the monoses.

Considerable improvements have been made in the apparatus employed for the polarimetric study of chemical changes, and these, together with the precautions which must be observed in accurate work, are described in detail. H. M. D.

Studies of the Processes Operative in Solutions. XXIII. Hydrolysis of Methyl Acetate by Acids. FREDERICK P. WORLEY (*Proc. Roy. Soc.*, 1912, *A*, **87**, 582—603. Compare Armstrong and Watson, A., 1907, ii, 849).—With the object of determining the apparent molecular hydration of the acid by the method employed in connexion with the hydrolysis of sucrose (P., 1910, **26**, 298), measurements have been made of the rate of hydrolysis of methyl acetate under the influence of hydrochloric acid. The experiments were carried out at 25°, the molecular proportions of the substances employed being 1 of methyl acetate, 120 of water, and from 0·6 to 4 of hydrochloric acid.

Under these conditions, the proportion of methyl acetate ultimately hydrolysed is never greater than 95%, and in consequence it is necessary to take the reverse change into account in calculating the velocity coefficient of the hydrolysis, the reaction taking place in accordance with the equation $dx/dt = k(a-x) - k^1x^2$, in which a is the initial concentration of the ester, and x the amount transformed after time t.

For a given ratio of water and methyl acetate, the proportion of the latter which is hydrolysed when equilibrium is attained decreases slightly as the concentration of the catalyst increases. In view of this it is suggested that the usual interpretation of the equation

$$k[CH_3{\cdot}CO_2CH_3][H_2O] = k^1[CH_3{\cdot}CO_2H][CH_3OH]$$

is incorrect, and that since hydrolysis is probably effected by the direct interaction of hydrated hydrolyte and hydrated catalyst, the factor $[H_2O]$ does not necessarily represent the active mass of one of the substances taking part in the reaction, but probably expresses the degree of dilution.

From the velocity coefficients, values representing the apparent molecular hydration of the hydrochloric acid have been obtained. Corresponding values have also been calculated for sodium, potassium and ammonium chlorides from the increase which these salts produce in the velocity coefficient. These molecular hydration values are much smaller than the corresponding numbers obtained when sucrose and raffinose are used as hydrolytes. Whereas with methyl acetate the apparent hydration value increases from 2·5 to 5 when the molecular

ratio of water to acid increases from 30 to 80, the corresponding series of numbers from the data for the hydrolysis of sucrose increases from 12·4 to 18·7. It is considered probable that the differences involved represent actual differences in the condition of the acid in presence of such different hydrolytes as methyl acetate and sucrose. H. M. D.

Studies of the Processes Operative in Solutions. XXIV. Nature of the Hydrolytic Process. Henry E. Armstrong and Frederick P. Worley (*Proc. Roy. Soc.*, 1912, *A*, **87**, 604—623).—The authors discuss the general character of the results obtained in this series of papers and their theoretical interpretation. As indicated in previous communications, the view is put forward that hydrolysis is essentially an associative process which involves the association and direct interaction of two complexes, one of which consists of the hydrated hydrolyte and the other of the hydrated catalyst. Such associated systems are being constantly produced, broken down and reformed in such a manner that while some give rise to the original components, others are resolved into the products of change. According to this view, hydrolysis is a bimolecular change, the second factor being the active mass of the hydrated catalyst, and not, as is generally supposed, the active mass or concentration of the water. The similarity of the results arrived at by the study of different properties, such as electrical conductivity, hydrolytic activity and osmotic effects, is quite consistent with this view, the similarity being due to the fact that the determining factor in all these cases is the interaction involved in the production of the electrolyte from water and the solute.

The increase of molecular conductivity to a maximum on dilution is attributed partly to a gradual increase in the extent of the interaction between the solute and water, and partly to the gradual simplification of the complexes formed by the dissolved substance. On the other hand, the decrease of electrical activity, as exemplified by the hydrolytic activity of the acids, to a minimum on dilution is considered to be the necessary result of a gradual weakening of the acid by further combination with water. The greater the extent to which the activity of the acid is used up in combining with water, the less must be the residual activity available for hydrolytic processes.

Stress is laid on the fact that this associative theory is directly opposed to the generally accepted dissociative hypothesis, and it is claimed that the facts disclosed in the investigation of the processes operative in solution go far to show that this hypothesis is no longer tenable. H. M. D.

Intercrystalline Cohesion in Metals and the Formation of Twinned Crystals in Silver. Walter Rosenhain and Donald Ewen (*J. Inst. Metals*, 1912, **8**, 149—185).—Many of the properties of metals, especially at high temperatures, may be accounted for by assuming the presence of an amorphous film between the crystals. The hypothesis has been tested in the following manner. The amorphous modification, being unstable, should have a higher vapour-

pressure than the crystalline. Two specimens of silver are taken, one having coarse and the other fine crystals. The latter, which has a larger area of intercrystalline boundaries in unit volume than the former, always loses weight more rapidly when heated in a vacuum. Similar results are obtained with zinc and copper. Microscopical examination shows that the intercrystalline boundaries are developed, as if by etching, by such treatment. Boundaries between twin crystals are not thus affected.

Cast silver, even without any mechanical treatment, shows numerous twinned crystals, which are revealed by heating in a vacuum.

C. H. D.

Formation of Twin Crystals by Quenching and its Influence on the Hardness of Metals. CHARLES A. EDWARDS (*Internat. Zeitsch. Metallographie*, 1912, **3**, 179—194).—The light and dark acicular structure observed in quenched alloys of copper and aluminium, containing 9—16% Al, is not due to the presence of two constituents, but to repeated twinning, brought about by the mechanical pressure due to quenching. The vitreous modification of the metal is formed at the surfaces of slip, thus increasing the hardness of the alloys. This explanation is extended to the general case of hardening of alloys by quenching. C. H. D.

Etching at High Temperatures. H. HANNEMANN (*Internat. Zeitsch. Metallographie*, 1912, **3**, 176—178).—The method of investigating the crystalline structure of alloys at a high temperature by exposure to etching vapours is faulty, because the surface etched is not a section through a crystal, but the surface of a crystal, and segregation is not thereby revealed. Further, recrystallisation may take place during the action of the reagent, thus producing a false structure. C. H. D.

Colloids. PAUL BARY (*J. Chim. phys.*, 1912, **10**, 437—453. Compare A., 1911, ii, 702).—Colloidal solutions comprise three classes, namely: (1) Jellies, which are solutions of liquids in solids of great cohesive power. (2) Electrical colloids, which are suspensions of very fine insoluble powders without solvent power, which acquire an electrical charge in contact with the liquid. Colloids of this class exhibit Brownian motions, and are coagulated by reducing their electrostatic charges. (3) Mixed colloids consisting of micella formed from irregular particles of jelly by the action of excess of liquid. These micella exhibit Brownian motions and may acquire an electrostatic charge. They can therefore be coagulated by altering the external osmotic conditions or by electrical methods, or by both combined according to circumstances.

The micella in class (3) are to be regarded as minute osmotic cells into which the surrounding liquid diffuses until its pressure is balanced by the surface tension or cohesion of the small particles. The surface tension of the colloidal substance is negative to start with and tends to approach zero as the jelly becomes saturated. Caoutchouc (Red Tonkin, unvulcanised) absorbs approximately the same volumes

of chloroform, benzene, carbon disulphide, and tetrachloroethane to form saturated jellies before breaking up into micella.

In some cases the surface tension does not attain zero, so that the limit of osmosis inwards is reached in the jelly stage, and the true solution of class (1) does not pass into a pseudo-solution of class (3) on further addition of liquid. Examples of this are the swelling of gelatin in cold water and of cellulose tetra-acetate in cold tetrachloroethane. In such cases micella can usually be obtained from the jellies by heating or even by violent agitation. The jelly separates out again on cooling, as with cellulose tetra-acetate, unless Brownian motion and electrification of the micella supervene as in the case of gelatin. R. J. C.

Determinations of the Volume of Voids in Silicic Acid Gels. WILHELM BACHMANN (*Zeitsch. anorg. Chem.*, 1912, **79**, 202—208).—The transient opacity of silica gels during dehydration has been considered by Tschermak and also by Tammann to indicate the appearance of a new hydrated phase. On the other hand, the fact that the same change is observed when such different liquids as cedar oil or a mixture of olive oil and chloroform are used, indicates that the process is one of mechanical imbibition. The view of Zsigmondy (A., 1911, ii, 880; Bachmann, A., 1912, ii, 145) that the gel is traversed by minute capillaries accords best with the facts. It is now shown that the weight of different liquids taken up by a gel is proportional to their density. The gel is prepared by exposing glassy silicic acid to steam, and then washing with water and drying over sulphuric acid. Three gels are examined, the liquid being generally introduced by exposure to its vapour.

Measurements with water, benzene, chloroform, ethyl iodide, and acetylene tetrabromide, the last being used in the liquid form only, give concordant results. C. H. D.

Theory of Emulsification. IV. WILDER D. BANCROFT (*J. Physical Chem.*, 1912, **16**, 739—758. Compare A., 1912, ii, 834).—Robertson's paper on emulsions of oil and water (A., 1910, ii, 697) and the article on emulsions in Remington's "Practice of Pharmacy" (1907) are reproduced in full.

Robertson's work is valuable because he was able to prepare emulsions of water in oil as well as of oil in water. Moreover, by means of an especially efficient shaker, he emulsified the whole of his ingredients in one operation instead of working in the dispersed phase gradually. The author holds that this successful preparation of emulsions of water in oil was due to the fact that the olive oil used has some solvent power for the emulsifier, sodium oleate, whereas kerosene and benzene, in which the soap is insoluble, give no such emulsions. The author does not accept the conclusion drawn by Robertson that one type of emulsion passes into the other at a definite concentration, but argues that there may be a range of concentrations within which no emulsion whatever is produced, or the emulsions may overlap.

The emulsions known to Pharmacy, which contain upwards of 95% of oil, are all of the oil in water type with gum acacia, egg-albumin, or

casein as emulsifying agents. The object of the pharmacist is to divide the oil into minute globules, and surround each one with an adhesive envelope. The exact proportions of oil, water, and gum are probably not so important as is generally supposed. R. J. C.

Composition of the Disperse Phase in Emulsoids. EMIL HATSCHEK (*Zeitsch. Chem. Ind. Kolloide*, 1912, **11**, 284—286).—On the assumption that the velocity of displacement of the juxtaposed layers exceeds a certain critical value, it has been shown (A., 1911, ii, 98) that the viscosity, η', of an emulsoid is given by the equation $\eta' = \eta\sqrt[3]{A}/(\sqrt[3]{A} - 1)$, in which η is the viscosity of the dispersive medium and A is the ratio of the volume of the emulsoid to that of the disperse phase. If the viscosity of the pure dispersive medium is taken as unity, this equation gives $A = \{\eta'/(\eta' - 1)\}^3$. From the viscosity data for a series of glycogen and sodium casein hydrosols, the author has calculated the values of A given by this formula. When these values are compared with the values of A', representing the ratio of the volume of the emulsoid to the weight of disperse phase present, it is found that the ratio of A' to A remains very nearly constant if the less concentrated hydrosols are left out of account. The constancy of this ratio indicates that the disperse phase consists, at a given temperature, of the dissolved substance together with a definite and constant quantity of the dispersive medium. H. M. D.

The Existence and Probable Thickness of Adsorption Envelopes on Suspensoid Particles. EMIL HATSCHEK (*Zeitsch. Chem. Ind. Kolloide*, 1912, **11**, 280—284).—The properties of suspensoid systems which depend on the movements of the particles indicate that the volume of the disperse phase is not independent of the degree of dispersity. On the assumption that this is due to the formation of an envelope of the dispersive medium round each suspensoid particle, and that the thickness of the covering film is constant for varying degrees of dispersity, it can be shown that the effective volume, V', and the actual volume, V, of the disperse phase are connected with one another by the equation $V'/V = (1 + 3t/r)$, where r is the radius of the nucleus of disperse phase and t is the thickness of the envelope of dispersive medium. From this, it is evident that the effective volume of the disperse phase will increase continuously as the degree of dispersity increases.

Experimental measurements have shown that the viscosity of highly disperse systems increases with the degree of dispersity when the proportion of disperse phase is kept constant, and this is probably due to the increasing importance of the surrounding envelope of dispersive medium.

From Odén's measurements of the viscosity of colloidal sulphur solutions of different degrees of dispersity (A., 1911, ii, 971; 1912, ii, 240), the author has calculated, by means of the above formula, the thickness of the surrounding envelope to be $0{\cdot}87\mu\mu$. Accepting this value, it follows that, for colloidal particles of diameter $10\mu\mu$, the volume of the envelope amounts to 62% of the volume of the colloidal sulphur. H. M. D.

The Equilibrium of a Gas in a State of Binary Dissociation. J. DE BOISSOUDY (*Compt. rend.*, 1913, **156**, 61—64).—A mathematical discussion of the equilibrium of a gas such as nitrogen peroxide, acetic acid vapour, etc., when partly dissociated into two identical constituents. The equilibrium is expressed by the equation

$$x^2/v(1-x) = MT^3e^{-\frac{\chi}{RT}}$$

where x is the degree of dissociation, v the volume containing one gram-molecule, T the temperature, χ the energy necessary to dissociate the normal molecules into their constituents, and M a constant coefficient. W. G.

Action of Temperature on the Equilibrium of Nitrous and Nitric Acids Formed from the Oxides of Nitrogen and Water. EMIL BRINER and E. L. DURAND (*Compt. rend.*, 1912, **155**, 1495—1497).—In a previous paper (A., 1912, ii, 1045) the authors studied the effect of pressure and concentration on various systems of oxides of nitrogen and water, the temperature remaining constant. They have now estimated the relative molecular amounts of nitrous and nitric acids formed in the solutions at varying temperatures, and find that increase in pressure of the nitric oxide and diminution of temperature favour the formation of nitrous acid. W. G.

The Equilibrium in Acid Solutions of Potassium Salts. II. ALBERT J. J. VANDEVELDE (*Bull. Soc. chim. Belg.*, 1912, **26**, 513—532. Compare A., 1912, ii, 30).—A continuation of the study of the constitution of the solid phase obtained from acid solutions of potassium salts. In the former communication the salt chosen was potassium sulphate and the three acids, hydrochloric, nitric and sulphuric. To complete this study the equilibrium has been determined (1) for solutions of potassium chloride, (2) for solutions of potassium nitrate, mixed in turn with one of the three abovementioned acids in such proportions as to produce a solid phase. In the systems studied the same results are obtained by having present the same ions in equal quantities, independently of the manner of their original combination; thus from solutions containing $20KCl : 10H_2SO_4$ or $10K_2SO_4 : 20HCl$, the solid phase in each case had the composition $8KCl : 4KHSO_4$.

In the system potassium chloride, sulphuric acid, and water, the solid portion was only a single phase, consisting of potassium chloride when the sulphuric acid was in the proportion $40KCl : 5H_2SO_4$ or less, the solubility of the chloride diminishing as the concentration of the acid diminished. On replacing the sulphuric acid in the system by hydrochloric acid, the solid phase was always potassium chloride, the solubility increasing with diminution in concentration of the acid. In the system potassium chloride, nitric acid, water, the solid phase in all cases contained both potassium chloride and nitrate, the amount of the former diminishing and of the latter increasing with rise in concentration of the acid.

In the case of potassium nitrate, sulphuric acid, and water, the

solid phase consisted solely of potassium nitrate, and its solubility seemed but very slightly affected by the concentration of the acid. On replacing the sulphuric acid with nitric acid, the nitrate was found to be less soluble, but to an extent independent of the acid concentration. In the system potassium nitrate, hydrochloric acid, water, the solid portion was a single phase, potassium nitrate, until the acid reached the concentration $20KNO_3 : 20HCl$. W. G.

Heterogeneous Equilibria between Aqueous and Metallic Solutions. II. Interaction of Mixed Salt Solutions and Liquid Amalgams. GEORGE McPHAIL SMITH (*J. Amer. Chem. Soc.*, 1913, **35**, 39—49. Compare A., 1910, ii, 401).—This work was undertaken for the purpose of studying by an independent method the ionisation relations existing in mixtures of salts. By agitating dilute sodium or potassium amalgam with successive portions of a solution of sodium and potassium chlorides or sulphates, a mixture is soon obtained in which at equilibrium the concentrations of the salts in the mixed solution are identical with those in the original salt solution; the amalgams are then analysed.

The ion fractions of sodium and potassium in experiments in which the salts were present in equivalent quantities have been calculated on the assumptions that (1) the reaction takes place according to the equation $KHg_m + Na^{\cdot} \rightleftharpoons NaHg_n + K^{\cdot} + (m-n)Hg$, and (2) that in the solutions containing a common ion and having a total salt concentration $0{\cdot}2N$, the relation Na salt/K salt $= Na^{\cdot}/K^{\cdot}$ is approximately true. The results show that the sodium ion fraction increases with the total salt concentration of a solution. In order to explain this phenomenon, it is suggested that sodium and potassium chlorides in mixed aqueous solution form the complexes Na(Cl·K·Cl) and K(Cl·Na·Cl). The formation of the latter complex would lower the value of the sodium ion fraction, and the conclusion is therefore drawn that the preponderating complex is Na(Cl·K·Cl), and that this ionises into $Na^{\cdot}$ and $(Cl{\cdot}K{\cdot}Cl)'$ ions. E. G.

Influence of Temperature on the Velocity of Chemical Reactions. I. B. SCHVECOV (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, *Phys. Part*, 470—474).—Owing to the inconstancy of the ordinary temperature-coefficient of chemical reactions which is represented by the expression $\gamma = (K_2/K_1)10/(t_2 - t_1)$, where K_1 and K_2 are the velocity constants at the temperatures $t_1°$ and $t_2°$ respectively, Plotnikov (A., 1905, ii, 376) suggested the use of the so-called logarithmic temperature-constant given by $a = (\log K_2 - \log K_1)/(t_2 - t_1)$. Comparison of these two equations shows that a would be constant only over intervals of temperature for which γ gives constant values. Auerbach (A., 1905, ii, 571) has, indeed, shown that Plotnikov's logarithmic temperature-constant is a variable magnitude.

From theoretical considerations, the author regards it as more likely that constant values will be obtained for the ratio between the velocities of reaction if these are calculated for absolute temperatures having a constant ratio (ρ). The logarithmic temperature-coefficient, η, would then be given by the equations: $\eta = K\rho T/KT$, $\eta = K\rho^2 T/K\rho T$,

. . . . . , $\eta = K\rho^n T / K\rho^{n-1} T$. The product of all these equations gives $\eta^n = K\rho^n T/KT$, or, if $K\rho^n T = K_2$, $KT = K_1$, $\rho^n T = T_2$ and $T = T_1$, $\rho^n = T_2/T_1$ or $n = (\log T_2 - \log T_1)/\log \rho$. Hence,

$$\eta = \sqrt[n]{K\rho^n T/KT} = (K_2/K_1) \log \rho / \log T_2 - \log T_1.$$

The relation between this logarithmic coefficient η and the ordinary coefficient γ is expressed by the equation:

$$\log \eta = \frac{\log \rho}{10} \cdot \frac{T_2 - T_1}{\log T_2 - \log T_1} \cdot \log \gamma.$$

Taking ρ to be 1·1, that is, an increase of 10% in the absolute temperature, the values $\gamma_1 = 2$ and $\gamma_2 = 3$ for the ordinary coefficient at ordinary temperatures give $\eta_1 = 7{\cdot}23$ and $\eta_2 = 23{\cdot}02$ respectively. On the assumption that the latter magnitudes remain constant, the corresponding values for γ at different absolute temperatures will be as follows:

T.	η_1, 7·23.	η_2, 23·02.
100	$\gamma_1 = 8{\cdot}00$	$\gamma_2 = 27{\cdot}02$
150	3·98	8·93
200	2·84	5·22
300	2·00	3·00
1000	1·23	1·38

These numbers are in agreement with the general variation of the ordinary temperature-coefficient, which diminishes with rise, and rapidly increases with fall, of the temperature. In the particular case of the decomposition of hydrogen iodide, the values of γ calculated by means of the above equation agree, within the limits of experimental error, with the observed values; thus for the temperature-intervals 300—400°, 400—500°, and 500—600°, Bodenstein (A., 1899, ii, 637) found 1·89, 1·64, and 1·53 respectively, the calculated values being 1·94, 1·64, and 1·49. T. H. P.

The Relation between Oxidation Potential and Oxidation Velocity JULIUS GRÓH (*Zeitsch. physikal. Chem.*, 1913, 81, 695—712. Compare Bodenstein, A., 1904, ii, 717; Bognar, A., 1910, ii, 282).—The oxidation of acetaldehyde and formic acid was effected by means of chlorine, and the velocity constants determined. Considerable difficulty was experienced owing to the reactions being complicated through the action of the chlorine on water; however, by effecting the changes in the presence of a known concentration of nitric acid, it became possible to bring the secondary reaction into the calculation, and obtain a moderately good velocity constant.

Other experiments, namely, the action of iodine on acetaldehyde, the oxidation of aldehyde by cerium ammonium nitrate, and the oxidation of chloral and bromal with bromine were tried, but were found to be too complicated to furnish results. The velocity of oxidation by chlorine in the two cases investigated when compared with Bognar's results for bromine (*loc. cit.*) show that they are just opposite to the oxidation potentials of chlorine and bromine, thus:

	Acetaldehyde.		Formic acid.	
	Br.	Cl.	Br.	Cl.
Velocity constants	1·205	0·648	3280	431
Oxidation potential ...	1·334	1·639	1·334	1·639

This anomaly can be explained in two ways: (1) The chemical resistance is greater in the case of chlorine than in that of bromine. (2) That the course of the reaction is different in the two cases. The first reason is held by the author to be unlikely, the second case becomes likely if it is supposed that the halogen forms an intermediate compound with the reducing substance, which breaks up with greater or lesser velocity to form the end products of the reaction. Attempts were made by spectrophotometric measurements to confirm the second conclusion, but they led to no definite results. J. F. S.

Velocity of Reaction of Different Bases with Halogen-substituted Acids. II. HJ. JOHANSSON (*Zeitsch. physikal. Chem.*, 1913, **81**, 573—589. Compare A., 1912, ii, 544; Holmberg, A., 1912, ii, 443; Senter, T., 1912, **91**, 460).—The velocity of reaction of the decomposition of monobromosuccinic acid is investigated in neutral and alkaline solution and also in the presence of neutral salts. It is shown that two reactions take place, the first unimolecular, in which the hydroxyl ion reacts with the ion of monobromosuccinic acid with the production of the ion of fumaric acid and bromine ion, thus:

$$'O\cdot CO\cdot CHBr\cdot CH_2\cdot CO\cdot O' + OH' = 'O\cdot CO\cdot CH\vdots CH\cdot CO\cdot O' + Br' + H_2O,$$

and the second, a bimolecular reaction in which the ion of monobromosuccinic acid forms first the ion of propiolactonecarboxylic acid and bromine ion, thus:

$$'O\cdot CO\cdot CHBr\cdot CH_2\cdot CO\cdot O' = 'O\cdot CO\cdot \underset{\displaystyle O\text{---}CO}{\underline{CH\cdot CH_2}} + Br',$$

and the lactone ion then reacts with the hydroxyl ion, giving the ion of malic acid, thus:

$$'O\cdot CO\cdot \underset{\displaystyle O\text{---}CO}{\underline{CH\cdot CH_2}} + OH' = 'O\cdot CO\cdot CH(OH)\cdot CH_2\cdot CO\cdot O'.$$

The reaction constants of both reactions are determined, the former being determined in neutral solution, using the sodium, potassium, barium, and strontium salts of the acid. The reaction constant is found to be $k = 0{\cdot}002403$, and is independent of the nature of the metal ion.

The addition of neutral salts causes the constant to increase slightly, but this is held to be due to the superimposing effect of the second reaction. The second reaction constant was determined in alkaline solution using the hydroxides of sodium, potassium, barium, strontium, both with and without the addition of the nitrate corresponding with the hydroxide. This reaction is shown to depend on the nature and concentration of the cation, and follows the empirical rule of Holmberg (*loc. cit.*): $C_M = C[M^{\cdot}]a$. It is found that $d = \frac{1}{3}C_{Na} = 0{\cdot}095$ $C_K = 0{\cdot}093$; $C_{ba} = 0{\cdot}197$, and $C_{sr} = 0{\cdot}196$. J. F. S.

Theory of Efflorescence. Influence of the Size of the Crystal. CH. BOULANGER and GEORGES URBAIN (*Compt. rend.*, 1912, **155**, 1612—1614. Compare this vol., ii, 34).—Starting from their law $\log(m_\theta - m_t) = \log a + A \log(\theta - t)$, the authors deduce the equation $\log a' = \log a + (1 - A/3) \log p'/p$ for the relationship between the efflorescence of two crystals of weights p' and p respectively.

They have applied this to two crystals of sodium sulphate, and consider that the values found and calculated are in agreement within the limits of experimental error. W. G.

Kinetics of Chemical Reactions of Combination, Deoxidation, and Oxidation. II. E. I. ORLOV (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1576—1597).—Examination of Spitalsky's results dealing with the catalytic decomposition of hydrogen peroxide (A., 1911, ii, 36) in the light of the considerations previously advanced by the author (A., 1912, ii, 243) leads to the following conclusions.

The catalytic decomposition of hydrogen peroxide by chromic acid furnishes an example of the transformation of a unimolecular reaction of the first order into a unimolecular one of the second order. This transformation is conditioned by the action of an intermediate form of the oxide formed during the reaction and entering the sphere of the catalysis only after the peroxide is decomposed to a certain extent.

The influence of this intermediate form is complicated by the fact that one form of catalysis is converted into the other, not suddenly, but gradually; when the intermediate form comes into action, the coefficient f appears in the differential equation:

$$dx/dt = k(A - fx)(B + fx).$$

This appearance of f is dependent on the consumption of a certain proportion (one-fifth to one-eighth part of the original amount remains) of the hydrogen peroxide, and the consequent difficulty of oxidation of Cr^{III} to C^{VI}; a more rapid process of oxidising $Cr_2O_3(O_3H_4)_4$ to $Cr_2O_7H_2$ is then initiated, $Cr(OH)_7$ being formed as an intermediate product in the change. It is hence necessary to assume, in the kinetics of chemical processes, the principle of least loss of time; chemical processes strive to take place in such a way that there occurs the least waste of time.

The reducing properties of hydrogen peroxide are explained as due to the quadrivalency of oxygen in the molecules of the peroxide and of water. The oxidation of the hydrogen ions is regarded as a combination with the molecule $H{\cdot}O{:}O{\cdot}H$, thus: $H{\cdot}O{:}O{\cdot}H + 2H^{\cdot} = H_2{:}O{:}O{:}H_2 = 2{}^{H}_{H}{>}O{<}^{\cdot}_{\cdot}$. The first stage of this reaction requires time, but the second proceeds instantaneously.

This hypothesis of the quadrivalency of oxygen necessitates the assumptions that aqueous solutions contain the complex, $H_2{:}O{<}^{O:H_2}_{O:H_2}$ possessing reducing properties, and that the ions Cr_2O_7'' and the molecules H_2O_2 give an intermediate oxide of the type

$$Cr_2O_3\left[\begin{matrix}-HO \\ -HO\end{matrix}{>}OH_2\right]_4 \quad \text{or} \quad Cr(OH)_7.$$

This oxide is the oxygen-carrier, and takes part in the conversion of Cr^{VI} into Cr^{III} and of the latter into Cr^{VI} again. After combination of the hydrogen ions with hydrogen peroxide, the remaining groups, $(Cr_2O_7){<}^{\cdot}_{\cdot}$, with free affinities, also combine with $H{\cdot}O{:}O{\cdot}H$,

giving $\underset{Cr_2O_7}{H\cdot O\!=\!O\cdot H}$, which is highly unstable under the conditions of Spitalski's experiments (*loc. cit.*) and decomposes into Cr_2O_7'', $2H^{\cdot}$, and O_2, but is comparatively stable under the ordinary conditions of room-temperature and absence of vigorous shaking.

If the catalytic decomposition of hydrogen peroxide by means of potassium dichromate proceeds under ordinary conditions, the stable compounds $\underset{Cr_2O_7}{H\cdot O\!=\!O\cdot H}$ and $\underset{HCrO_4\quad HCrO_4}{H\cdot O\text{———}O\cdot H}$, are obtained, and the decomposition follows the differential equation: $dx/dt = k(A-x)(B+x)$. This equation is applicable to reactions of combination. The form $dx/dt = k(A-x)$ represents a particular case. T. H. P.

Kinetics of Chemical Reactions of Combination, Deoxidation, and Oxidation. III and IV. E. I. Orlov (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1598—1623, 1623—1658).—The considerations advanced in previous papers (see preceding abstract) are applied to other reactions.

The decomposition of hydrogen peroxide by an iodide in aqueous solution is shown to be a unimolecular reaction of the second order, decomposition by means of potassium dichromate or molecular platinum proceeding similarly. The mechanism of these changes is discussed.

T. H. P.

Universal Significance of the Elementary Quantum. Otto Sackur (*Ann. Physik*, 1913, [iv], **40**, 67—86. Compare A., 1912, ii, 145, 1151).—By a process of reasoning similar to that adopted in the previous papers, equations have been deduced for the energy and entropy of ideal monatomic solid substances and of monatomic gases. The reasoning is based on a more precise definition of the (physical) conception of probability, and not on the usual assumption of elementary energy quanta. The only quantities occurring in the equations are certain general constants, and also the atomic vibration frequency in the case of the solids and the molecular weight in the case of the gases.

The values of the "chemical constants," which determine the chemical behaviour of the gases and the vapour pressures of their condensation products, are calculated for helium, neon, argon, krypton, xenon, and mercury, In atmospheres, this constant C is given by the equation $C = -2{\cdot}055 + 1{\cdot}5 \log M$, where M is the molecular weight of the gas. It is shown that the calculated vapour pressures of mercury between 0° and 360° are in fairly good agreement with the observed values when the "constant" for mercury given by this equation is applied in the calculation of the vapour pressure curve. The calculated and observed vapour pressures of argon at 84° abs. are also concordant. H. M. D.

The "Chemical Constants" of Di- and Tri-atomic Gases. Otto Sackur (*Ann. Physik*, 1913, [iv], **40**, 87—106. Compare preceding abstract).—On the assumption that the di- and tri-atomic gases have

the structure assigned to them by Boltzmann, formulæ are deduced from which the entropy and the "chemical constants" of these gases may be calculated. The values obtained for hydrogen, oxygen, nitrogen, the halogen and halogen acids, carbon monoxide, nitric oxide, water, hydrogen sulphide, carbon dioxide and sulphur dioxide are recorded. The "chemical constants" are applied in the calculation of the vapour-pressure curves of iodine and ice, and of the dissociation constants corresponding with the equilibria: $2HCl \rightleftharpoons H_2+Cl_2$, $2HBr \rightleftharpoons H_2+Br_2$, $2HI \rightleftharpoons H_2+I_2$, $2H_2O \rightleftharpoons 2H_2+O_2$, $2CO_2 = 2CO+O_2$, and $2NO \rightleftharpoons N_2+O_2$. From a comparison of the calculated vapour pressures and dissociation constants with experimental data, it is found that the values obtained for the "chemical constants" may be regarded in most cases as approximately correct. The existence of considerable discrepancies between theory and experiment which is found in certain cases, for example, the dissociation of carbon dioxide and nitric oxide, indicates, however, that the values of the "constants" cannot be regarded as final, and that it will probably be necessary to modify the theory of polyatomic molecules before the true values can be derived. H. M. D.

Volume and Valency. M. SEBALDT (*Zeitsch. physikal. Chem.*, 1913, 81, 749—753).—A theoretical paper in which the relationship between valency and atomic volume and also other properties of the elements is shown to be periodic. In one diagram the logarithms of the atomic volumes are plotted as ordinates, the elements being placed on lines parallel to the ordinate axis which represent the eight groups of the periodic system. This arrangement shows clearly the relationship between the electroaffinity and the volume; atomic magnetism and compressibility are also shown to be functions of the atomic volume. In another arrangement the elements are placed round a polar co-ordinate ring in order of atomic weight, those of even valency to the left of the ordinate axis and those of odd valency to the right; the logarithm of the atomic volume is plotted on the ordinate. This arrangement brings out most of the relationships between the elements very clearly. J. F. S.

The Nature of Auxiliary Valencies. II. Metal Ammonias. FRITZ EPHRAIM (*Zeitsch. physikal. Chem.*, 1913, 19, 513—538. Compare A., 1912, ii, 546).—The present paper contains further details on ammonia derivatives of the metal salts. It is shown that errors are likely to come into the pressure measurements of ammine derivatives, owing to incomplete drying and absorption of air by the finely divided compounds. Precautions for avoiding these errors are indicatad. The gaseous pressure at a series of temperatures is determined for the hexammine derivatives of the halogen salts of cadmium, zinc, manganese, nickel, cobalt, iron, copper, calcium, and magnesium. It is found that the ratio T_{Cl}/T_I is a constant for a given pair of salts at all pressures, where T is the temperature at which the two compounds have the same gaseous pressure. Compounds of this type, therefore, obey the Ramsay-Young rule. The value of the factor varies from 0·988 for $ZnI_2/ZnBr_2$ to 1·232 for $MnI_2/MnCl_2$. The temperature at

which the dissociation pressure of the various salts is 500 mm. is given, and it is seen that the pressure generally decreases as the atomic volume of the central atom increases. The hexammines of zinc iodide, cupric bromide, and those of the chloride, bromide and iodide of cadmium being exceptional. The value $\sqrt[3]{Tv}$ is shown to be constant for all the hexammines except those mentioned above, and in this connexion it is shown that taking the mean value of $\sqrt[3]{Tv}=14{\cdot}0$, it is possible to calculate the atomic volume of the central atom with fair approximation when T is the absolute temperature at which the dissociation pressure is 500 mm. It is found that when the absolute temperatures for pressures of 700 mm. and 200 mm. are taken the ratio is approximately constant (1·085—1·073). Moduli are calculated for the pressure-temperature relationship of I : Cl, I : Br, Br : Cl, and from these it is seen that generally at a given temperature the tension is greatest for the chlorides and least for the iodides. From calculations from the Nernst equation, $\log p = -Q/(4{\cdot}571T) + 1{\cdot}75 \log T + 3{\cdot}3$, it is shown that the dissociation of the hexammines of the bivalent metals occurs by first splitting off one molecule of ammonia:

$$R''(X)_2 6NH_3 \rightleftharpoons R''(X)_2 5NH_3 + NH_3.$$

The heats of formation of the various ammines are calculated both from the Nernst formula and the van't Hoff formula. A series of notes on the preparation of the ammines used in the investigation is given.

J. F. S.

The Nature of Auxiliary Valencies. III. The Region of the Existence of Auxiliary Valency Compounds. FRITZ EPHRAIM (*Zeitsch. physikal. Chem.*, 1913, **81**, 539—542. Compare preceding abstract).—The dissociation of the hydrates and ammines is theoretically considered. It is shown that whilst the ammines dissociate by successively splitting off one molecule of ammonia this is not analogous to the hydrates. The reason is the formation of solutions in the case of the hydrates. It is concluded that all the possible hydrates exist if only in a labile condition and in solution. It is also shown why the dissociation curves of the ammines show no transition points, whilst those of the hydrate do. J. F. S.

What are Bases and Acids? DANIEL VORLÄNDER (*J. pr. Chem.*, 1913, [ii], **87**, 84—91).—Theoretical. F. B.

New Shaking Apparatus. WILHELM STEINKOPF and HANS WINTERNITZ (*Chem. Zeit.*, 1913, **37**, 40).—The apparatus resembles a retort stand where the upright is fitted, by means of ball-bearings, into a heavy cast-iron base. A short horizontal arm is attached to the upright and connected with the eccentric of a small motor. The usual retort stand clamps may be used for holding water- and hot-air baths, and flasks for the distillation of viscous liquids which otherwise have a tendency to bump. The apparatus may also be used for holding burettes for the titration of boiling liquids.

On account of the gentle rotating movement imparted to the contents of the vessels, it is not necessary to use stoppers, and hence any risk of introducing impurities is avoided. H. B. H.

Shaking Apparatus, which can be Exhausted, Fitted with an Inner Temperature Regulator. RICHARD KEMPF (*Chem. Zeit.*, 1913, **37**, 58—59).—A modification of the apparatus previously described (A., 1906, ii, 433), the principle remaining the same. The method by which the apparatus may be used in investigating catalytic reductions with colloidal or finely divided platinum is described.

T. S. P.

A Simple Experiment Illustrating the Luminosity of Phosphorus. DOUGLAS F. TWISS (*Chem. News*, 1913, **107**, 16).—A vertical glass tube, 2—2½ cm. internal diameter and about 120 cm. long, is fitted at the lower end with an indiarubber bung carrying a glass tube, which is bent upwards so as to be parallel to, and of approximately the same height as, the wider tube. A solution of phosphorus in olive oil is introduced into the wider tube so as to reach about 6 inches from the top, and steady suction is applied at the mouth of this tube by means of a water pump. Air enters through the narrow tube, and a beautiful series of bell-shaped phosphorescent air bubbles rises through the column of oil. T. S. P.

Inorganic Chemistry.

Early Work on Hydrofluoric Acid and the Isolation of Fluorine. FREDERICK D. CHATTAWAY (*Chem. News*, 1913, **107**, 25—26).—Historical.

Reactions of Ozone with Certain Inorganic Salts. YOSHITO YAMAUCHI (*Amer. Chem. J.*, 1913, **49**, 55—68).—A study has been made of the action of ozone on certain inorganic salts with the object of ascertaining whether the oxidation is effected by only one oxygen atom of the ozone molecule or whether all three atoms take part in the process. A method has been devised by which each sample of ozonised oxygen can be divided into two parts, one for carrying out the experiment, and the other for analysis.

The salts employed included potassium arsenite, stannous chloride, sodium thiosulphate, thallous nitrate, mercurous nitrate, and ferrous ammonium sulphate. In the case of stannous chloride, the oxidation takes place according to the equation

$$3SnCl_2 + 6HCl + O_3 = 3SnCl_4 + 3H_2O,$$

but in all the other cases only one oxygen atom of the ozone molecule reacts with the salt, the ozone decomposing, thus : $O_3 = O_2 + O$. When sodium thiosulphate is treated with ozone, two reactions occur, one involving the catalytic decomposition of the salt,

$$3Na_2S_2O_3 = 3Na_2SO_3 + 3S,$$

and the other effecting a partial oxidation of the sulphite formed $2Na_2SO_3 + 2O_3 = 2Na_2SO_4 + 2O_2$. Thallous salts are rapidly and com pletely oxidised by ozone, and the thallic oxide produced can be readil

collected and weighed; the reaction is therefore applicable to the estimation of ozone. E. G.

The Dynamic Allotropy of Sulphur. IV. HUGO R. KRUYT (*Zeitsch. physikal. Chem.*, 1913, **81**, 726—748. Compare A., 1908, ii, 1028; 1909, ii, 228, 802).—The paper is chiefly polemical. It is shown that mixed crystals are formed by $S\mu$ and $S\lambda$, and that the transition $S_{rh.} \rightarrow S_{mon.}$ takes place at a higher temperature in the presence of $S\mu$. The transition point of pure $S_{rh.}$ is 95·3°, whereas the generally observed transition point is 95·5°, and the triple point $S_{rh.}$, $S_{mon.}$ and $S_{liq.}$ lies at 95·9° ± 0·1°. Attempts are made to calculate the transition point of rhombic sulphur on the basis of Nernst's theorem, but this led to results which are in no way like the experimentally-determined values. An answer is given to the papers of Wigand (A., 1910, ii, 602, 1055), Smits and Leeuw (A., 1912, ii, 40), Leeuw (this vol., ii, 40), Preuner and Schupp (A., 1909, ii, 997), and to Wo. Ostwald (*Grundriss der Kolloidchemie*, p. 132). The following thermal constants of sulphur are collected in the paper; these are held to be trustworthy.

M. p. monoclinic sulphur (free from $S\mu$), 119·25°.
M. p. monoclinic sulphur, as usually prepared, 114·5°.
M. p. rhombic sulphur (free from $S\mu$), 112·8°.
M. p. rhombic sulphur, as usually obtained, 110·2°.
M. p. of nacreous variety of sulphur (free from $S\mu$), 106·8°.
M. p. of nacreous variety of sulphur, as generally obtained, 103·4°.
Transition point $S_{rh.} \rightarrow S_{mon.}$ (free from $S\mu$), 95·3°.
Transition point usually obtained, 95·5° (3·1% $S\mu$ present).

J. F. S.

The Chemistry of the Formation of Nitric Oxide in the High Tension Arc. FRANZ FISCHER and EMIL HENE (*Ber.*, 1912, **45**, 3652—3658).—The purely thermal formation of nitric oxide from nitrogen and oxygen has been questioned by various investigators (compare Haber and Koenig, A., 1908, ii, 34, 940; Grau and Russ, A., 1907, ii, 753). Escales, in a discussion before the German Bunsen Society (*Zeitsch. Elektrochem.*, 1906, **12**, 539), raised the question whether the formation of nitric oxide might not be preceded by the activation of the nitrogen, but Strutt has since shown (A., 1912, ii, 153) that active nitrogen does not react with oxygen. The authors now show that the energy of the discharge is probably used up in dissociating the oxygen molecules, this being an endothermic process. Outside the arc the following processes, which are exothermic, then take place: (1) re-formation of molecular oxygen, (2) oxidation of molecular oxygen to ozone, (3) formation of nitric oxide. The latter may be a direct reaction between the active oxygen atoms and the nitrogen, or may be due to a reaction between the ozone and the nitrogen, which reaction would be exothermic.

The above conclusions are based on the following experiments. When pure oxygen is sparked as it passes out of a quartz capillary and mixes with pure nitrogen in a closed apparatus, six and a-half times more nitric oxide is produced than when the nitrogen is sparked and mixes with

oxygen. Similarly, when air is sparked and blown into oxygen, four times as much, when blown into nitrogen, twice as much, nitric oxide is produced as when pure nitrogen is sparked and blown into pure unsparked oxygen.

A high-tension arc was produced in a quartz apparatus cooled with water. When air was sent through the arc and then mixed immediately with oxygen, air, and nitrogen respectively, the volume percentages of nitric oxide produced were respectively 7·8, 7·4, and 5·9.

When air is submitted to the silent discharge in a quartz Siemens ozone tube heated at varying temperatures (20—700°), the percentage of nitric oxide produced increases with rise in temperature, owing to the increased velocity of reaction between any ozone produced and the nitrogen, reaction taking place before the ozone is destroyed by the high temperature.

The above results indicate that better results would be obtained on a manufacturing scale if oxygen were passed through the arc flame instead of air, using magnetite electrodes, and then rapidly mixed with nitrogen and cooled. T. S. P.

The Inner Cone of Hydrocarbon Flames. FRITZ HILLER (*Zeitsch. physikal. Chem.*, 1913, **81**, 591—625. Compare A., 1910, ii, 122).—A further investigation of the inner cone of certain flames. The ether and coal-gas flames are chiefly investigated, and the analyses of the products of combustion at the point of the cone, the side of the cone, and at different positions above the cone in the space between the inner and outer cone are made. Temperature determinations were made by means of an iridium, iridium-rhodium couple, and these values were compared with the temperatures calculated from the composition of the gas in the space between the two cones and the known specific heats and heats of combustion on the one hand, and with those obtained from the equilibrium constant and its relation to temperature on the other.

Considerable difficulty was experienced in the calculations owing to the uncertainty of the thermal data required for obtaining the temperature. The constant $K = (H_2O/CO_2) \cdot (CO/H_2)$ is given for all experiments, the various values being obtained by gas analytical processes. The equilibrium constant is found to be about 3·4 when the gases coming from the inner cone are cooled to a temperature which allows of no further change, but when the coal gas has been previously mixed with carbon dioxide, the equilibrium constant is considerably lower than 3·4. In the case of the ether flame, this constant is often found to be as low as 2·8, the higher value only being obtainable when a very small flame is employed. J. F. S.

The Various Forms of Silica and their Mutual Relations. CLARENCE N. FENNER (*J. Washington Acad. Sci.*, 1912, **2**, 471—480).—The velocity of transformation of one form of silica into another is extremely slow, and the different forms may exist together over considerable ranges of temperature. The inversions may be hastened

by employing a catalytic agent (sodium tungstate). The following inversion points were determined from the heating curves :

α-Quartz (tetartohedral hexagonal) $\rightleftarrows$ β-quartz (hemihedral hexagonal), 575°.

β-Quartz $\rightleftarrows$ β-tridymite (holohedral hexagonal), 870° ± 10°.

β-Tridymite $\rightleftarrows$ β-cristobalite (cubic), 1470° ± 10°.

On cooling, β-tridymite and β-cristobalite promptly pass at the following temperatures into metastable forms possessing lower optical symmetry :

β-Tridymite $\rightleftarrows$ α-tridymite (biaxial, perhaps orthorhombic), 115—120°.

β-Cristobalite $\rightleftarrows$ α-cristobalite (biaxial), 180—270°.

Chalcedony possibly represents a seventh form of silica. L. J. S.

The Transformations of Silica at High Temperatures. KURD ENDELL and REINHOLD RIEKE (*Zeitsch. anorg. Chem.*, 1912, **79**, 239—259).—The present investigation deals with pure temperature changes in the absence of mineralisers. The specimens of native silica, in fragments of 1—3 c.c. and also in powder, are heated in an electric furnace, and the direction of the transformation determined by measurements of the density, using the data D (quartz) 2·65, (cristobalite) 2·33, (silica glass) 2·21.

Quartz and chalcedony which have been heated at 1450° have often been described as optically isotropic, owing to the microscopic cracks produced during the transformation, which also give rise to an error in the determinations of density. Cristobalite is best recognised by its change of volume at about 230°, measured in a mercury dilatometer. This is the only means of distinguishing it from tridymite.

Quartz and amorphous silica are converted into cristobalite by heating above 800°, but an exact temperature of transformation has not been found. The velocity of conversion increases with the temperature. Between 1200° and 1600° the transformation of silica glass is proportional to the time. Twinned quartz is converted more rapidly than simple crystals, and chalcedony still more rapidly. Using an iridium furnace, β-cristobalite is found to have m. p. 1685° ± 10°.

The factor determining the rate of transformation is the extent of surface, a twinned crystal having a greater effective surface than a simple one, and fibrous varieties, such as chalcedony, a still greater surface. The quartz of pegmatite and graphic granite is often repeatedly twinned. Chalcedony may be regarded as an unstable transitional form of quartz. Massive rock crystal may probably be melted by rapid heating, without previous conversion into cristobalite. The present data do not allow of the construction of an equilibrium diagram for silica, but an attempt is made to classify the various modifications in accordance with Tammann's hypothesis (A., 1912, ii, 149). C. H. D.

Capacity of Potassium Haloids for Forming Solid Solutions at High Temperatures. MARIO AMADORI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 606—610. Compare A., 1912, ii, 758).—The author has repeated some of his former experiments with results which con-

firm those obtained by him and Pampanini (A., 1912, ii, 48), and do not agree with those of Vrshesnevsky (A., 1912, ii, 137). The author's conclusions are further supported by recent work of Nacken and Schobert (*Diss.*, Leipzig, 1912) and Nacken and Flack (unpublished).

R. V. S.

Some Properties of Alkali Nitrites. MARCEL OSWALD (*Compt. rend.*, 1912, **155**, 1504—1506).—The author has prepared sodium and potassium nitrites in a high state of purity and examined their properties. Sodium nitrite, when heated in a vacuum, melts at 217° (compare Divers, T., 1899, **75**, 86) and decomposes at 320°; potassium nitrite melts at 297·5° and decomposes at 350°. After fusion and resolidification they have respectively D_0^0 2·168 and 1·912. The densities of their solutions at various concentrations are given.

W. G.

The Silver-Zinc Equilibrium. HENRY C. H. CARPENTER and W. WHITELEY (*Internat. Zeitsch. Metallographie*, 1912, **3**, 145—169).—The equilibrium diagram given by Petrenko (A., 1906, ii, 284) is incompatible with the phase rule. It is shown that the errors in the diagram are due to the use of insufficient quantities of material, to want of uniformity, and to the absence of proper annealing. The system has now been reinvestigated, using larger quantities and employing greater precautions. The actual diagram is of a much simpler character. The liquidus has been determined accurately by Heycock and Neville (T., 1897, **71**, 407). The limits of the α-solid solution at 220° (determined on samples annealed for six weeks) are 100 and 62·7 atomic % of silver. The β-constituent is unstable below 264°, at which temperature there is a eutectoid point, $\beta \longrightarrow \alpha + \gamma$. The γ-constituent is the compound Ag_2Zn_3; it is highly brittle and develops conspicuous cleavage cracks. At 220° the γ-range is from 40 to 37·3 atomic % Ag. The δ-constituent (probably Ag_2Zn_5), which is also brittle, has a range 29 to 14·3 atomic % Ag, whilst the η-constituent is confined to the immediate neighbourhood of the zinc end of the series. The ϵ-constituent does not exist below 310°. There is thus a very close resemblance, throughout the whole system, between the copper–zinc and silver–zinc series. C. H. D.

The Copper–Zinc, Silver–Zinc, and Silver–Cadmium Equilibria HENRY C. H. CARPENTER (*Internat. Zeitsch. Metallographie*, 1912, **3**, 170—175).—A remarkable similarity is observed between the equilibria in the systems copper–zinc (A., 1912, ii, 764), silver–zinc (preceding abstract), and silver–cadmium (Petrenko and Fedorov, A., 1911, ii, 281, 800).

In each case a compound of similar composition,

$$Cu_2Zn_3,\ Ag_2Zn_3,\ Ag_2Cd_3,$$

determines the form of the diagram. The α-solid solutions have a similar range of stability, and near to the compositions CuZn, AgZn, and AgCd, β-constituents occur, having a comparatively wide range of composition at a high temperature, narrowing with falling temperature until a eutectoid point is reached at or about 50 atomic %. The γ-constituent is in each case the pure compound. It is remarkable

that the systems copper–tin and copper–aluminium also include a β-constituent stable only above a certain temperature, and then undergoing a eutectoid inversion.

The copper–cadmium diagram does not show any close analogy with the above. C. H. D.

The Preparation and Investigation of Silver Oxide. E. HÖST MADSEN (*Zeitsch. anorg. Chem.*, 1912, **79**, 195—201).—Silver oxide has not hitherto been obtained in a pure condition. A concentrated solution of silver nitrate is precipitated with a dilute solution of sodium hydroxide, and the precipitate is washed with water, previously freed from carbon dioxide. It is then dried at 85—88° in a stream of air free from carbon dioxide. The product contains 1·75% of silver hydroxide (0·125% of water), and about 0·5% of silver carbonate. Some reduction takes place, as, whilst the moist precipitate yields a white chloride with hydrochloric acid, even after exposure to light, the dry solid always yields a red chloride, the colour of which is deeper the higher the temperature of drying.

The oxide dried at 85° is dark brown with a violet shade. At 280° the water is almost completely expelled, but it is not possible to obtain a product of constant weight, as appreciable dissociation of the oxide takes place. C. H. D.

Cement Limestones of Santa Marinella. NICOLA PARRAVANO (*Gazzetta*, 1912, **42**, ii, 610—617).—The paper records analyses of a number of specimens from this district (which lies south of Civitavecchia) carried out to determine the suitability of the stones for the manufacture of Portland cement, and gives the results of tests applied to the cements made from them. R. V. S.

Gelatinous Calcium Sulphate and the Setting of Plaster. CAVAZZI (*Gazzetta*, 1912, **42**, ii, 626—632).—When calcined calcium sulphate is treated with water, a gelatinous calcium sulphate is first formed, which in a few minutes at low temperatures, and more rapidly at higher temperatures, turns into crystals of $CaSO_4,2H_2O$. The gelatinous salt can be observed to crystallise under the microscope, and it is identical with that produced by the addition of alcohol to a supersaturated solution of calcium sulphate. That the setting of plaster is not due to the crystallisation of $CaSO_4,2H_2O$ from a supersaturated solution is shown by the fact that the increase of volume on setting is very much less than that which is found to occur when this salt is allowed to crystallise from a supersaturated solution.

R. V. S.

The Rôle of Calcium Sulphate and Barium Sulphate in the Reduction of Zinc Minerals. EUGÈNE PROST and MAURICE UBAGHS (*Bull. Soc. chim. Belg.*, 1912, **26**, 532—541. Compare A., 1911, ii, 283).—In the presence of silica the sulphates of calcium and barium have a marked influence on the reduction of zinc minerals. They consume a large amount of heat for their decomposition or reduction, and, in the presence of silica, react with it generating sulphurous

vapours, which in contact with the zinc vapour cause the formation of zinc sulphide, which remains in the distillation residue, thus increasing the loss of zinc, the sulphide only being reduced at a much higher temperature. The presence of silica is necessary for the formation of zinc sulphide, as, in its absence, the calcium and barium sulphides formed by the reduction of the corresponding sulphates do not yield their sulphur to the zinc oxide of the roasted blende at the experimental temperature of 1200° (compare *Metallurgie*, 1911, **8**, 763).

W. G.

Glucinum Phosphates, and Glucinum Phosphite and Hypophosphite. BENNO BLEYER and BR. MÜLLER (*Zeitsch. anorg. Chem.*, 1912, **79**, 263—276. Compare A., 1912, ii, 644).—*Monoglucinum orthophosphate*, $GlH_4(PO_4)_2$, prepared from the hydroxide and orthophosphoric acid, forms colourless, hygroscopic leaflets. Diglucinum orthophosphate, $GlHPO_4,3H_2O$, has not been obtained free from adhering phosphoric acid. *Triglucinum orthophosphate*, $Gl_3P_2O_8,6H_2O$, obtained from disodium phosphate, acetic acid, and glucinum sulphate, forms a loose precipitate. A basic *salt*,

$$2Gl_3P_2O_8,GlO,13H_2O,$$

is obtained when trisodium phosphate is used for precipitation.

Potassium glucinum orthophosphate, and also the corresponding sodium and ammonium salts, have only been obtained as precipitates of variable composition. The glucinum phosphates previously described in the literature are mixtures.

Glucinum pyrophosphate, $Gl_2P_2O_7.9H_2O$, is precipitated by means of sodium pyrophosphate. Sodium glucinum pyrophosphate,

$$Gl_2P_2O_7,2Na_4P_2O_7,5H_2O,$$

is a soluble, hygroscopic salt. *Glucinum metaphosphate*, $Gl(PO_4)_2$, forms colourless crystals, and must be prepared in absence of water, otherwise a basic salt is obtained. Glucinum phosphite,

$$4GlHPO_3,GlO,7H_2O,$$

and hypophosphite, $GlH_4P_2O_4$, have also been prepared. C. H. D.

Magnesium Ions as Oxygen Carriers. OTTO HAUSER (*Chem. Zeit.*, 1913, **37**, 58).—The rusting of iron is accelerated by the presence of magnesium ions. In general, reactions which take place with absorption or evolution of oxygen are similarly accelerated. The effect of magnesium ions is best shown in the oxidation of hydrochloric acid or chlorides by permanganate. T. S. P.

Thermal Analysis of Binary Mixtures of Chlorides of Bivalent Elements. IV. CARLO SANDONNINI (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 634—640. Compare A., 1912, ii, 1172).—The present paper deals with the thermal analysis of the systems $MgCl_2$–$SrCl_2$, $MgCl_2$–$BaCl_2$, and $MgCl_2$–$MnCl_2$. The magnesium chloride used contained 1·11% of oxide, which was allowed for in calculating the compositions of the mixtures dealt with.

Magnesium chloride and strontium chloride do not seem to form solid solutions; there is an eutectic corresponding with 535° and 50 mols. % of strontium chloride.

The system $MgCl_2$–$BaCl_2$ is analogous to the system $MnCl_2$–$BaCl_2$ already studied. There is an eutectic corresponding with 36 mols. % of barium chloride and about 556°. Mixtures containing more barium chloride show a pause at 590°, as well as that of the eutectic; if the amount of barium chloride is increased, only this upper pause is observed, but if the amount is still further raised the pause falls again until it coincides with the eutectic. These indications point to the production of a compound decomposing on fusion.

Magnesium chloride and manganese chloride are completely soluble both in the solid and in the liquid state, and mixtures of them melt at temperatures intermediate between those of the constituents.

The author discusses the regularities which may be perceived in the thermal behaviour of the binary mixtures of chlorides of bivalent elements investigated by himself and others. R. V. S.

[Metastable Metals.] E. B. WOLFF (*Zeitsch. Elektrochem.*, 1913, **19**, 19—23. Compare Cohen, A., 1909, ii, 1008).—Polemical. The author shows that an etching solution does not convert a metal, which has been rendered metastable by deformation, into the stable condition. The action is shown to be the removal of the deformed and metastable surface layer with the exposure of the stable underneath layer.

It is also stated in opposition to Cohen (*loc. cit.*) that a metal which has been rendered stable by etching is unable to innoculate other metal which has been subjected to deformation. J. F. S.

[Metastable Metals.] ERNST COHEN (*Zeitsch. Elektrochem.*, 1913, **19**, 23).—Polemical. An answer to Wolff (preceding abstract). J. F. S.

Physico-chemical Studies on Red Lead. JAROSLAV MILBAUER (*Chem. Zeit.*, 1912, **36**, 1436—1437, 1484—1485).—By means of a specially designed apparatus the author has investigated the formation of red lead from lead oxide under oxygen pressures varying from 1 to 12 atmospheres, and at temperatures from 325° to 520°. The results show that the equilibrium is independent of the pressure, but is attained more rapidly with increasing pressure. One hundred % of red lead is formed at 470—480°, the percentages being less above and below this temperature, the time of experiment being in all cases three hours. T. S. P.

The Structural Resolution of the Pure Copper–Zinc β-Constituent into $\alpha+\gamma$. HENRY C. H. CARPENTER (*J. Inst. Metals*, 1912, **8**, 51—58).—The β-constituent of alloys of copper and zinc, which undergoes transformation at 470° during cooling (A., 1912, ii, 764), does not segregate even after annealing for several months at 445°, although the presence of minute quantities of either the α- or γ-constituent brings about segregation much more rapidly. Repeated quenching in liquid air brings about the transitory development of a duplex structure, the nature of which is unknown. Resolution of the β-alloy at 445° is brought about by contact with an $\alpha\gamma$-alloy of copper and zinc containing 0·95% of vanadium. C. H. D.

The Effect of Other Metals on the Structure of the β-Constituent in Copper–Zinc Alloys. HENRY C. H. CARPENTER (*J. Inst. Metals*, 1912, 8, 59—85).—The resolution $\beta \rightarrow \alpha + \gamma$, which takes place in alloys of copper and zinc at 470° (A., 1912, ii, 764), is affected by the presence of other metals in the alloy. Metals which are insoluble in the solid alloy, such as lead and chromium, are without influence, but bismuth has been found in one case to accelerate the resolution Antimony, tin, aluminium, silicon, and vanadium, which enter into solid solution, displace the eutectoid composition to the γ-side, and assist the resolution. Iron has much less effect. Nickel and manganese have little effect. C. H. D.

Copper–Zinc–Nickel Alloys. LÉON GIULLET (*Compt. rend.*, 1912, 155, 1512—1514. Compare A., 1905, ii, 168).—A study of the influence of nickel when added to certain brasses. It is found that the addition of nickel considerably improves their mechanical properties and gives them a "fictitious" proportion of zinc considerably higher than their real proportion (compare A., 1906, ii, 357). W. G.

Constitution of Aluminates. EDWARD G. MAHIN, D. C. INGRAHAM, and O. J. STEWART (*J. Amer. Chem. Soc.*, 1913, 35, 30—39).—The solubility of aluminium hydroxide in alkali hydroxide solutions and the existence of minerals containing the oxides of aluminium and certain other metals in apparently constant proportions have led to the hypothesis that aluminium hydroxide is amphoteric. Most of the investigations on the aluminates have been directed to the determination of their formulæ, and have given varying results; they have also shown that the quantitative relations between the alkali metal and aluminium differ according to the method of preparing the solution. In view of these facts the present work was undertaken in order to ascertain whether the solubility of aluminium hydroxide in alkali hydroxides is not due rather to its colloidal properties than to its amphoteric character.

Measurements of the heat of solution of aluminium hydroxide in solution of sodium hydroxide, a quantitative study of the action of ammonium nitrate on a solution of sodium aluminate, and observations on the behaviour of sodium aluminate on electrolysis have been made. The results indicate that the solubility of aluminium hydroxide in alkali hydroxide solutions depends very largely on its colloidal properties, and that it is doubtful whether aluminates have any existence as definite salts. E. G.

The Heusler Ferromagnetic Alloys of Manganese. FRIEDRICH HEUSLER (*Zeitsch. angew. Chem.*, 1912, 25, 2651—2653).—A claim for priority against Wedekind (this vol., ii, 55). C. H. D.

The Formation of Nitrogen Oxides by Heating Manganese Dioxide in Air. PAUL ASKENASY and E. L. RÉNYI (*Zeitsch. Elektrochem.*, 1913, 19, 23—32).—The statement made by Odier (*J. phys. chim.*, 1798, 464) that oxides of nitrogen are produced when manganese

dioxide is heated in oxygen is investigated. The authors heated natural and artificial manganese dioxide in a current of air at various temperatures. It was found that very small quantities of oxides of nitrogen were evolved, which never amounted to more than 0·2 mg. nitric oxide from 10 grams of manganese oxide. The oxides made their appearance at 280°, but on heating for several hours ceased to be formed. On raising the temperature, a fresh quantity was produced. Above 700° no oxide could be obtained. The authors draw the conclusion that the oxides of nitrogen are not formed from atmospheric nitrogen, since the same results could be obtained by substituting a current of carbon dioxide for that of air. They are of the opinion that the nitrogen is furnished by the manganese dioxide, which probably contains a nitrogen compound to the extent of 0·002%.

J. F. S.

The Passive State of Iron. JAMES MACLEOD-BROWN (*Chem. News*, 1913, **107**, 15).—It is frequently asserted that, if part of an iron nail or wire is rendered passive, the remainder of the nail or wire also assumes this state. That this is not so may be shown as follows: An iron nail, three inches long, is immersed to a depth of one inch in concentrated nitric acid. The nail is allowed to drain, and the other end immersed to a depth of one inch in dilute nitric acid, when it will be found to be active; the passive end remains passive. If the nail is lowered into the dilute nitric acid, passive end first, the whole of it becomes passive after a short time.

Other experiments are described in which it is shown that when a passive iron nail is connected by means of a platinum or copper wire to a nail of ordinary iron, the two nails being immersed in dilute nitric acid, that part of the ordinary iron which dips into the nitric acid becomes passive after a short time, the passivity being produced by anodic polarisation.

The author considers that the passive state is conditioned by some definite arrangement of the particles at the surface of the iron.

T. S. P.

Equilibria in Quaternary Systems. VI. Quaternary Alloys of Iron, Nickel, Manganese, and Copper. NICOLA PARRAVANO (*Gazzetta*, 1912, **42**, ii, 589—609. Compare A., 1912, ii, 1175; this vol., ii, 33, 55, 58).—In the present paper, which does not lend itself to abstraction, the author summarises the results which he has already obtained (*loc. cit.*) in the thermal study of the binary and ternary systems included in the above quaternary system, and referring to a former theoretical discussion of quaternary systems (this vol., ii, 33), he establishes theoretically the characteristics which should be displayed by this quaternary system. The experimental part, which is accompanied by numerous tables, diagrams, and photomicrographs, gives the results of the experimental verification of these theoretical previsions. R. V. S.

Determination of the Atomic Weight of Uranium. WILLIAM ŒCHSNER DE CONINCK (*Compt. rend.*, 1912, **155**, 1511—1512).—A

determination of the atomic weight of uranium by ignition of anhydrous uranyl oxalate, and weighing the residual uranium dioxide. The mean of seven determinations gives the value 238·4 for the atomic weight of uranium. W. G.

The Oxides of Uranium. WILLIAM ŒCHSNER DE CONINCK and ALBERT RAYNAUD (*Bull. Soc. chim.*, 1912, [iv], 11, 1037—1038).—When uranium formate, covered with a layer of methyl alcohol, is exposed to the action of diffused daylight for three months, uranous oxide (UO_2) is deposited and formic acid formed.

When uranous oxide is heated in the air to a bright red heat, the oxide U_4O_{10} is produced. T. S. P.

The Basicity of the Tungsto-acids. HIPPOLYTE COPAUX (*Compt. rend.*, 1913, **156**, 71—75. Compare *Ann. Chim. Phys.*, 1912, [viii], **25**, 22).—The author has determined the conductivity of acids of the type of phosphotungstic acid in very dilute solutions, and from his results deduced the basicity of the acids. Silicotungstic acid is tetrabasic, and even at high orders of dilution is practically unhydrolysed. Its isomeride, tungstosilicic acid, and its isomorph, silicomolybdic acid, are also tetrabasic and not hydrolysed on dilution. Borotungstic acid is pentabasic, this being in agreement with its known sodium, barium, and cadmium salts. Metatungstic acid is hexabasic, but is appreciably hydrolysed in very dilute solutions. Phosphotungstic acid is freely hydrolysed on dilution, and whilst the composition of its ordinary salts and its analogy to other acids point to its being tribasic, the conductivity seems to reach a limit for a basicity of five. Phosphomolybdic acid is tribasic, but in moderately dilute solutions gives values for a tetrabasic acid, seemingly due to hydrolysis of the acid yielding two dibasic acids, which the author suggests is represented by the equation:

$$H_3[P(Mo_2O_7)_6H_4] + 2H_2O = H_2[P(Mo_2O_7)_5(OH)_2H_5] + H_2Mo_2O_7.$$

In general, the composition of the soluble salts of strong bases is a criterion of the basicity of tungsto- and molybdo-acids, and the value so obtained is in accord with that obtained by conductivity methods. Disagreement is a sign of hydrolysis of the acid on dilution. W. G.

The System Tin. ANDREAS SMITS and H. L. DE LEEUW (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 676—681).—The probable existence of a transition point for tin in the neighbourhood of 200° is indicated by a number of observations, and in particular by the experiments of Werigin, Lewkojev, and Tammann (*Ann. Physik*, 1903, [iv], **10**, 147) on the rate of flow of tin under pressure.

The fact that Cohen and Goldschmidt (A., 1905, ii, 168) obtained no evidence of the existence of the transition point in dilatometric experiments is now shown to be due in all probability to the slowness with which the change in question takes place, and new observations with a dilatometer are recorded which indicate that the temperature of the reversible change tetragonal tin $\rightleftarrows$ rhombic tin is 202·8°. Small

quantities of mercury act as a catalyst, but at the same time the transition temperature is depressed

In the presence of 0·12 and 0·22% of mercury, the temperatures obtained by the dilatometric method were 173° and 151° respectively. The occurrence of this change at 202·8° accounts for the brittleness developed when tin is heated to about 200°

The transition temperature of 170° deduced by Cohen and Goldschmidt from the flow experiments referred to above, is based on an erroneous interpretation of the data in question, there being no evidence whatever for the occurrence of any change at this temperature. H. M. D.

The System Tin–Iodine. H. S. VAN KLOOSTER (*Zeitsch. anorg. Chem.*, 1912, **79**, 223–229. Compare Reinders and de Lange, this vol., ii, 60).—Stannous iodide, SnI_2, m. p. 321°, is practically immiscible with molten tin at 400°. Stannic iodide, SnI_4, m. p. 143°, mixes in all proportions with iodine, the eutectic point being at 12 atomic % of tin and 76°. Stannous iodide is only slowly formed from its components, even at 440° in a sealed tube.

Stannous iodide crystallises in ruby-red needles, D_{15}^{15} 5·21. Crystallographic measurements [by F. M. Jaeger] show that the crystals are monoclinic, $a:c=1:0·5911$, $\beta=82°55''$. C. H. D.

Thorium Compounds. FRANZ HALLA (*Zeitsch. anorg. Chem.*, 1912, **79**, 260–262).—A mixture of anhydrous thorium sulphate and magnesium carbonate with a little water yields a sandy precipitate of *basic thorium sulphate*, $ThOSO_4,5H_2O$. The same salt is obtained as a flocculent precipitate by the action of magnesium sulphate on a boiling solution of thorium sulphate or nitrate. The titration of thorium nitrate with potassium hydroxide and phenolphthalein is complete when 3·5 mols. KOH are present for 1 atom Th. With the basic sulphate the hydrolysis proceeds to the same stage:

$$ThOSO_4 : KOH = 1 : 1·75.$$

It is not possible to wash thorium hydroxide free from sulphate by means of dilute ammonia.

The addition of ammonium carbonate to a mixed solution of magnesium chloride and thorium nitrate yields a transparent emulsion, the globules of which change to a hard glass on drying. Magnesium hydroxide and thorium sulphate, or magnesium sulphate and thorium hydroxide, yield an opalescent jelly. C. H. D.

The Preparation of Metallic Vanadium. III. WILHELM PRANDTL and HERMANN MANZ (*Zeitsch. anorg. Chem.*, 1912, **79**, 209–222. Compare A., 1909, ii, 1022; 1910, ii, 1075).—The vanadium obtained by Ruff and Martin (A., 1912, ii, 166) by heating the trioxide with carbon in an electric vacuum furnace is only apparently purer than that obtained by the aluminothermic process, the slag which is always present having been deducted in the course of Ruff's analyses.

The addition of calcium fluoride in the aluminothermic process is not essential. Vanadium pentoxide gives better results than the

trioxide, the higher temperature obtained favouring the elimination of slag. The presence of alkali is harmful, as alkali vanadate passes into the slag, and an excess of aluminium remains. The attempt has been made to remove oxygen from the product by the addition of vanadium hydride, prepared by heating electrolytically disintegrated vanadium in hydrogen at 1000° (Muthmann, Weiss, and Riedelbauch, A., 1907, ii, 781), but a hydride has not been obtained, the increase in weight being due merely to combination with oxygen and nitrogen.

The reduction of vanadium trichloride with sodium in slight excess also yields a product containing about 96% of metal. Aluminothermic vanadium (95%) has D_{20} 5·987, and 96% metal from the chloride and sodium has D_{20} 5·819. C. H. D.

The Annealing of Coinage Alloys. Thomas K. Rose (*J. Inst. Metals*, 1912, 8, 86—125).—The softening of metals and alloys hardened by mechanical treatment takes place at any given temperature at first rapidly and then more slowly, but at temperatures approaching the melting point it is almost instantaneous. The change is accompanied by recrystallisation. The formation of new crystals, at 200° in the case of gold, is too rapid to be accounted for by diffusion. The softening is accompanied by expansion, which is greater in alloys than in pure metals. C. H. D.

Condition of Gold in Gold Quartz. P. P. von Weimarn (*Zeitsch. Chem. Ind. Kolloide*, 1912, **11**, 287—290).—If 0·1 to 1% solutions of sodium auric chloride and sodium silicate are mixed, a clear solution is obtained, which gradually develops a reddish colour, and this changes slowly and finally becomes blue. Coagulation commences after several months, and the microscopic examination of the coagulum has shown a close similarity in structure with that presented by the gold in auriferous quartz. H. M. D.

Some Anomalies Observed in the Assay of Platinum Ores from Ural. H. C. Holtz (*Ann. Chim. Phys.*, 1912, 27, 559—566).—The process employed is briefly as follows: the mineral is treated with *aqua regia*, which leaves a residue composed of sand and a compound of osmium and iridium. The solution is evaporated to dryness, the residue treated with hydrochloric acid, and again evaporated and dried at 130° to reduce the iridium chloride to the ous-state. After dissolving in water, the platinum is precipitated quantitatively by addition of excess of ammonium chloride, and from the filtrate the other metals (iron excepted) are then precipitated by adding a little hydrochloric acid, and a sufficiency of pure zinc.

After weighing, the deposit ("blacks") is treated with dilute nitric acid (1 : 1), which dissolves the palladium and copper. From this solution the palladium is precipitated by means of mercuric cyanide; the excess of mercury is got rid of by ignition, preferably after evaporation with hydrochloric acid, and the copper precipitated finally as copper thiocyanate. Now, on applying the process to a mixture of the chlorides of platinum, iridium, palladium, rhodium, and copper, the

results were quite satisfactory, but when assaying the "Ural ore" the following anomalies were observed.

(1) The "blacks" are not totally dissolved by the nitric acid. (2) The copper oxide (after expelling the excess of mercury) is not completely soluble in hydrochloric acid. (3) The filtrate from the copper thiocyanate is yellow, and gives a dark precipitate on addition of zinc. From further experiments it seems that: (*a*) The oxide of this mysterious substance is insoluble in hydrochloric, nitric, nitrohydrochloric, and sulphuric acid. (*b*) The oxide dissolves in aqueous sodium hydroxide with a yellow colour. This solution remains bright yellow on adding hydrochloric acid, and does not react with potassium iodide; stannous chloride decolorises it. (*c*) When fused with oxidising mixture the oxide is not attacked and a colourless mass is obtained. (*d*) The dark product (3) is reduced to metal by ignition in a current of hydrogen, with slight loss in weight. (*e*) The metal is dissolved by melting with potassium hydrogen sulphate, yielding a brownish-red mass which does not give a white turbidity with water (absence of rhodium). (*f*) It is soluble in nitric acid, and its hydrochloric acid solution is not precipitated by ammonium chloride.

These properties taken in conjunction with similar experiences of other writers lead the author to believe that another unidentified element is present in the Ural ore. L. DE K.

Mineralogical Chemistry.

The Native Elements of the Earth's Crust. VLADIMIR I. VERNADSKI (*Centr. Min.*, 1912, 758—765).—The author reproduces with some modifications and extensions a table from his recent Russian treatise on mineralogy (*Opuit Opisatelnoĭ Mineralogii*, part I, St. Petersburg, 1908). The main headings in this table are: (I) Solid crystalline chemical elements, A, metals, B, metalloids; (II) solid colloidal elements; (III) fluid elements; (IV) gaseous elements. By including such modifications and combinations as α-, β-, and γ-ferrite, α- and β-ferroplatinum, bismuth-gold, etc., this list is extended to 106 minerals found in the state of native elements. The following forty-seven chemical elements as such occur native: Ag, Ar, As, Au, Bi, Br, C, Cd, Cl, Co, Cr, Cu, Fe, H, He, Hg, Ir, I, K?, Kr, Mn, N, Na?, Ne, Ni, Nt, O, Os, P?, Pb, Pd, Pt, Ra?, Ru, S, Sb, Se, Si?, Sn, Ta, Te, Tl, Zn, Xe, thorium emanation and actinium emanation.

L. J. S.

Optical Investigation of Ural Naphtha. MICHAEL A. RAKUZIN (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1737—1738).—A sample of naphtha from Dos-Sor, D^{15} 0·8754, showed distinct dichroism, had a carbonisation constant (K) in benzene (200 mm.) of 3·75—4%, and yielded distillates which were in all cases inactive. The naphtha is regarded as a perfect natural filter-distillate, and the lack of distillate below 150° indicates communication with the atmosphere.

T. H. P.

White Sublimates of the Volcano Chinyero (Canaries). ANGEL DEL CAMPO (*Anal. Fis. Quim.*, 1912, **10**, 431—449).—The sublimates arising from the eruption of November, 1909, are pale yellow, or pure white, crystalline masses interspersed with specks of lava, and consist of ammonium chloride (96·20%), ammonium fluoride (2·45%), ferrous chloride (0·25%), and chlorides of magnesium, aluminium, etc. (0·70%). Spectrographic examination revealed traces of tin, lead, silver, titanium, manganese, sodium, and, perhaps, tantalum. G. D. L.

An Aluminium Arsenate from Utah. FRANK W. CLARKE (*J. Washington Acad. Sci.*, 1912, **2**, 516—518).—A white, amorphous mineral found with orpiment in the Sunshine mine, Mercur district, Utah, gave (anal. by W. F. Hillebrand):

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	SrO.	MgO.	$(K,Na)_2O$.	As_2O_5.
7·08	26·46	0·64	10·29	2·10	trace	0·12	33·82

P_2O_5.	SO_3.	CO_2.	F.	Cl.	H_2O.	Total.
0·94	0·27	0·88	0·21	trace	17·23	100·04

Of the water, 3·22% is lost at 110°, and the remainder below redness. Deducting silica, strontianite, and gypsum, these results correspond with $3(AlO_2H_2)_3AsO_4,3H_2O + Ca_3(AsO_4)_2$ or with

$$Ca_2(AlO_2H_2)_5(AsO_4)_3,5H_2O.$$

Whether the substance is to be regarded as a simple mineral or as a mixture of liskeardite $[(AlO_2H_2)_3AsO_4,5H_2O]$ and berzeliite $[Ca_3(AsO_4)_2]$ is left undecided. L. J. S.

Preslite [=Tsumebite], a New Mineral from Tsumeb, German South-West Africa. VOJTECH ROSICKÝ (*Zeitsch. Kryst. Min.*, 1912, **51**, 521—526).—The mineral was observed in small, emerald-green crystals associated with chessylite, cerussite, calamine, and dolomite. The crystals are imperfectly developed, and appear to be orthorhombic ($a:b:c = 0·977:1:0·879$) with complex twinning; D 6·09, H = $3\frac{1}{2}$. A partial analysis by J. Frejka gave:

PbO.	CuO.	P_2O_5.	H_2O.
65·09	11·97	10·26	not det.

In a postscript it is admitted that this mineral is identical with the recently-described tsumebite of K. Busz (this vol., ii, 65). L. J. S.

Chemical Composition of the Haüynite of the Albanian Hills. NICOLA PARRAVANO (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 631—633).—The mineral has the following composition:

SiO_2.	Al_2O_3.	CaO.	Na_2O.	K_2O.	SO_3.	Cl.	Total.
32·18	27·11	10·26	16·34	0·08	14·10	0·31	100·31

The total being arrived at by deducting 0·07 for oxygen replaced by chlorine. This analysis agrees with the formula suggested by Brögger and Bäckström (A., 1891, 25). R. V. S.

Alunogen and Halotrichite. JOHANNES UHLIG (*Centr. Min.*, 1912, 723—731, 766—776).—A review is given of the literature of these

minerals, and the following formulæ are considered as the most probable: alunogen, $Al_2S_3O_{12},16H_2O$; halotrichite, $FeAl_2S_4O_{16},24H_2O$. A sample of "hair-salt" from a cave in the Waitopu valley in the Rotorua volcanic district, New Zealand, is yellowish-white and finely fibrous. Under the microscope it is seen to consist of a mixture of fibres of halotrichite (with oblique extinction of 38°, and $n = 1·49$) and scales of alunogen ($n = 1·47$). D 1·735—1·899. The following analysis corresponds with 48·30% alunogen, 41·98 halotrichite, with a little free sulphuric acid, etc. The material is soluble in water, and the insoluble residue consists of 0·70 sulphur, 4·15 silicates.

Al_2O_3.	Fe_2O_3.	FeO.	Na_2O.	K_2O.	SO_3.	H_2O.	Insol.	Total.
11·59	1·24	3·26	0·86	0·53	35·43	42·43	4·85	100·19

Microscopical examination of similar materials from other localities shows the frequent intermixture of alunogen and halotrichite, together often with some gypsum. L. J. S.

Analysis of Garnet from Tavolato. G. SIROVICH (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 643—645 *).—Two garnets analysed had the following compositions, respectively:

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	Na_2O.	H_2O.	Total.
I.	36·74	1·04	5·23	21·10	2·21	31·65	0 96	0·38	0·10	99·41
II.	37·88	0·96	5·46	21·13	2·17	31·02	0·84	0·29	0·08	99·83

These correspond with the accepted formula for the composition of this mineral. R. V. S.

Kragerite, a Rutile-bearing Rock from Krageroe, Norway. THOMAS L. WATSON (*Amer. J. Sci.*, 1912, [iv], **34**, 509—514).—This is a medium-grained rock of light colour and granitic texture, consisting mainly of felspar (albite-oligoclase, with some microcline and orthoclase), much rutile, some quartz, and a little ilmenite. It is a rutile-bearing aplite, and was named kragerite by W. C. Brögger in 1904. Analysis I, by J. W. Watson, is of the rock, and II, by W. M. Thornton, of the rutile, D 2·225, isolated from it:

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	Na_2O.	K_2O.	H_2O.	P_2O_5.	S.	Total.
I.	50·52	25·00	13·98	0·49	0·16	0·34	1.05	6·18	1·00	0·50	trace	0·12	99·34
II.*	1·06	97·68	—	—	0·81	—	—	—	—	—	—	—	100·49

* Also Cr_2O_3, 0·39; V_2O_3, 0·55.

L. J. S.

Analytical Chemistry.

Extraction Apparatus. HENRY J. CARY-CURR (*J. Ind. Eng. Chem.*, 1912, **4**, 535).—This apparatus consists of a short metallic spiral-tube reflux condenser, the inlet and outlet tubes of which project through a metal plate which serves the double purpose of a support for

* and *Gazzetta*, 1913, **43**, i, 36—38.

the condenser and a closure for the glass extraction flask. The flask is of somewhat conical form, with a long neck and flat bottom. A porcelain Gooch crucible is suspended from the condenser (in the neck of the flask) by means of platinum wire fastened into two holes bored on opposite sides of its upper rim, and in it is placed the material to be extracted. The whole apparatus is only six inches high and three inches wide. F. M. G. M.

Alundum not Constant in Weight. E. B. FORBES (*J. Ind. Eng. Chem.*, 1912, **4**, 544—545).—It is found that the porous earthenware material "alundum" in use for extraction vessels does not remain of constant weight when heated in contact with water; one of its constituents combines with water, forming a compound which is stable at 160°, but destroyed at considerably below 1000°, whilst a second factor, which results in a gain of weight, is also present.

F. M. G. M.

A Modification of the Frary Electrodynamic Stirring Device. J. M. KNOTE and W. R. WORKE (*J. Ind. Eng. Chem.*, 1912, **4**, 534).—The use of a solenoid in the rapid electrolytic estimation of metals has been proposed by Frary (A., 1908, ii, 68), and the essential improvement now described consists in putting the coil of the solenoid round an iron core, covering the top with a suitable material, and placing the beaker containing the electrolyte on it; whilst the use of electrodes with bent stems fastened to a block which can be raised facilitates inspection during the course of the reaction.

F. M. G. M.

Apparatus for Testing Water by Measurement of its Electrical Conductivity. LEONARD ARCHBUTT (*Analyst*, 1912, **37**, 538—542).—The apparatus described is known as the Digby and Biggs' "Dionic" water-tester, and its usefulness depends on the fact that the conductivity of pure water is extremely small, whilst the presence of any salt, acid, or base, in solution at once increases the conductivity. The water to be tested is filled into a U-tube, the two electrodes being fitted into the tops of the two limbs respectively. The current is supplied by a hand-driven dynamo provided with a constant-speed friction clutch which maintains a constant *E.M.F.* of 100 volts. The current passing through the water is measured by a direct-reading conductivity meter. Boiled distilled water shows a conductivity of about 1·5; distilled water saturated with carbon dioxide, 44; Glasgow (Loch Katrine) water, 34; spring water of 18·4 hardness, 552. The standard temperature of testing is 20°. The author gives results of many experiments, and mentions instances where the apparatus would be of practical use. W. P. S.

Colour Reactions of Hydrogen. JOSÉ GIRAL PEREIRA (*Anal. Fis. Quim.*, 1912, **10**, 370—381).—Hydrogen gas, rapidly at 80°, more slowly in the cold, produces a blue coloration on passing into 2 c.c. of saturated phosphomolybdic acid, 1 c.c. of 1% palladium chloride, and 3 c.c. of water. In the cold the reaction is slower. With 2 c.c. of

10% sodium tungstate, 2 c.c. of glacial acetic acid, and 2 drops of palladium chloride, a blue colour is given similarly, and in both cases finely divided palladium is separated.

The presence of much free strong acid, the use of a saturated solution of phosphomolybdic acid, or the addition of too large a proportion of palladium all retard or reduce the intensity of the reaction.

Carbon monoxide reduces less readily and does not give a pure blue coloration. G. D. L.

Use of Selenic Acid in the Estimation of Bromine Associated with Chlorine in Haloid Salts. FRANK A. GOOCH and PHILIP L. BLUMENTHAL (*Amer. J. Sci.*, 1913, [iv], 35, 54—62).—About 0·07 gram of the mixed salt is distilled in an atmosphere of carbon dioxide with 30 c.c. of water and 5 c.c. of 40% selenic acid, or a mixture of 1·8 grams of sodium selenate and 3 c.c. of dilute sulphuric acid (1 : 1). The vapours are conducted into a relay flask containing 2·5 c.c. of selenic acid and 10—15 c.c. of water, or 0·2—0·3 gram of the selenate and 1—2 c.c. of the dilute sulphuric acid; this flask is placed in an oil-bath heated at 110—115°. The vapour is then absorbed in a special receiver containing 4 grams of potassium iodide dissolved in 250 c.c. of slightly acid water and surrounded by cold water.

When the liquid in the distilling flask has boiled down to about 10—15 c.c., the boiling is stopped; and a moderately strong current of carbon dioxide passed to prevent regurgitation.

The iodine liberated by the bromine set free is then titrated as usual. L. de K.

Preparation of Selenic Acid and Sodium Selenate Used in the Estimation of Bromine in Haloid Salts. PHILIP LEE BLUMENTHAL (*Amer. J. Sci.*, 1913, [iv], 35, 93—96).—Selenic acid is best prepared by oxidising selenium dioxide with nitric acid and potassium bromate. After the bromine liberated has been completely expelled, the solution is made slightly ammoniacal, and precipitated at boiling heat with barium chloride. The precipitate when heated with a calculated amount of sulphuric acid yields selenic acid. Sodium selenate may be prepared by mixing 1 part of selenium with 5 parts of sodium peroxide, and heating this, by degrees, in a nickel crucible. The mass is dissolved in water, evaporated to a pasty condition, and most of the sodium hydroxide removed by extraction with alcohol. The residue, consisting of sodium selenate and carbonate, is dissolved in water and carefully neutralised with sulphuric acid; on evaporation, sodium sulphate crystallises first, then a mixture of this with sodium selenate, which after being dried at 108° is then tested as to its true selenate content.

The salt may also be prepared by fusing barium selenate with an insufficiency of sodium carbonate and recrystallising the product from water. L. DE K.

Oxygen in Brass. THOMAS TURNER (*J. Inst. Metals*, 1912, 8, 248—257).—It is not possible to estimate oxygen accurately in brass by heating in a current of hydrogen. Some zinc is always reduced, volatilised, and again oxidised at a lower temperature by the water

vapour, which thus does not reach the drying tube. This effect is also observed when hydrogen is passed over zinc oxide at 1000°.

C. H. D.

Comparison of Some Methods for the Estimation of Sulphur in Vulcanised Caoutchouc, with Especial Reference to Electrolytic Oxidation. DAVID SPENCE and J. YOUNG (*J. Ind. Eng. Chem.*, 1912, **4**, 413—416).—As a result of the comparison of numerous methods for estimating combined sulphur in caoutchouc with a standard Carius method, a modification of the electrolytic oxidation method introduced by Gasparini (A., 1907, ii, 650) is advocated as being exceedingly accurate, simple, and rapid.

About 0·5 gram of the sample in a 200 c.c. beaker is covered with nitric acid (D 1·4), and gently warmed until solution is complete; about 30 c.c. of nitric acid (D 1·5) are added, and a current of about 3 amperes with a potential of 6—8 volts passed through the solution between electrodes of platinum foil until oxidation is complete (one to four hours).

A diagram of the electrical connexions is given, and the further simplification by introducing a subsequent volumetric process (Pennock and Morton, A., 1904, ii, 206) for estimating the sulphur is discussed in the original.

F. M. G. M.

Estimation of Sulphurous Acid in Sugar Cane and Beetroot Products. HENRI PELLET (*Bull. Assoc. chim. Sucr. Dist.*, 1912, **30**, 337—338).—The apparatus described for the estimation of sulphurous acid in sugar products consists essentially of a cylinder bearing marks which indicate the quantity of sugar solution to be taken for the estimation, the volume of acid, etc., to be added for neutralisation, the quantity of indicator, and the volume of standard iodine solution required to oxidise the sulphurous acid.

W. P. S.

Estimation of Nitrites in Water. MAURICE DUYK (*Ann. Chim. anal.*, 1912, **17**, 445—447).—One hundred c.c. of the water are acidified with 20 c.c. of 10% hydrochloric acid, 4 grams of potassium hydrogen carbonate are added in small quantities at a time, a crystal of potassium iodide is then introduced, and, after the further addition of 1 gram of potassium hydrogen carbonate, the liberated iodine is titrated with thiosulphate solution. The addition of the potassium hydrogen carbonate is for the purpose of expelling air from the water and vessel in which the experiment is carried out; the liberated nitric oxide is also expelled, and there is, therefore, no risk of the latter combining with oxygen and reacting further with the potassium iodide.

W. P. S.

Detection of Nitric Acid in Presence of Nitrous Acid. V. N. IVANOV (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1772—1775*).—As little as 0·0001 gram of nitric acid may be detected in presence of one hundred times as much nitrous acid by the blue coloration which it yields with a quadrivalent iridium compound. The reagent may be prepared conveniently from 0·025 gram of iridium in the form of

* and *Chem. Zeit.*, 1913, **37**, 157.

iridichloride or dioxide, which is dissolved in 3—5 c.c. of water, 100 c.c. of concentrated sulphuric acid (98—99%) being then added to the solution with constant stirring. The liquid is heated to boiling to decolorise it, and when cold is stored in a well-stoppered bottle. It should contain 96—96·5% of sulphuric acid.

To make a test, 5 c.c. of the reagent are heated to incipient boiling, and the substance to be tested, which must be in the solid state, quickly added. If, for example, a water is to be examined, it is first evaporated to dryness with a slight excess of alkali. The test-tube is not heated while the substance is being added, owing to the danger of converting the nitrous acid into nitric acid; on the other hand, if the reagent is insufficiently heated, a yellow and not a blue coloration is obtained.

With a large amount of nitrous acid, a coloration may appear after a time as a result of the reaction between nitrogen peroxide and water-vapour: $N_2O_4 + H_2O = HNO_3 + HNO_2$. By means of a tube fitted with a ground stopper and with two side-tubes for the passage of a current of carbon dioxide, the gas formed is rapidly removed and satisfactory results are obtained. T. H. P.

Analysis of Mixtures of Nitric Acid, Carbamide, and Water. A. MASSINK (*Chem. Weekblad*, 1912, **9**, 1000—1002).—To estimate nitric acid in presence of carbamide, the author titrates with potassium hydroxide and methyl-orange. The carbamide is estimated by evaporating the neutralised liquid to dryness, removing the last traces of water by repeated evaporation with 96% alcohol, and weighing the residual carbamide and potassium nitrate. The amount of nitrate present in the mixture is calculated from the volume of alkali employed in the titration. The method is rapid and accurate.

A. J. W.

Detection and Estimation of Free White Phosphorus in Phosphorus Sesquisulphide. THEOPHILE SCHLŒSING, jun. (*Compt. rend.*, 1912, **155**, 1461—1464).—The phosphorus sesquisulphide is shaken for several minutes with sufficient light petroleum (b. p. $<45°$) to dissolve any free phosphorus present, the liquid quickly filtered, and an aliquot portion taken and quickly evaporated in a vacuum at 15—20°. The residue is oxidised with nitric acid, and the sulphur and phosphorus estimated according to Berger's method (compare A., 1907, ii, 129). In order simply to detect the presence of phosphorus, the residue, after evaporating off the petroleum, is shaken with some fine sand in a flask in the dark and carefully examined for any phosphorescent glow, which is given by minute traces of free phosphorus. W. G.

Reduction of Manganese Dioxide by Nitrous Acid. Application of this Reaction in the Estimation of Phosphorus in Iron and Steel without Separation of Silicon. EUGEN R. E. MÜLLER (*Chem. Zeit.*, 1912, **36**, 1490).—A slight modification of the author's process described previously (A., 1911, ii, 1132).

Instead of reducing the manganese dioxide formed by means of sodium peroxide, 0·5 c.c. of absolute alcohol and 1 c.c. of 10% sodium

nitrite are added, which causes the liquid rapidly to clear. After adding 1 c.c. of ammonia and boiling for a short time, the solution is ready for the molybdate precipitation. L. DE K.

The Estimation of Phosphorus in Lecithin. PAUL FREUNDLER (*Bull. Soc. chim.*, 1912, [iv], **11**, 1041—1043).—Two to three grams of lecithin are heated with 50 c.c. of fuming nitric acid in a 500 c.c. flask on a water-bath. After two to three hours the reaction stops; 25—30 c.c. of water are then added, and 25—35 grams of finely powdered permanganate in portions of one gram at a time. When the oxidation is complete, the solution is diluted to 150—200 c.c., the manganese dioxide dissolved with sodium nitrite, and the whole evaporated to a syrup to expel the excess of acid. The phosphorus is then precipitated, without it being necessary to filter the liquid, with ammonium molybdate in the presence of ammonium nitrate, and estimated in the usual way. The method is accurate and preferable to that described by Bordas (A., 1902, ii, 587). T. S. P.

Accurate Volumetric Estimation of Phosphoric Acid in Phosphate Rock. JOHN G. FAIRCHILD (*J. Ind. Eng. Chem.*, 1912, **4**, 520—522).—A modification of Pemberton's (*Pharm. Zentr.-h.*, 1911, **50**, 1288) method of estimating phosphoric acid by titration with alkali hydroxide in which Sutton's (*Volumetric Analysis*) suggestion of first precipitating the phosphoric acid with barium chloride is carried out. This method is claimed to be accurate and very rapid, as, after allowing twenty minutes for the solution of the rock, about one hour is needed to finish the experiment. F. M. G. M.

Use of "Activated" Aluminium in the Detection of Arsenic. ÉMILE KOHN-ABREST (*Ann. Falsif.*, 1912, **5**, 384—388. Compare A., 1912, ii, 768).—The hydrogen required in the Marsh test for the detection of arsenic may be obtained by the action of water on activated aluminium foil, and the following method of carrying out the test is recommended: Four grams of aluminium foil in small pieces are cleaned with nitric acid, and then immersed for three or four minutes in 25 c.c. of a 1% mercuric chloride solution. The pieces of foil are now washed with water and introduced, together with 220 c.c. of water, into the flask of the Marsh apparatus. At the end of about two hours, the solution to be tested for arsenic is added; the latter solution should be neutral in reaction and measure about 20 c.c. W. P. S.

Detection and Estimation of Arsenic in the Earth of a Cemetery. GINO ZUCCÀRI (*Gazzetta*, 1912, **42**, ii, 633—638).—In view of the fact that in cases of suspected poisoning it has been suggested that arsenic may have reached a corpse from the soil of the cemetery in which it was buried, the author has made experiments on the soil of a cemetery known to contain arsenic. From samples of the soil, extracts were made with water, aqueous ammonia (1%), aqueous sodium carbonate (1%), and sulphuric acid. In all these extracts small quantities of arsenic could be detected by Bressanin's method (*Atti R.*

Ist. Ven. S. L. A., 1911, **70**, 951), the organic matter being previously removed by Breteau's method (A., 1911, ii, 226). R. V. S.

Estimation of Arsenic in Pyrites. E. SCHÜRMANN and WILHELM BÖTTCHER (*Chem. Zeit.*, 1913, **37**, 49—51).—Three grams of the sample are heated in a reflux apparatus with 12 grams of chromic acid and 30 c.c. of dilute sulphuric acid (1 : 1) for four hours at boiling heat. When cold, 50 c.c. of water are added, and then 1·1 gram of cuprous chloride. After further addition of two grams of potassium bromide and 100 c.c. of fuming hydrochloric acid, the arsenic is distilled off in a current of hydrogen chloride and collected in an Erlenmeyer flask containing 150 c.c. of water and cooled by means of ice and salt. When two-thirds of the liquid has distilled over, the arsenic has generally passed over completely. This reduction with cuprous chloride is preferable to the use of sulphur dioxide.

The arsenic is now precipitated as sulphide by means of hydrogen sulphide. This is then converted in the usual manner into silver arsenate. To effect complete precipitation, the authors add a little ammonium acetate so as to remove free nitric acid, or the sulphide may be converted into arsenious acid, which is then titrated with iodine. L. DE K.

Phenolphthalein as a Double Indicator in the Estimation of Carbon in Castings, Steel, and Alloys by Direct Combustion. P. BRÈS (*Mon. Sci.*, 1912, [v], **2**, 501—502).—The carbon dioxide obtained in the ordinary combustion process is absorbed in a U-tube, one limb of which is filled with a mixture consisting of soda-lime, 80 grams, sawdust, 20 grams, potassium hydroxide solution, D 1·18, 20 c.c., and phenolphthalein, 0·3 gram. This mixture is colourless, but a red coloration develops as the carbon dioxide is absorbed by the soda-lime, and the course of the absorption may thus be observed. The other limb of the U-tube is filled with calcium chloride to prevent loss of moisture from the first limb. Any escape of unabsorbed carbon dioxide may be detected by subsequently passing the gases through a solution containing 1 part per 100,000 of potassium hydroxide and a small quantity of phenolphthalein; 10 c.c. of this solution are decolorised by as little as 0·0002 gram of carbon dioxide.

W. P. S.

Phenolphthalein as an Indicator of the Presence of Sodium Carbonate in Sodium Hydrogen Carbonate. R. RICHTER. (*Pharm. Zeit.*, 1912, **57**, 998—999).—According to the author, phenolphthalein is an untrustworthy indicator for the detection of sodium carbonate in sodium hydrogen carbonate, as the latter itself exhibits an alkaline reaction when the indicator is concentrated. At the same time, the presence of less than 4% of the normal carbonate in the hydrogen carbonate does not produce a pink coloration when the solution of the salt is treated with a small quantity of phenolphthalein (0·2 c.c. of a 0·05% solution). W. P. S.

The Use of Potassium Palmitate in Water Analysis. CARL J. BLACHER, P. GRÜNBERG, and M. KISSA (*Chem. Zeit.*, 1913, **37**, 56—58).—When potassium stearate is used in water analysis (compare Blacher and Jacoby, A., 1908, ii, 897), certain side reactions occur which are objectionable. The authors consequently recommend the use of potassium palmitate, and give the following directions for determining the temporary and permanent hardness of water. The carbonates are first titrated with $N/10$-hydrochloric acid, using dimethylaminoazobenzene as indicator, the carbon dioxide being removed by a current of air. The slight excess of acid is then neutralised with $N/10$-alcoholic potassium hydroxide, using phenolphthalein as indicator, and the total hardness is determined by titrating with $N/10$-potassium palmitate until the liquid turns decidedly red. When the water contains salts of weak acids, the neutral points of the two indicators are divergent, and the number of c.c. of alcoholic potassium hydroxide used give a measure of the content of the water with respect to these weak acids.

The estimations of sulphates and magnesium are carried out in a manner similar to that described for potassium stearate (*loc. cit.*).

T. S. P.

Quantitative Separation of Calcium and Strontium. RAMÓN LLORD Y GAMBOA (*Anal. Fis. Quim.*, 1912, **10**, 389—394).—In the author's experience the indirect method of estimation by precipitation of the oxalates, conversion into carbonates, and determination of carbonic anhydride, yields more accurate results than either of the direct separations, by means of the nitrates with ether-alcohol or by means of ammonium sulphate. G. D. L.

Qualitative Separation of Barium, Strontium, and Calcium. J. L. M. VAN DER HORN VAN DEN BOS (*Chem. Weekblad*, 1912, **9**, 1002—1003. Compare *ibid.*, 5).—To detect barium, strontium, and calcium, the mixed carbonates are dissolved in dilute acetic acid, the solution boiled to expel carbon dioxide, and diluted with water. Ammonium acetate is added, any precipitate formed being filtered off, and the barium precipitated quantitatively by addition of ammonium dichromate to the boiling solution. The cold filtrate is made slightly ammoniacal, and the strontium chromate precipitated by addition of 96% alcohol. The presence of calcium in the filtrate can be detected by addition of ammonium oxalate. The method is rapid and accurate, and can also be applied to the quantitative separation of the metals.

A. J. W.

Estimation of Lead in Tin. L. VANNIER (*Ann. Falsif.*, 1912, **5**, 477—478).—For the estimation of small quantities of lead in tin it is recommended that exactly 1 gram of the metal be dissolved in nitric acid, and the metastannic acid separated in the usual way. The filtrate from the metastannic acid is then diluted to 200 c.c., and 20 c.c. of this solution are treated with 1 c.c. of a 40% potassium iodide solution. If less than 0·5% of lead is present in the metal, the mixture will remain clear; 0·6% of lead will cause a precipitate of lead iodide to separate within five minutes, whilst 0·8% yields a

large quantity of precipitate. The quantity of lead may be estimated by comparison with solutions containing known amounts of lead.

W. P. S.

Use of Meyer's Reagent. UMBERTO PAZIENTI (*Boll. chim. farm.*, 1912, 51, 661—666).—The author confirms the statement of Tixier (*Bull. sci. pharm.*, 1910, 82), that the oxidation of phenolphthalin to phenolphthalein (which is the basis of the action of this reagent) is shown by water containing very slight traces of copper (one part in one million), but the reaction is entirely prevented by the addition of 0·001 gram-mol. of hydrogen cyanide. The author suggests a possible mechanism for the reaction with copper salts, which is apparently an example of catalysis involving the formation of intermediate substances. The sensitiveness of the reagent towards copper salts depends on circumstances: 0·01—0·001% of copper sulphate causes almost instantaneous oxidation of the phenolphthalin without the intervention of hydrogen peroxide, whilst when the solutions contain 0·0001—0·00001%, the oxidation is very slow unless hydrogen peroxide is added. The maximum dilution at which copper can be detected with the reagent (hydrogen peroxide being also added) is 0·000001%, and it is thus much more sensitive than other tests for copper. Manganese, cobalt, lead, iron, platinum, and various inorganic and organic compounds also affect the reagent, which was originally suggested as a test for blood. Discussing its value for the last-named purpose, the author is of opinion that it may be used to detect blood in urine, if the latter is first "defæcated" to remove any substances which might interfere with it.

R. V. S.

A Case of Mercurial Poisoning, and the Estimation of Mercury in Textile Materials. LORENZO L. LLOYD and WALTER M. GARDNER (*J. Soc. Chem. Ind.*, 1912, 31, 1109—1111).—Cases of mercurial poisoning having occurred recently amongst the operatives in a hat factory, the authors have investigated the matter and record the results obtained. The source of the mercury was not far to seek, since the great bulk of the rabbit and other fur constituting the raw material used in the manufacture of hats is treated with an acid solution of mercuric nitrate by the fur dealers. Although much of the mercury is removed in the processes which the furs undergo, considerable quantities remain in the finished product; at the same time, portions of the mercury compounds volatilise during the operations, and the vapours may be inhaled by the workers. A hat which had been in use for about twelve months was found to contain 0·0015% of mercury. For the detection of mercury in textile materials, a portion of the latter is treated with dilute *aqua regia*, a slight excess of zinc dust is added, and the mixture is submitted to distillation with superheated steam at a temperature of 160°; the volatilised mercury is collected on a piece of copper gauze placed in the condenser. The gauze is then dried, and heated in a tube which is drawn out to a capillary, the mercury globules collecting in the latter being then identified by the iodine test. The quantity of mercury present may be estimated by extracting the material with dilute *aqua regia*, rendering

the extract slightly alkaline by the addition of sodium hydroxide, precipitating the mercury as sulphide, and then adding acetic acid. The mercury sulphide is collected on a filter, washed with water and nitric acid, and dissolved in *aqua regia*. This solution is neutralised and treated with a solution containing 0·2 gram of potassium iodide, 6 grams of sodium hydroxide, and 2 grams of ammonium chloride per 100 c.c., the coloration obtained being compared with that produced by known amounts of mercury. A kaolin filter for collecting the mercury sulphide is described. W. P. S.

Estimation of Manganese by the Bismuthate Method. HARRY F. V. LITTLE (*Analyst*, 1912, **37**, 554—557).—The author records results which show that this method (compare A., 1902, ii, 107) is trustworthy in the case of both small and large amounts of manganese. The theoretical factor should be employed for calculating the quantity of manganese present, and the author prefers to dilute the oxidised solution, before titration, with an equal volume of 3% nitric acid. W. P. S.

The Estimation of Total Manganese in Soils. ROSS A. GORTNER and CLAYTON O. ROST (*J. Ind. Eng. Chem.*, 1912, **4**, 522—524).—It is found that the methods of Marshall (A., 1901, ii, 350) and Walters (*Chem. News*, 1901, **84**, 239), as described by Washington and Hillebrand (*The Chemical Analysis of Rocks*; and *Bull.* **422**, U.S. Geol. Survey) for the estimation of manganese are not applicable to Nebraska soils, and the following modification is found to give accurate results.

The soils are fused with sodium carbonate, the solution of the fused mass acidified with sulphuric acid, and oxidised with sodium bismuthate, thus converting the whole of the manganese into permanganic acid, which is then estimated colorimetrically by comparison with a standard solution of permanganic acid prepared by the reduction of potassium permanganate with sulphurous acid and subsequent re-oxidation with bismuthate. F. M. G. M.

Manganese and Phosphoric Acid Content of Honeys. ARTHUR GOTTFRIED (*Pharm. Zentr.-h.*, 1912, **53**, 1440—1443. Compare A., 1911, ii, 823).—The author has determined the amount of ash, and the phosphoric acid and manganese contained therein, of a number of honeys and honey substitutes and tabulated the results. These prove that the composition of the ash of honey differs widely, and this is particularly so as regards the amounts of manganese and phosphoric acid. Whether these variations are due to the different origin of the honeys is a matter for future research. L. DE K.

Estimation of Iron in Waters. EUGENE TASSILLY (*Bull. Soc. chim.*, 1913, [iv], **13**, 34—37. Compare Rosenheim and Cohn, A., 1901, i, 455; Oerum, A., 1904, ii, 449; Stokes and Cain, A., 1907, ii, 581).—The author finds that on examining solutions of ferric salts to which potassium thiocyanate has been added by Féry's spectrophotometer, (1) the absorption of light becomes constant for a definite

quantity of iron when the salts are present in the proportion

$$FeCl_3 : 11(KCNS)_3;$$

(2) the maximum absorption takes place in the bluish-violet, but the maximum sensitiveness is in the green, and (3) in presence of great excess of the thiocyanate the absorption, as measured by the instrument, is proportional to the amount of iron in the coloured solution.

The estimation is made by heating 100 c.c. of the water with 20 c.c. of hydrochloric acid and 0·5 to 1 gram of potassium chlorate until chlorine is no longer evolved. On cooling, 20 c.c. of thiocyanate solution (1·7%) are added, the volume is made up to 100 c.c., and the solution examined in the spectrophotometer, the percentage of iron being determined by reference to a curve prepared from data obtained by the examination of iron solutions of known strength. If a precipitate forms, this is dissolved in hydrochloric acid and added to the liquid, which is then evaporated to 100 c.c. if necessary.

T. A. H.

Estimation of Traces of Iron in Cane and Beet Sugar Factory and Refinery Products. JOHN J. EASTICK, JAMES P. OGILVIE, and JAMES H. LINDFIELD (*Internat. Sugar J.*, 1912, **14**, 428—435).—The sulphide colorimetric method described by Winkler (A., 1903, ii, 108) is recommended for the estimation of iron in sugar and sugar products. The process may be applied directly to sugar solutions or to the ash obtained from them. The standard iron solution used for comparison should be prepared from ferrous sulphate, and it has been found that if, instead of water alone, a 50% sucrose solution is employed for the preparation of this solution, the latter will keep almost indefinitely. W. P. S.

Rapid Estimation of Chromium in Chrome Mordants. S. JAKUBOWSKI (*Färb. Zeit.*, 1912, **23**, 415—416).—The estimation of chromium can be rapidly and conveniently effected by first oxidising it to chromic acid, treating with potassium iodide, and subsequently titrating with sodium thiosulphate in acid solution.

The following oxidising agents can be employed, hydrogen or sodium peroxides or sodium percarbonate in alkaline solution. F. M. G. M.

Estimation of Stannous Chloride and of Chlorates by means of Methylene-blue. FREDERICK W. ATACK (*J. Soc Dyers*, 1913, **29**, 9—10).—The process is based on the fact that, in presence of a sufficiency of free hydrochloric acid, stannous chloride has a quantitative reducing action on methylene-blue.

About 1·4 gram of the salt are dissolved up to 250 c.c. in dilute hydrochloric acid (1 : 1), and 25 c.c. are then titrated with $N/50$-methylene-blue (about 4 grams per litre) until the blue colour persists. This solution is checked as follows: About 0·7 gram of the pure metal is dissolved in 50 c.c. of dilute hydrochloric acid (1 : 1) and made up with air-free water to 250 c.c., 25 c.c. are withdrawn, 25 c.c. of hydrochloric acid are added, and titrated in a current of carbon dioxide with the methylene-blue solution. The result is not affected by the presence of antimony.

Chlorates may be estimated indirectly by this method by adding excess of stannous chloride and warming the solution in a current of carbon dioxide. When cold, an equal volume of hydrochloric acid is added, and the excess of stannous chloride titrated as directed. L. DE K.

A Volumetric Method for the Estimation of Thorium in the Presence of Other Rare Earths. The Analysis of Monazite Sand. FLOYD J. METZGER and F. W. ZONS (*J. Ind. Eng. Chem.*, 1912, 4, 493—494).—When an excess of ammonium molybdate solution is added to a cold acetic acid solution of a thorium salt, the thorium is precipitated quantitatively as molybdate. Other rare earths, such as cerium, lanthanum, neodymium, praseodymium, erbium, yttrium, and gadolinium give no precipitate under similar conditions.

The ratio of thorium to molybdenum indicates that the precipitate is a normal thorium molybdate.

As indicator, diphenylcarbazide (the solution of which must have been prepared at least two weeks previously) is employed, being used "outside" on a white tile, and at the end of the titration furnishes a pink colour which lasts about fifteen seconds and requires some experience to identify.

The analysis is carried out as follows: About 1 gram of monazite sand is treated with 10—15 c.c. of concentrated sulphuric acid in a porcelain crucible, and, after several hours' heating, carefully transferred to about 700 c.c. of cold water and left overnight; the solution is filtered, the filtrate nearly neutralised with dilute ammonium hydroxide, followed by the addition of 50 c.c. of a cold saturated solution of oxalic acid, and again left overnight.

The mixed oxalates are collected, washed with dilute oxalic acid, transferred to a beaker, and boiled with 20—25 c.c. of a concentrated solution of potassium hydroxide, diluted, the precipitate of rare earth hydroxides collected, washed, redissolved in hot dilute nitric acid, and evaporated to dryness several times with small quantities of water to remove free nitric acid. The dry residue is treated with 20 c.c. of glacial acetic acid, 300 c.c. of water and 1 gram of sodium acetate, and, when completely in solution, titrated with standard ammonium molybdate solution. F. M. G. M.

Analysis of Bismuth Subnitrate. MAURICE FRANÇOIS (*J. Pharm. Chim.*, 1912, [vii], 6, 536—542; *Ann. Falsif.*, 1912, 5, 569—573).—To determine whether a sample of bismuth subnitrate contains an admixture of oxide, it is recommended that the results of analysis should be calculated into percentages of water, bismuth oxide, and nitrogen pentoxide. For the pure substance, the ratio of the percentage amounts of nitrogen pentoxide to bismuth oxide (Bi_2O_3) should be 1 to 4·296. The authors find that commercial bismuth subnitrate frequently contains less water than the quantity mentioned in the French Codex, namely, 5·8%. W. P. S.

New Apparatus for the Examination of Mine Air. LEONARD A. LEVY (*J. Soc. Chem. Ind.*, 1912, 31, 1153—1155).—For

the combustion of small quantities of methane in the estimation of this gas in air, the author uses a silica capillary containing a platinum wire. The silica tube is about three inches long, and has a diameter of 1 mm., whilst the platinum wire is one inch in length, and is stretched axially in the middle of the tube; a spring at one end of the platinum wire prevents the latter from touching the sides of the tube when it is heated. The wires supplying the electric current are fused into the ends of the silica tube, and the platinum wire is heated to a white incandescence during the passage of the gas through the apparatus. The gas is admitted through a capillary side-tube near one end of the platinum wire, and a capillary side-tube near the other end is provided for the exit of the gas. Two portable forms of apparatus are described for the estimation of methane and carbon monoxide, etc., respectively, in mine air. W. P. S.

The Estimation of Benzene in Coal Gas. ELLEN S. McCARTHY (*J. Gasbeleuchtung*, 1912, **55**, 891—892).—A description of the method of estimating benzene in coal gas by means of the additive compound formed with ammoniacal nickel cyanide (compare A., 1903, i, 469). F. M. G. M.

Estimation of Methyl Alcohol in Spirits. JOSEF HETPER (*Zeitsch. Nahr. Genussm.*, 1912, **24**, 731—737).—In the method proposed, the quantity of methyl alcohol is estimated by oxidation with permanganate in phosphoric acid solution; 1 gram of methyl requires 187·5 c.c. of *N*/1-potassium permanganate solution, and 1 gram of ethyl alcohol 87 c.c. of this solution for complete oxidation. The spirit under examination is distilled, and the distilate is either diluted or concentrated by further distillation until it has D 0·910 to 0·925; between these limits, solutions of either methyl or ethyl alcohols have the same density, and the quantity of total alcohol present may be found by reference to tables. A weighed portion of about 1·5 c.c. of this alcoholic solution is then diluted to 200 c.c., and 10 c.c. are introduced into a flask containing 30 c.c. of *N*/2-permanganate solution (containing 40 grams of crystallised phosphoric acid per litre) and 60 c.c. of water. The flask is then heated on a water-bath in a reflux apparatus for two hours. After cooling, the excess of permanganate is titrated with oxalic acid solution, and the amount of methyl alcohol calculated from the quantity of permanganate reduced. The method cannot be applied to spirits containing large quantities of furfuraldehyde or ethyl acetate. W. P. S.

The Bromine and Iodometric Methods for the Volumetric Estimation of Cresol. C. M. PENCE (*J. Ind. Eng. Chem.*, 1912, **4**, 518—520).—A description of experiments from which the author draws the conclusion that the usual bromine methods for the estimation of cresols depend on certain fixed conditions, presupposing a previous knowledge on the part of the operator which renders them undesirable. Tribromo-*o*- and tribromo-*p*-cresols cannot be formed in an analogous manner to 2:4:6-tribromophenol, but *m*-cresol can be estimated by conversion into tribromo-*m*-cresol. *o*- and *p*-Cresols form

di-iodo-compounds, and this can be made the basis of a method for their estimation, but *m*-cresol does not combine quantitatively with iodine.

F. M. G. M.

The Behaviour of Blood-Sugar in Normal and Pathological Cases. I. The Technique of the Estimation of Sugar in Blood. FR. ROLLY and FR. OPPERMANN (*Biochem. Zeitsch.*, 1913, **48**, 50—63).—Details are given of the experimental methods for separation of the proteins, for which the dialysed iron hydroxide method of Michaelis and Rona forms the basis, and for estimation of sugar in the protein-free filtrate by Bertrand's method. S. B. S.

Analysis of Cane Molasses. Study of the Different Methods of Estimating Sucrose. C. FRIBOURG (*Bull. Assoc. chim. Sucr. Dist.*, 1912, **30**, 312—327).—The following results were obtained by using different methods for the estimation of sucrose in a sample of molasses: Direct polarisation, after clarification with basic lead acetate, 35·90%; with normal lead acetate and calcium hypochlorite, 33·93%. Double polarisation, with basic lead acetate, 42·58%; with normal lead acetate, 41·86%. Fehling's gravimetric method, 41·44%. Double polarisation, after treatment with carbamide and hydrochloric acid, 41·52%; after treatment with sulphurous acid, 41·62%. Direct polarisation after the reducing sugars had been destroyed by means of hydrogen peroxide, 41·65%; double polarisation of this solution showed 41·57%, whilst Fehling's method yielded 41·32%. The invertase method gave 41·36%. Excluding the results obtained on solutions clarified with basic lead acetate, the average of the other figures was 41·54%. The difference between the amount of sucrose actually present and that found by the direct polarisation emphasises the necessity of employing the more trustworthy methods which are mentioned. W. P. S.

Estimation of Sugar in "Bagasse" and in Sugar Cane. Estimation of Water in "Bagasse." HENRI PELLET (*Bull. Assoc. Chim. Sucr. Dist.*, 1912, **30**, 305—312).—The total sugar may be estimated by treating a weighed portion of the substance with small quantities of calcium hydroxide and sodium carbonate, and extracting it with successive quantities of hot water. The solution thus obtained is clarified with basic lead acetate, and examined in the polarimeter. The small quantity of sugar which remains in the "bagasse" after this extraction is estimated in the liquid which is recovered from the moist mass by pressure. An alternative method consists in heating the "bagasse" with water in a closed vessel, and, after cooling, separating the solution by decantation and pressure; this solution is then clarified with basic lead acetate, and polarised. The method is suitable for the estimation of sugar in sugar cane provided that the latter is finely-divided previously. The moisture in "bagasse" may be estimated by heating 50 grams of the sample in a wire-gauze basket to a temperature of 110° until no further loss in weight takes place.

W. P. S.

Polarimetric Estimation of Sugar in Beetroots, using the Cold and Hot Extraction Methods of Pellet. HENRI PELLET (*Bull. Assoc. chim. Sucr. Dist.*, 1912, **30**, 328—333).—Results of experiments are recorded which show that exactly the same figures are obtained, whether the beetroots are treated by the cold diffusion or by the hot digestion methods for extracting the sugar. W. P. S.

Determination of the Polarisation of Beetroot Sugar Products by Double Polarisation. Comparison between the Carbamide–Hydrochloric Acid and Sulphurous Acid Methods. HENRI PELLET (*Bull. Assoc. chim. Sucr. Dist.*, 1912, **30**, 335—337).—The double polarisation method, using for the direct polarisation a sugar solution containing carbamide and hydrochloric acid, yields lower results than is the case when the sugar solution is treated with sulphurous acid. This is due to the action of the hydrochloric acid on the sugar. The carbamide method yields about 0·25% less sugar than the sulphurous acid method in the case of beetroot juice containing 20% of sugar, whilst with raw sugar the difference between the two methods amounts to 2·5% of sugar. A similar difference is obtained in the case of molasses, and the carbamide method cannot, therefore, be considered as trustworthy. W. P. S.

The Gelatinising Temperature of Starch Grains. MAX NYMAN (*Zeitsch. Nahr. Genussm.*, 1912, **24**, 673—676).—Various starches were found to gelatinise at slightly different temperatures when mixed with water and heated gradually, for instance, rye starch gelatinised at 57°, barley starch at 58°, and wheat starch at 59°. The gelatinising point was taken as being the temperature at which the starch grains ceased to polarise light when examined under the micropolariscope. The larger starch grains gelatinised more quickly than the smaller. It was also found that the starches gelatinised at different rates when maintained at a temperature a few degrees below the actual gelatinising point. At 53°, rye starch is gelatinised completely in six minutes, whilst wheat starch requires twenty-four minutes. This difference may afford some slight means of identifying these two starches in mixtures of the same, as any ungelatinised grains remaining after about seven minutes' heating at 53° would indicate the presence of wheat starch. W. P. S.

New Method of Estimating Glycogen in the Liver. HENRI BIERRY and (Mme.) Z. GATIN-GRUZEWSKA (*Compt. rend.*, 1912, **155**, 1559—1561).—A rapid method of estimating glycogen in liver. Twenty-five grams of the liver are crushed and heated to solution on a water-bath with 25 c.c. of 35% aqueous potassium hydroxide. The solution is then heated in an autoclave at 120° for half an hour, cooled, and neutralised with hydrochloric acid. Five c.c. of hydrochloric acid (D 1·18) are added, the liquid made up to 100 c.c., and again heated in the autoclave at 120° for half an hour. After cooling, it is neutralised with sodium hydroxide, the proteins precipitated by mercuric nitrate, the solution made up to 300 c.c., filtered, and the dextrose estimated in the filtrate by Bertrand's method. The

results so obtained were, in all cases, higher than those given by Pflüger's method, but the difference was shown not to be due to the formation of *l*-xylose by hydrolysis of nucleo-proteins in the liver.
W. G.

The Estimation of Cellulose in Wood and Spinning Fibres. Charles F. Cross and Edward J. Bevan (*Zeitsch. Farb. Ind.*, 1912, **11**, 237—238).—Polemical, a further reply to König and Hühn (A., 1912, ii, 1105).
F. M. G. M.

Detection of Formic Acid in Fruit Products. F. L. Shannon (*J. Ind. Eng. Chem.*, 1912 **4**, 526—528).—The formic acid is isolated by steam distillation, the volume of liquid reduced by evaporation (after neutralisation with sodium hydroxide), and the formic acid either reduced to formaldehyde with magnesium and dilute sulphuric acid, or converted into the lead salt which is readily identified by its crystallographic habit.
F. M. G. M.

Estimation of Acetyl Groups. Wilhelm Normann (*Chem. Rev. Fett. Harz. Ind.*, 1912, **19**, 205—206).—The following method for the estimation of acetyl groups can be completed in about two hours. Two grams of the accurately weighed fat or oil are acetylated by boiling with 4—6 c.c. of acetic anhydride during 0·5—1 hour, and the excess of acetic anhydride expelled by heating in a stream of a neutral gas such as hydrogen or carbon dioxide. The acetyl groups are then eliminated by the action of standard alcoholic potassium hydroxide, and the excess of alkali subsequently titrated with a standard solution of acid.
F. M. G. M.

The Fractional Precipitation of Mixtures of Fatty Acids. Hans Kreis and Emil Roth (*Chem. Zeit.*, 1913, **37**, 58).—An alcoholic solution of the mixture of fatty acids is precipitated by about one-tenth of the theoretical quantity of lead acetate, and the acids obtained from the precipitate by boiling with hydrochloric acid. The melting point, refractivity, iodine value, and molecular weight of the acids can then be determined.

The results obtained with a number of oils are given, and it is shown that the first fraction from rape-seed oil consists mainly of erucic acid. Arachidic acid can be obtained from a mixture of acids by one fractionation, and this is made use of in testing for earth-nut oil, the details for which are to be given later.
T. S. P.

Estimation of Total Tartaric Acid in Wines. Philippe Malvezin (*Bull. Soc. chim.*, 1912, [iv], **11**, 1043—1045; *Bull. Assoc. Chim. Sucr. Dist.*, 1912, **30**, 342—343).—Twenty-two c.c. of the wine are distilled in a conical flask until 2 c.c. only remain. The flask does not come directly into contact with the flame, but is placed about 3 cm. above a thin metal plate, which is heated directly. To the contents of the flask are then added 1 c.c. of a 10% solution of potassium bromide and 40 c.c. of a mixture of alcohol and ether in equal volumes, in order to favour the precipitation of the tartaric acid present, either

in the free or combined state. The flask is then immersed for fifteen to twenty minutes in a freezing mixture made from equal weights of water and ammonium nitrate. The precipitate is collected, washed several times with the ether-alcohol mixture, then dissolved in water, and titrated with *N*/10-sodium hydroxide in order to determine the amount of tartaric acid present.

The volatile acids and the alcohol can be determined in the 20 c.c. of distillate obtained. T. S. P.

Estimation of Citric Acid in the Presence of Certain Other Acids. L. GOWING-SCOPES (*Analyst*, 1913, **38**, 12—19).—The reagent used is prepared by pouring 68 c.c. of strong nitric acid on to 51 grams of mercuric nitrate and 51 grams of manganese nitrate. One hundred c.c. of water are then added, and when all is dissolved, the solution is made up to 200 c.c. and filtered.

A quantity of the substance containing not more than 0·04 gram of citric acid is carefully neutralised with *N*/10-alkali, using phenolphthalein as indicator. Ten c.c. of the reagent are added, and the whole diluted to 200 c.c. The liquid is then boiled in a reflux apparatus for three hours, and the mercurial precipitate is collected on a Gooch crucible, washed with cold water, dried in the water-oven for two hours, and weighed. The weight divided by six equals citric acid.

The following acids when present do not interfere: tartaric, succinic, oxalic, benzoic, phosphoric, sulphuric and acetic acids; malic, lactic and salicylic acids, however, cause the results to be less accurate. L. DE K.

Estimation of Salicylic Acid and Benzoic Acid in Fruit Juices, Jams, Lemonades, etc. A. VAN RAALTE (*Chem. Weekblad*, 1912, **9**, 1004—1005).—For the estimation of salicylic and benzoic acids and "saccharin" in the articles cited, the author recommends boiling for five hours with dichloroethylene, followed by titration with decinormal alkali and phenolphthalein. After separation from the dichloroethylene, the neutralised liquid is examined for salicylic and benzoic acids. "Saccharin" can be extracted with ether from another portion of the aqueous liquid after addition of phosphoric acid. A. J. W.

Nuclein Metabolism. ALFRED STEPHAN (*Chem. Zentr.*, 1912, ii, 1783; from *Apoth. Zeit.*, 1912, **27**, 816—818).—A review of the subject. A method for estimating uric acid in blood as a copper urate is described. The method for estimating uric acid in urine recommended is a modification of Folin's. W. D. H.

A New Colorimetric Method for the Estimation of Uric Acid in the Blood. OTTO FOLIN and W. DENIS (*J. Biol. Chem.*, 1913, **13**, 469—476).—The phosphotungstic method yields positive evidence of the presence of uric acid in the blood. All previous evidence is regarded with suspicion. Quantitatively it gives accurate results. W. D. H.

Comparison of the Hübl and Wys Methods for Estimating the Iodine Numbers of Fats. AUGUET (*Ann. Falsif.*, 1912, **5**, 459—475).—The Hübl method yields low results as compared with the Wys method when the reagent used in the former method is freshly prepared, owing to the absence of hydriodic acid. This acid forms gradually in the alcoholic iodine solution, and the solution should not be used until it is at least twenty-five days old. The same result is attained by adding 3·5 grams of hydriodic acid to each litre of the iodine solution; the reagent itself should be prepared immediately before being required for use by mixing equal volumes of the iodine and mercuric chloride solutions. If these precautions be taken, the iodine numbers obtained by the Hübl method will agree closely with those obtained by the Wys method. The results obtained by either method are not influenced by variations in temperature varying from 10° to 25°, and for most oils one hour's contact is sufficient in the case of Hübl's reagent; a much shorter time suffices with Wys' reagent. The difference in the results yielded by the two methods does not exceed 1% for oils having an iodine number below 130. In the case of linseed oil, the absorption of iodine is only complete after eighteen hours' contact with Hübl's reagent, or two hours with Wys' reagent.

W. P. S.

Relation between the Saponification, Iodine, and Refractometer Numbers of Fats and Oils. OTTO RICHTER (*Milch. Zentr.*, 1913, **42**, 7—12).—It is shown that there is a definite relation between the saponification number and the refractive index of triglycerides of the stearic acid series; from tributyrin to trimelissin, the refractive index increases by 0·001 for each increase of 28·02 (C_2H_4) in the molecular weight. In the case of unsaturated glycerides, the refractive index increases by 0·0112 for every two atoms of iodine absorbed by the glyceride molecule. Formulæ are given for calculating the refractive index, the saponification number, or the iodine number of a glyceride when the other two constants have been estimated.

W. P. S.

Detection of Earthnut Oil in Olive Oil by the Franz-Adler Test. HEINRICH LÜERS (*Zeitsch. Nahr. Genussm.*, 1912, **24**, 683—684).—Samples of olive oil which contain a large proportion of myristin yield a turbidity with the Franz-Adler test (A., 1912, ii, 815), indicating the presence of earthnut oil. The turbidity is due, however, not to arachidic acid derived from the latter oil, but to the formation of a potassium hydrogen salt of myristic acid, ($KC_{14}H_{27}O_2,C_{14}H_{28}O_2$). The production and precipitation of this salt in the test may be prevented by adding 3 drops of glacial acetic acid (in addition to the prescribed quantity of dilute acetic acid) to the saponified oil. W. P. S.

A New Colorimetric Method for the Determination of Epinephrine (Adrenaline). OTTO FOLIN, W. B. CANNON, and W. DENIS (*J. Biol. Chem.*, 1913, **13**, 477—484).—Adrenaline, like uric acid, gives a colour reaction with phosphotungstic acid, and the quantitative results are almost identical with those obtained by physiological (blood-pressure) methods. W. D. H.

Detection of Histidine. KATSUJI INOUYE (*Zeitsch. physiol. Chem.*, 1913, **83**, 79—82).—Histidine in aqueous solution reacts with diazobenzenesulphonic acid in presence of excess of sodium carbonate to give a dark red coloration, which is definite in great dilution. Histidine reacts also when combined in the protein molecule. Tyrosine, however, gives a similar coloration (compare Pauly, A., 1904, i, 1068).

Benzoylhistidine still shows the coloration; dibenzoyltyrosine no longer gives it, or does benzoylhistidine when fixed in the protein molecule. It is thus possible to distinguish between free and fixed histidine.

It is necessary to allow the excess of benzoyl chloride, with which the protein or its decomposition product is treated, to decompose before adding the diazobenzenesulphonic acid. E. F. A.

Estimation of Lipoids in Blood-Serum. LÉON GRIMBERT and M. LAUDET (*Compt. rend.*, 1912, **155**, 974—976).—A rapid and moderately accurate method of estimating cholesterol, phosphorus-containing lipoids, fatty acids, and neutral fats in a small sample of blood-serum.

The serum (20 c.c.) is treated with excess of alcohol, and after twelve hours' contact it is extracted with a further quantity of alcohol. The combined extract is concentrated by distillation, the residue treated with ether, and filtered, the filtrate on evaporation leaving a residue which contains the constituents to be estimated. The residue is saponified with $N/5$-alcoholic potassium hydroxide, the alcohol removed, the liquid acidified with nitric acid, and extracted with ether, the ethereal extract on evaporation giving the cholesterol and a mixture of fatty acids. In this mixture the cholesterol is estimated by Kumagawa's method (compare A., 1908, ii, 331), the acids being obtained by difference. The aqueous layer is evaporated to dryness and calcined, the residue treated with nitric acid, filtered, and the phosphorus estimated in the filtrate as ammonium phosphomolybdate according to Villier's method (compare A., 1893, ii, 438). The weight of the precipitate divided by 2·3 gives the weight of phosphorus-containing lipoids expressed as lecithin distearate. W. G.

Mett's Method for Estimating Pepsin and the Optimal Conditions of Peptic Activity. JOHANNE CHRISTIANSEN (*Biochem. Zeitsch.*, 1912, **46**, 257—287).—Satisfactory results were obtained by Mett's method, when a soft coagulum of egg-white was used. With weak acids the amount digested is nearly proportional to the time. Hydrochloric acid has a deleterious action on pepsin, and on this account, when higher concentrations of acid are used, the amount digested is not proportional to the time. Schütz's law, $y^2 = kx$, where y = length of column of egg-white digested, x = the amount of pepsin, does not hold on account of the diffusion and the injurious action of acid on the ferment. For concentrations of acid between $N/10$ and $N/20$, the relation between the amount digested and quantity of pepsin can be approximately expressed by the formula $y^{2 \cdot 45} = kx$. The acidity for optimal activity of human pepsin is less than that of animal pepsins. S. B. S.

General and Physical Chemistry.

Refractive Index of Metals. P. A. Ross (*Jahrb. Min.*, 1912, ii, Ref. 314—316; from *Physical Review*, 1911, **33**, 549—556).—Prisms of the metals, with a refracting angle of 15·3″, were deposited on glass by means of the cathode rays; and the refractive indices determined for red, yellow, and blue light by the methods of deviation, interference, Newton's rings, and immersion in liquids of known refractive index. The results obtained by the different methods show some variation, but they are of the same order. The following are selected as examples (for sodium-light): copper, 0·46—0·57; iron, 1·85; lead, 1·95; platinum, 1·75—1·88; silver, 0·28—0·34; zinc, 2·11; magnesium, 0·40; gold, 0·58—0·65; bismuth, 1·98; nickel, 1·88; brass, 0·66. L. J. S.

Further Remarks on a Formula for the Index of Refraction of Binary Mixtures. Arrigo Mazzucchelli (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 701—707).—The author sustains and develops his former criticism (A., 1911, ii, 781) in view of the reply of Schwers (A., 1912, ii, 1). R. V. S.

Optical Constants of Certain Metals in the Ultra-Red. K. Försterling and Vsévolod Fréedericksz (*Ann. Physik*, 1913, [iv], **40**, 201—232).—The optical constants of silver, copper, gold, platinum, and iridium have been calculated from observations on the influence of the metals on the polarisation of the light reflected from the polished metal surfaces. These observations were made with monochromatic light of wave-length varying from $\lambda = 1000\ \mu\mu$ to $5000\ \mu\mu$.

According to the electro-magnetic theory, if the dielectric constant may be neglected in comparison with the conductivity, it is to be expected that the relations $\kappa = 1$ and $n = \sqrt{\sigma\tau}$ will hold good, where κ is the index of absorption, n the refractive index, σ the conductivity, and τ the period of vibration of the incident light.

It has already been shown that these relations are not satisfied in the case of ultra-violet and visible rays, and the data now obtained lead to the same result for ultra-red radiation. H. M. D.

The Spectra of Nebulæ and the Analogies to be Drawn From Them. Jean Meunier (*Compt. rend.*, 1913, **156**, 391—393. Compare A., 1912, ii, 432; this vol., ii, 24).—The greater part of the nebulæ present continuous spectra, but there are some which show a number of definite lines. The author considers that these lines all coincide with definite lines in the solar spectrum, attributed to various elements, namely, hydrogen, iron, and titanium, there being thus a marked analogy between the solar spectrum and that of the nebulæ. Finally, from Watts' examination of the spectrum from the flame of a Bessemer converter, he draws the conclusion that iron and titanium can exist in flames which are absolutely

gaseous, and developed under physical conditions comparable to those existing at the surface of the sun and in the nucleus of the nebulæ. W. G.

Influence of Different Gases and of Variations in Gas Pressure and Current Strength on the Appearance of the First Ultra-violet Band Spectrum of Oxygen. WALTER STEUBING (*Ann. Physik*, 1912, [iv], **39**, 1408—1430. Compare A., 1910, ii, 913; 1911, ii, 558).—In previous papers it has been shown that the so-called water-vapour bands in the ultra-violet region are probably due to oxygen. Further observations have now been made with different gases, purified and dried with the utmost care. Some of these experiments were made with an arc burning between platinum electrodes at atmospheric pressure, and others at pressures of less than 1 cm. of mercury, the current being also varied considerably in intensity. The gases examined were oxygen, nitrogen, air, hydrogen, and carbon dioxide.

Both at high and low pressures, the spectral observations indicate that the ultra-violet band spectrum in question is due to oxygen and not to water vapour. Pure oxygen, which has been dried for weeks in contact with phosphoric oxide, shows the band very clearly, although the conditions of the experiment preclude the possibility of interaction of the gas with traces of either hydrogen or hydrocarbons. In comparative experiments with nitrogen and hydrogen the band was not in evidence. In air and carbon dioxide, which both show the band quite clearly, its intensity increases with pressure and temperature. H. M. D.

Systems of Series in the Spectra of Zinc, Cadmium, and Mercury. JOHANNES STARK (*Ann. Physik*, 1912, [iv], **39**, 1612—1616). —The views of Paschen (A., 1911, ii, 833) relative to the existence of certain series in the mercury spectrum are adversely criticised. According to Paschen, the lines $\lambda = 2536$ and $\lambda = 4078$ belong to the same combination series. This is not in agreement with the general behaviour of the two lines. The flame spectrum of mercury shows only the former, and in the arc spectrum the relative intensities are very different. In regard to the manner in which they are resolved by a magnetic field, there is no similarity between them and the Doppler effect for the two lines in the canal-ray spectrum afford no evidence of a series relationship. On the other hand, the behaviour of $\lambda = 2536$ and $\lambda = 1848$ is similar, and it is probable that they belong to one and the same series.

The conclusion that the zinc line $\lambda = 2138$, the cadmium line $\lambda = 2288$, and the mercury line $\lambda = 1848$ are homologous is also inadmissible. It is contradictory to the rule that the wave-length of homologous lines of elements belonging to the same periodic group increases with the atomic weight, and, in the author's opinion, the line $\lambda = 1848$ should be replaced by $\lambda = 2536$. The members of this group behave quite similarly in many ways.

The nature of certain ultra-violet doublets in the zinc and cadmium spectra is also discussed. H. M. D.

Absorption Spectra of Some Uranyl Salts. ARRIGO MAZZUCCHELLI and OLGA GRECO D'ALCEO (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 850—854; 1913, [v], **22**, i, 41—43).—In a recent paper (this vol., i, 160) the authors have shown that a number of uranyl and uranous salts do not form complexes with certain nitrogenous compounds. The present papers record the results of photographic measurement of the absorption bands of solutions of these salts both before and after the addition of the nitrogenous substances, and the results confirm those obtained in the former paper by purely chemical methods. As a control, similar measurements were made with sodium uranyl tartrate and pyridine; the reaction (of whatever nature) which occurs between these substances is indicated by the absorption spectra.

Uranous chloride shows the same absorption spectrum alone and after addition of carbamide, so that no additive compound is formed. The spectrum of $M/20$-uranous sulphate is figured, and also the spectrum of the same solution after addition of glycine in the proportion of 24 mols. to 1 mol. of uranium salt; the only difference observable is a slight displacement of the maxima of the bands. The spectra of the two corresponding solutions of uranous chloride (which are also reproduced) do exhibit differences, and in this case the existence of an additive compound has been shown to be probable by chemical means. R. V. S.

Spectrographic Studies in the Triphenylmethane Group. RICHARD MEYER and OTTO FISCHER (*Ber.*, 1913, **46**, 70—84).—The hypothesis that only such quinonoid substances of the triphenylmethane group as contain an auxochrome group in the para-position to the methane carbon atom can possess the properties of a dye (Meyer and Fischer, A., 1911, i, 723; von Baeyer, A., 1907, i, 757) is not in accord with further experiment.

Fuchsone, $CPh_2:C_6H_4:O$, in alcoholic solution gives an absorption spectrum (bands with maxima at 380 and 260 $\mu\mu$) resembling that of the salts of phenolphthalein, and a hot alcoholic solution of benzaurin gives a similar curve (maxima 440 and 275 $\mu\mu$); the deepening in the colour of the benzaurin solution on warming is attributed to a change into the quinonoid structure, $OH\cdot C_6H_4\cdot CPh:C_6H_4:O$, and from the similarity of the absorption of this and fuchsone it is evident that the para-hydroxyl group is not essential to selective absorption. This is confirmed by a comparison of fuchsonimonium chloride, $CPh_2:C_6H_4:NH_2Cl$ (obtained by warming fuchsonimonium carbinol hydrochloride, $OH\cdot CPh_2\cdot C_6H_4\cdot NH_2,HCl$, in alcoholic solution), and Döbner's violet, $NH_2\cdot C_6H_4\cdot CPh:C_6H_4:NH_2Cl$, each giving similar curves with three absorption bands (maxima at 440, 330, and 260 $\mu\mu$, and at 570, 400, and 300 $\mu\mu$ respectively); an alkaline solution of benzaurin gives a similar curve with maxima at 550, 375, and 290 $\mu\mu$.

The elimination of a molecule of water is not necessary to the existence of colour in a triphenylmethane compound (compare von Baeyer, *loc. cit.*; *p*-hydroxytriphenylmethane, di-*p*-hydroxytriphenylmethane, and *p*-diaminotriphenylmethane hydrochloride in

alcoholic solution all exhibit an absorption band between 250 and 300 $\mu\mu$.

The alkali salts of hydroxyphenyl- and hydroxydiphenyl-phthalide give only one-sided absorption, resembling in this a colourless solution of phenolphthalein containing excess of alkali; it is possible therefore that these compounds exist in the solutions in the carbinol structure; this view is supported by the fact that the yellow solution of hydroxydiphenylphthalide is, like phenolphthalein, decolorised by excess of alkali, the colour re-appearing on warming.

Phenolphthalein and hydroxydiphenylphthalide both dissolve in concentrated sulphuric acid to coloured solutions of which the absorption curves run roughly parallel, but that of the former contains an additional point of maximum absorption (maxima at 500 and 390 $\mu\mu$ and at 470 $\mu\mu$); the former curve is quite different from that of the alkali salt of phenolphthalein.

Fluorane, $O<\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}>C<\begin{smallmatrix}C_6H_4\\CO-\end{smallmatrix}>O$, and dithiofluoran,

$$O<\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}>C<\begin{smallmatrix}C_6H_4\\CS-\end{smallmatrix}>S,$$

when dissolved in a mixture of acetic acid and alcohol give different types of absorption band, the former having one point of maximum absorption (at 290 $\mu\mu$) and the latter three (at 515, 360, and 300 $\mu\mu$). D. F. T.

Spectrographic Studies in the Anthraquinone Group. Richard Meyer and Otto Fischer (*Ber.*, 1913, **46**, 85—92).—An investigation of the absorption spectra of the hydroxyanthraquinones.

The alkali salts of 1- and 2-hydroxyanthraquinone give curves which are quite different in character, the former having one large band (maximum absorption at 500 $\mu\mu$), whilst the other has three bands (maxima at 492, 300, and 238 $\mu\mu$); a neutral solution of the alkali salt of alizarin (1 : 2-dihydroxyanthraquinone) gives a similar absorption curve to 2-hydroxyanthraquinone (maxima at 527, 330, and 260 $\mu\mu$), but an alkaline solution gives a quite different curve (absorption maxima at 612, 560, and 266 $\mu\mu$).

The alkali salts of 1 : 4-dihydroxyanthraquinone (quinizarin) and 1 : 5-dihydroxyanthraquinone show similar absorption to 1-hydroxyanthraquinone, giving maxima at 565 and 500 $\mu\mu$ respectively; the former substance in alkaline solution gives two bands with maxima at 605 and 560 $\mu\mu$.

2 : 6- and 2 : 7-Dihydroxyanthraquinones in alkaline solution exhibit four bands, whilst 1 : 2 : 4-trihydroxyanthraquinone (purpurin), whether in excess of alkali or not, is similar to alizarin in excess of alkali.

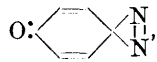
A neutral solution of the alkali salt of 1 : 2 : 3-trihydroxyanthraquinone shows three decided bands (maxima at 510, 430, and 290 $\mu\mu$) with a much weaker one (at 620 $\mu\mu$), which develops more sharply on the addition of more alkali. The alkali salt of 5 : 6-dihydroxy-1 : 4-naphthaquinone in absorption resembles the alkaline solution of alizarin.

A comparison of these results indicates that hydroxyl in the 2-, 3-, 6-, or 7-position is more strongly auxochrome than in one of the other positions. The difference between the spectra of the alizarin and quinizarin salts in neutral and alkaline solution is probably due to the neutralisation of one hydroxyl or two, according to the conditions.

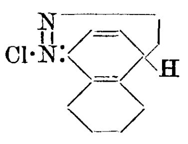
From a comparison of the above hydroxyanthraquinones with anthraquinone itself (Baly and Stewart, T., 1906, **89**, 511), all in sulphuric acid solution, the conclusion is drawn that the introduction of hydroxyl in the 2- or 3-position influences the absorption spectrum more strongly than introduction in the 1-position.

D. F. T.

Optical Investigation of Diazo-compounds. JOHN C. CAIN (*Ber.*, 1913, **46**, 101—102).—The author draws attention to the similarity between the absorption curves of *p*-benzoquinonediazide,



and of *a*-naphthalenediazonium chloride, on which Hantzsch and Lifschitz (A., 1912, ii, 1116) fail to comment. The similarity must indicate an analogy of structure which is best explained by the author's diazonium formula for the latter substance (annexed formula); from the general resemblance of the curves for the above and other diazonium compounds (*loc. cit.*), the structure should be common to all.



A consideration of the author's diazonium formula would have foretold the fruitless character of certain experiments of Hantzsch and Lifschitz.

D. F. T.

Absorption of Light and Fluorescence of Aliphatic Acid Imides (Fluorescence Phenomena among Non-aromatic Compounds. I.) HEINRICH LEY and W. FISCHER (*Ber.*, 1913, **46**, 327—335).—The authors have investigated the absorption spectra and fluorescence of imides of the general formula $R<^{CO}_{CO}>NH$, since, by suitable substitution in the group R, the substances show considerable change in colour.

Succinimide only shows absorption at the boundary of the visible field, whilst *magnesium succinimide* is still more transparent. Dimethylmaleinimide shows distinct selective absorption. The introduction of bromine into the molecule of maleinimide has the effect of shifting the absorption towards the region of greater wave-length. The presence of an amino-group causes the absorption to shift towards the red end of the spectrum, whilst, on the addition of acid to solutions of amino-imides, the absorption is moved towards the region of shorter wave-length. In the case of amino-imides, however, it is probably that salt-formation is accompanied by intermolecular re-arrangement.

Fluorescence of Imides.—Diphenylmaleic anhydride, diphenylmaleinimide, chloroaminomaleinimide, and methylaminocitraconic

methylimide yield fluorescent solutions when dissolved in water, alcohol, ether, or benzene, and, further, the nature of the fluorescence is found to be dependent on the particular solvent employed. Under the experimental conditions adopted, no fluorescence was observed with dimethylmaleinimide. Since, also, ethyl 5-amino-3-cyanofuran-2-carboxylate (Wislicenus, A., 1908, i, 965; Dieckmann, A., 1911, i, 457) is fluorescent, the authors are led to the conclusion that the systems $\begin{array}{l}\cdot C{-}C{:}X \\ \;\| \quad\;\; >Y \\ \cdot C{-}C{:}X\end{array}$ and $\begin{array}{l}\cdot C{=}C\cdot \\ \;| \quad\;\; >X \\ \cdot C{=}C\cdot\end{array}$ can occasion fluorescence, if an amino-group is also present.

Chloroaminomaleinimide (compare Ciamician, A., 1890, 24) was prepared by warming dichloromaleinimide with a concentrated alcoholic solution of ammonia during two hours at 70°. It had m. p. 219°.

Methylaminocitraconmethylimide, $\begin{array}{r}MeC{-}CO \\ \| \quad >NMe \\ NHMe{\cdot}C{-}CO\end{array}$, m. p. 140°, was obtained by heating an alcoholic solution of methyloxalacetic ester with aqueous methylamine during three to four hours at 70°.

Diphenylmaleinimide was obtained in the form of its *copper* salt, $(C_{16}H_{10}O_2N)_2Cu$, when diphenylmaleic anhydride and copper acetate were warmed with 20% ammonia. When warmed with dilute acid, the copper salt yielded the free imide. H. W.

Stark's Theory of Fluorescence. HANS VON LIEBIG (*Zeitsch. Elektrochem.*, 1913, **19**, 117—122).—Polemical. The author criticises Stark's statement (this vol., ii, 2) "that fluorescence is not a constitutive property of the molecule, but a property of the atom." The author, whilst admitting Stark's statement that fluorescence is due to loosened valency electrons, maintains, in opposition to Stark, that it is strictly scientific to consider the question of the relation between constitution and colour or fluorescence, only so far as the visible spectrum is concerned, and not over the whole spectrum. It is also shown that Stark's statement, based on Hartley's work, "that the colour of benzene derivatives is due only to a shift of the ultra-violet absorption bands toward the red by substitution and condensation," is not in accord with chemical facts. Stark's experiments on the fluorescence of acetone, diacetyl, etc., are held to be untrustworthy on account of the fact that such substances undergo chemical change under the influence of ultra-violet light, and that the products of such changes or the changes themselves might easily occasion the fluorescence observed. The reasons offered by Stark to explain the non-observance of fluorescence with glycerol, *p*-benzoquinone, anthraquinone, and violuric acid are regarded as insufficient to justify the statement that such substances are fluorescent. Finally, it is shown that the action attributed to the loosened valency electrons and the chromophoric groups, by Stark, is directly opposed to the main point in Stark's theory, namely, that constitution and fluorescence are entirely unconnected. J. F. S.

The Law of Elementary Photochemical Absorption. VICTOR HENRI and RENÉ WURMSER (*Compt. rend.*, 1913, **156**, 230—233 Compare A., 1912, ii, 882, 883).—The examination of a number of photochemical reactions to see whether Grotthus's law of photochemical absorption, that the photochemical susceptibility is proportional to the absorption, holds good in all cases. For acetone and ethyl acetate the maximum decomposition corresponds with the region of maximum absorption. In the case of acetaldehyde the absorption curve presents a maximum at $\lambda = 2775$, then diminishes to a minimum, and finally increases steadily for the extreme ultraviolet rays, whilst the decomposition is a maximum at $\lambda = 2775$, and then diminishes, showing no minimum, and being very feeble in the extreme rays. In explanation of this the following law is enunciated. The photochemical susceptibility of a substance depends only on that part of the absorption spectrum which corresponds with the same molecular groupings as those on which the action is produced. W. G.

Relation between the Velocity of a Photochemical Reaction and the Incident Radiant Energy. MARCEL BOLL (*Compt. rend.*, 1913, **156**, 138—140. Compare A., 1912, ii, 384, 407, 1119).—The author has studied the rate of hydrolysis of tetrachloroplatinic acid when submitted to rays of different energy. The light from a mercury-vapour lamp was dispersed by two quartz prisms, and certain of the resulting rays were used as a source of energy, the amount reaching the acid solution being controlled by a screen, consisting of a cell containing a dilute solution of caffeine, the concentration and thickness of the layer being varied. The coefficient of absorption of caffeine, as obtained from photometric measurements, was in close agreement with the value calculated from these results, on the hypothesis that the velocity coefficient of a chemical reaction is proportional to the incident radiant energy, even if the reaction is bimolecular. W. G.

Action of the Medium and Extreme Ultra-violet Rays on Acetaldehyde: Acidification, Polymerisation, Resinification. DANIEL BERTHELOT and HENRY GAUDECHON (*Compt. rend.*, 1913, **156**, 233—236).—A more detailed study of the photolysis of acetaldehyde (compare this vol., ii, 90). Initial ultra-violet rays do not convert the aldehyde into acetic acid in the absence of oxygen. Under the influence of medium and extreme rays oxidation takes place even in the absence of oxygen, a portion of the aldehyde being converted into acetic acid, and the amount of acid produced is far greater when the aldehyde is in the form of vapour than when it is liquid. With rays ($\lambda < 0{\cdot}25\mu$) polymerisation is rapid, both para- and meta-acetaldehyde being formed. No resinification results from the action of initial ultra-violet rays, and it is only slowly produced by the medium and extreme rays. The presence of water checks polymerisation and resinification, but favours acidification, formic acid being formed in this case and in amount almost equal to that of the acetic acid. W. G.

Photo-electric Behaviour of Iron in the Active and Passive State. H. STANLEY ALLEN (*Proc. Roy. Soc.*, 1913, *A*, **88**, 70—74).—The photo-electric activity of chemically active iron is found to be much greater than that of iron which has been rendered passive by the action of concentrated nitric acid or by anodic polarisation in a dilute sulphuric acid solution. It is considered that this observation affords support for the theory which attributes passivity to the occurrence of a layer of gas at the surface of the metal. H. M. D.

Photo-electric Effect in Some Compounds. A. LL. HUGHES (*Phil. Mag.*, 1913, [vi], **25**, 332).—It has been suggested by Willows (this vol., ii, 4) that the photo-electric activity of moist zinc chloride may be connected with the fact that moist halogen salts of zinc emit large quantities of ions when heated to 300°, whereas the dry salts are inactive. In reply to this, the author points out that the procedure adopted in the photo-electric experiments was such as to ensure that the effect is a direct result of ultra-violet illumination. H. M. D.

Arc and Spark Lines (Uni- and Multi-valent Lines) in the Canal-Ray Spectra. JOHANNES STARK (*Physikal. Zeitsch.*, 1913, **14**, 102—109).—The conditions under which the so-called arc and spark lines of an element make their appearance indicate that the spark lines are due to carriers moving with much greater velocities than those possessed by the carriers which give rise to the arc lines. Both kinds of lines are found in the canal-ray spectra, and from observation of the canal-ray spectra of oxygen, nitrogen, chlorine, iodine, helium, sulphur and aluminium, it is found that the two groups of lines behave differently in regard to the Doppler effect. Photographs of the spectra show that in the case of the spark lines, the maximum intensity of the displaced line is separated from the undisplaced line by an intervening region of minimum intensity, whereas this region is not found in the case of the arc lines at the dispersion which was employed in the production of the photographs. The ratio of the intensity of the displaced line to that of the undisplaced line is, moreover, very much greater for spark lines than for arc lines. These facts seem to show that the difference in the two groups of lines is attributable to a difference in the magnitude of the electric charge carried by the ions. It is supposed that the carriers giving rise to the arc lines have a single positive charge, whereas the spark lines are due to carriers with two or more positive charges. H. M. D.

Doppler Effect of Canal Rays. HEINRICH WILSAR (*Ann Physik*, 1912, [iv], **39**, 1251—1312).—The canal-ray spectra of hydrogen, oxygen, and nitrogen have been examined, and experiments made to determine the dependence of the velocity of the particles on the discharge potential, the magnitude of the Doppler effect, and the electric charges of the carriers. Other observations have reference to the influence of a magnetic field on the Doppler effect, the reflexion of the canal rays from a metal or glass surface, and the nature of the reflected rays.

The canal ray spectrum of hydrogen shows none of the lines belonging to the principal series, and lines belonging to the many-lined spectrum exhibit no Zeeman effect.

All the spark spectrum lines of oxygen which appear in the canal ray spectrum give rise to a Doppler effect of the same magnitude, and are presumably due to the same curve. On the other hand, no Doppler effect is obtained with the series lines of oxygen.

Certain nitrogen lines show the Doppler effect, and since the magnitude of this varies from one line to another, it is inferred that there are two or more carriers. The magnitude of the Doppler effect increases at first with the discharge potential, but not, as might be expected, in the ratio of the square root of the potential difference, the effect attaining a maximum at an applied potential which varies with the nature of the gas. In the case of hydrogen, the canal rays carry a single unit of charge, but multiple charges are carried by the oxygen and nitrogen canal ray particles.

The hydrogen canal rays are reflected to an appreciable extent at both glass and metal surfaces, and the reflected rays are found to behave quite similarly to the normal rays.

The carriers which give rise to the displaced lines in the canal-ray spectrum originate in the cathode region, where the rapid fall of potential occurs, and travel through the surrounding gas at practically constant speed. The luminous particles, to which the undisplaced lines are due, are accordingly unaffected by collision with the rapidly moving carriers in so far as the Doppler effect is concerned.

The excitation of a gas by the canal-ray particles of a second gas appears to be of a mutual character as a general rule. In the case of mercury, however, which is readily excited by the canal ray particles of other gases, this relationship does not exist, for the canal ray particles of mercury are apparently incapable of exciting the luminosity due to rapidly moving particles when they are allowed to pass through other gases. H. M. D.

Comparison of the Spectra of Fluorescent Röntgen Radiations. J. CROSBY CHAPMAN (*Proc. Roy. Soc.*, 1913, *A*, **88**, 24—37. Compare A., 1912, ii, 316, 518).—Measurements have been made of the absorption in aluminium, copper, silver, and platinum of the characteristic radiations which are emitted by elements belonging to the *K* and *L* groups. The results indicate that any radiation characteristic of an element of group *K*, and having a certain penetrating power in aluminium, is absorbed by any other element to just the same extent as the radiation from an element of group *L* which has the same penetrating power in aluminium.

From experiments with bromine and bismuth which belong to the two different groups, it has been found that their radiations are equally transformed into corpuscular radiation, and that the corpuscles ejected by the radiations have the same ionising and penetrating power. Other observations show that the radiations of bromine and bismuth are identical in type in regard to their ionising power in different substances.

The fact that radiations from elements belonging to different groups are identical in nature shows that properties, which are dependent on electronic structure, are repeated in atoms of different elements containing different numbers of electrons. The observations may therefore be regarded as affording support for the theory that the corpuscles in the heavy atoms are arranged in bundles, the distribution of the corpuscles in each bundle being similar to the distribution in the atom of some lighter element. There is no relation between the elements of different atomic weight which emit identical radiations and the grouping of the periodic system.

H. M. D.

Measurement of the Ionisation Potential in Different Gases. J. FRANCK and G. HERTZ (*Ber. Deut. physikal. Ges.*, 1913, **15**, 34—44).—The magnitude of the ionisation potential has been determined for a number of gases by a modification of Lenard's method (*Ann. Physik*, 1903, [iv], **8**, 149), an electrically heated wire being employed as the source of the electrons. In all cases the gases were carefully purified, and the following values obtained: helium, 20·5; neon, 16; argon, 12; hydrogen, 11; oxygen, 9; and nitrogen, 7·5 volts.

The data are insufficient to decide the question as to the manner in which the energy required for ionisation depends on the dimensions of the gas molecules.

H. M. D.

The Occlusion of the Products [of Disintegration] of Radium. GIOVANNI COSTANZO (*Compt. rend.*, 1913, **156**, 126—127).—A comparison of the results of introducing disks of palladium, rubber, and brass of varying thickness into an atmosphere activated by barium chloride containing radium. The results show (1) that brass obeys Curie's laws for the induced radioactivity of metals, (2) that palladium occludes the products of disintegration of radium almost to the same degree as rubber when in thin sheets, (3) that the thickness of the activated disks seems to have an influence on the occlusion, (4) that with disks under like conditions, the activity, immediately after withdrawal from the sphere of activation, is greater with palladium than with rubber. This radioactive occlusion could be used as a means of estimating radium in an activating atmosphere.

W. G.

The Valency of the Radio-elements. GEORG VON HEVESY (*Physikal. Zeitsch.*, 1913, **14**, 49—62*).—From the theory of the diffusion of a cation in presence of a great excess of its anion, and assuming for the mobility of the cation a mean value of 55·7, from which none of the known cations widely depart, it is deduced that the diffusion coefficient of the cation is expressed by $1{\cdot}25/n$ (cm.^{2}, day^{-1}), where n is the valency. A series of measurements of the diffusion coefficients, D, of several of the radioactive cations in $N/100$-hydrogen chloride has been carried out by the Graham-Stephan method, using the apparatus of Scheffer, and from these the valency of the ion is deduced. The results are expressed in the following table:

* and *Phil. Mag.*, 1913, [vi], **25**, 390—414.

Cation.	D (cm.^{2}, day^{-1}) at 18°.	Valency.	Cation.	D (cm.^{2}, day^{-1}) at 18°.	Valency.
Uranyl (UO_2'')	0·576 (in water)	II	Radium-F	0·760	II
Uranium-X	0·400	IV	Thorium	0·329	IV
Ionium......................	0·327	IV	Radio-thorium	0·333	IV
Radium	0·667	II	Thorium-X	0·659	II
Radium-D	0·651	II	Thorium-B (RaB, AcB)	1·21	I
Radium-E	0·646	II	Thorium-C (RaC, AcC)	0·625	II
			Actinium-X	0·664	II

For some of these the mobility (u in 10^5 cm., sec.$^{-1}$) has been directly determined. The value of u varies between the extremes of 54·0 for thorium-C and 68·8 for radium-F, and the more exact value of the valency, deduced by combining with u the value of D, confirm those given above. Thorium-B, which appears univalent, has a value for u 55·4, which shows that it is not an alkali metal, but is in the silver group, and is probably between mercury (univalent) and thallium in properties.

The known rule that the expulsion of an α-particle lowers the valency by two units, is, as the result of these measurements, extended and supplemented by the further rule that the expulsion of a β-particle acts in the opposite direction. After the emanation, or zero group, is reached, the opposite takes place, the change of valency with the expulsion of the positively charged α-particle always being in the direction of increasing the electro-positive character, and of the β-particle the electro-negative character. This is quite analogous to the reduction of a multivalent ion, such as the ferric or stannic ion, to the condition of lower valency, ferrous or stannous, by the loss of positive charges. The α- and β-changes have polar consequences for the residual atom. F. S.

The Diffusion of Uranium. GEORG VON HEVESY and L. VON PUTNOKY (*Physikal. Zeitsch.*, 1913, **14**, 63—65*).—The diffusion of uranous and uranyl salts has been studied by chemical and radioactive methods, as if there were any difference in the rates of diffusion of uranium I and uranium II, it should be made manifest by a difference in the two methods of measurement. In three experiments a one-fifth molar solution of uranyl nitrate in eight times molar nitric acid, the same in water, and a one-sixth molar uranous sulphate in water were diffused. The values of the diffusion coefficient D (cm.^{2}, day^{-1}) were respectively 0·442, 0·576, and 0·480, and there was in no case any difference between the results by the chemical and radioactive methods. This proves that uranium I and II diffuse at exactly the same rate, and are extremely closely allied in chemical properties. To bring the uranium disintegration scheme completely in accord with the rules as regards change of valency following α- and β-ray changes (preceding abstract), it is only necessary to assume that uranium-X is the product of uranium I, and is intermediate between it and uranium II as shown:

$$\underset{\text{(VI.)}}{\text{Ur-I}} \xrightarrow{\alpha} \underset{\text{(IV.)}}{\text{Ur-}X} \xrightarrow{\beta} \underset{\text{(VI.)}}{\text{Ur-II}} \xrightarrow{\alpha} \underset{\text{(IV.)}}{\text{Io}} \xrightarrow{\alpha} \underset{\text{(II.)}}{\text{Ra.}}$$

F. S.

* and *Phil. Mag.*, 1913, [vi], **25**, 415—418.

The Radioactivity of Solutions of Uranium Salts. L. MICHIELS (*Le Radium*, 1912, **9**, 432—434).—The ionisation produced by solutions of uranium salts of known concentration and density has been studied by means of an electroscope with amber insulation. These solutions lend themselves readily to the production of α-ray standards of greater uniformity than can be produced by films of solid uranium compounds. For a given volume and area of solution of given density, the α-radiation is proportional to the uranium content. If the density of a number of solutions of uranium of different concentration is made the same by the addition of ferric chloride, the activity is proportional to the concentration. This allows the content of uranium in a solution to be obtained by a radioactive method in the presence of other metals in the solution, provided that no other radioactive material is present. F. S.

Change in Activity of a Sample of Uranium Nitrate. M. LA ROSA (*Nuovo Cim.*, 1913, [vi], **5**, i, 73—82).—A sample of this salt was found to undergo changes in radioactivity (which are described in detail) under the influence of proximity to an electric arc, of slight heating, or of variations in the humidity of the air with which it was in contact. The changes observed are to be attributed to the hygroscopic nature of the substance, and to the solubility of the emanation which it produces in the absorbed water. R. V. S.

Behaviour of Uranium-*X* with Regard to the Usual Methods of Electrochemical Separation. PAOLO ROSSI (*Nuovo Cim.*, 1913, [vi], **5**, i, 5—14).—The electrochemical separation of uranium-*X* and uranium is more difficult than is the case with the radium group. This would seem in agreement with Lucas's law, according to which the radioactive elements transform themselves into electrochemically more noble elements, but in contradiction with this, uranium-*X* is not more easily separable than uranium. When uranium solutions are electrolysed with increasing *E.M.F.*, no uranium-*X* separates at the cathode, but it may be possible to obtain deposits at the anode which contain uranium-*X* and very little uranium, if the solution contains traces of impurities, and the deposition is probably due to these or to deposits arising from them by electrolysis. If substances are intentionally added to the solutions to produce anodic and cathodic deposits, the former contain only uranium-*X*, whilst the cathodic deposits are inactive or contain both uranium and uranium-*X*. The presence of uranium-*X* in the anodic deposits cannot be explained by the phenomenon of cataphoresis. It is more probably an adsorption phenomenon, and this explanation is supported by the fact that precipitates and colloidal metals acquire activity due to uranium-*X* when placed in contact with uranium solutions, and the author also finds on calculating the relative amounts of uranium and uranium-*X* which should be adsorbed, that the activity of the uranium would be masked by the much greater activity due to the uranium-*X* present. R. V. S.

Synthetic Observations on the Activity of Rain Water. JOSE MUÑOZ DEL CASTILLO and JOSÉ BARRIO FERNÁNDEZ (*Anal. Fis. Quim.*, 1913, **11**, 89—91).—Various specimens of rain-water were shown to give in volts per litre-hour values ranging from −3·6 to 175·0. G. D. L.

The Atmospheric Electricity and Radioactivity of the Atlantic and Pacific Oceans. I. Determination of the Emanation Content of Ocean Water. J. LAUB (*Physikal. Zeitsch.*, 1913, **14**, 81—83).—A series of fifty measurements of the emanation content of the ocean water was undertaken on a voyage in the Atlantic Ocean from Montevideo through the Magellan Straits into the Pacific Ocean to Callao. The mean of all the results showed the content to be 0·1 Mache unit, the mean for the Atlantic being 0·14, for the Magellan Straits 0·09, and for the Pacific, 0·08. No dependence of the value on the place, the neighbourhood of the coast, or the temperature of the water was observed. F. S.

Electrical Excitation in the Spraying of Liquids (Balloelectricity). II. CHRISTIAN CHRISTIANSEN (*Ann. Physik*, 1913, [iv], **40**, 233—248. Compare this vol., ii, 297).—In continuation of the experiments on the electrical excitation which accompanies the spraying of liquids, observations have been made on aqueous solutions of halogen substituted fatty acids, amines, amides, esters, hydroxybenzenes, alkaloids, and certain other substances.

From the data obtained with mixed aqueous solutions it is found that solutions of two different electrolytes, which change the balloelectrical effect exhibited by a solution of a non-electrolyte to a given extent, are also equivalent in respect of other non-electrolytes. In a similar way, solutions of non-electrolytes which are equivalent in their action towards a particular electrolyte are also equivalent in respect of other electrolytes.

The influence of the nature and the pressure of the surrounding gas on the electrical effect has also been examined. The effect increases in all cases with the pressure, and for carbon dioxide, air, coal-gas and hydrogen it increases as the density of the gas diminishes. H. M. D.

Improved Apparatus for Measuring the Conductivity of Electrolytes. EDWARD W. WASHBURN and J. E. BELL (*J. Amer. Chem. Soc.*, 1913, **35**, 177—184).—In order to obtain an accurate method for determining the conductivity of aqueous solutions of strong electrolytes between 0·001*N* and 0·000001*N*, a study has been made of the sources of error inherent in Kohlrausch's method when applied to such solutions. Apparatus has been devised by means of which great precision can be attained, not only in the measurement of very large resistances, but also of very small ones, and which possesses the advantages of greater rapidity and convenience of manipulation. The chief modifications introduced into the usual apparatus are the substitution of a high frequency generator for the induction coil as a source of current, and of special film

resistance units for the ordinary resistance box. These resistances are made by sealing platinum wires into the ends of a glass rod and connecting them by a film of platinum deposited on the glass. A tuned telephone is employed and an extended bridge wire, all measurements being made at the middle of the bridge.

Experiments have been made with this apparatus which show that by its means the conductivity of any solution of an electrolyte from conductivity water itself up to a $6N$-solution can be readily determined with a precision of 0·01%, and that with care the precision can be increased to 0·001% in most cases. The method should prove of considerable value for the exact analytical control of pure solutions of electrolytes. E. G.

The Molecular Conductivity and Viscosity in Mixtures of Methyl Alcohol or Acetone with Benzene and Nitrobenzene. J. FISCHLER (*Zeitsch. Elektrochem.*, 1913, **19**, 126—132).—The molecular conductivity and viscosity of solutions of potassium iodide and lithium bromide were measured in solutions of mixtures of methyl alcohol and benzene, methyl alcohol and nitrobenzene, acetone and benzene, and acetone and nitrobenzene. The conductivity at infinite dilution was calculated from the results by the Kohlrausch extrapolation formula, $\lambda_\infty = (\lambda_1 \sqrt[3]{v_1} - \lambda_2 \sqrt[3]{v_2})/(\sqrt[3]{v_1} - \sqrt[3]{v_2})$, in which λ_1 and λ_2 are the molecular conductivities at dilutions v_1 and v_2. It is shown that with lithium bromide the value λ_∞ is greater the larger the values of v_1 and v_2; the same is observed for potassium iodide, but not to so marked an extent. This irregularity is explained by the existence of complexes in the concentrated solutions which dissociate in the more dilute solutions. Walden (A., 1912, ii, 23) showed that the product $\lambda_\infty \eta$, where η is the viscosity, is a constant, and equal about 0·700. For solutions of potassium iodide in mixtures methyl alcohol–nitrobenzene, acetone–nitrobenzene, the value 0·650 is obtained, whilst the benzene mixtures give much lower values. With lithium bromide in methyl alcohol–nitrobenzene the value is low, but in the 50% acetone–50% benzene mixture it falls to 0·0487. This is no doubt due to the complexity of lithium bromide in the solution (see Serkov, A., 1909, ii, 372; 1910, ii, 177). The complexity of lithium bromide in the methyl alcohol and nitrobenzene mixtures is calculated by the Serkov formula, and it is seen to be strongly complex. J. F. S.

Aqueous Solutions of Ammonia Soaps. I. FRANZ GOLDSCHMIDT and LÉON WEISSMANN (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 18—31. Compare A., 1912, ii, 728).—The electrical conductivity and viscosity of solutions of an ammonia soap, prepared from the fatty acids of palm oil, has been examined in regard to the influence of concentration, temperature, and of the addition of ammonia and ammonium salts. The results are compared with those obtained in a previous investigation (*loc. cit.*) of the properties of solutions of a similarly prepared potassium soap.

The relationship between the conductivity and concentration is represented by a straight line which cuts the concentration axis

at a point on the positive side of the origin. The molecular conductivity, which is only about half as large as that of the potassium soap, increases with the concentration, and appears to approach asymptotically to a limiting constant value. The viscosity increases with the concentration at a gradually increasing rate, and the concentrated solutions are characterised by viscosity values which are extremely sensitive to changes of temperature.

The addition of ammonium chloride in small quantities increases the viscosity considerably, and causes a diminution in the conductivity. Larger quantities give rise to the precipitation of acid soaps. On addition of successive quantities of ammonia, the viscosity rises slightly at first, then falls, and finally increases until the viscosity becomes much greater than that of the pure soap solution. The effect of an addition of ammonia on the conductivity is to increase it at first, but a maximum value is soon reached, and further quantities result in a continuous fall in the conductivity.

From observations made with solutions to which both ammonium chloride and ammonia were added, it has been found that the increase in the viscosity produced by the addition of a given quantity of ammonium chloride is enormously magnified when ammonia is also present in the solution. For each concentration of ammonium chloride there is a particular ammonia concentration for which this effect has a maximum value. If this quantity of ammonia is exceeded, the viscosity falls very rapidly. H. M. D.

Electrochemistry of Non-aqueous Solutions. X. Schützenberger's Etherobromide. VLADIMIR A. PLOTNIKOV (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1919—1929).—The author challenges McIntosh's statements (T., 1905, **87**, 784; A., 1911, i, 256) that the electrical conductivity of Schützenberger's etherobromide (ether tribromide) (*Annalen*, 1873, **167**, 86) is due to the presence of hydrogen bromide developed in consequence of the gradual bromination of the ether, and that, in addition to the tribromide, a dibromide also exists.

As regards the first point, seven separate series of observations of the conductivity give concordant results (A., 1907, ii, 152), and the magnitude of the conductivity diminishes with lapse of time. Secondly, measurements of the viscosity of the system ether–bromine give no indication of the existence of a dibromide of the empirical formula Et_2OBr_2 (compare Kurnakov and Anisimov, *J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1005).

Solutions of ether dibromide in chloroform and ethyl bromide exhibit conductivities of the same order of magnitude as those of aqueous salt solutions, the specific conductivity increasing approximately in proportion to the concentration. On electrolysis, ether is liberated at the cathode, and bromine, in amount corresponding with the formation of the ion Br', at the anode. These results are in agreement with the hypothesis that the electrolytic conductivity of a solution is conditioned by the electrochemical relations of the solute with the solvent, and not by any special property, such as the dielectric constant, of the solvent.

Assuming the double formula for ether dibromide, a represen-

tation of its structure according to the co-ordination theory is suggested. T. H. P.

The Apparent Potential Difference of Contact of a Metal and Electrolytic Solutions. J. GUYOT (*Compt. rend.*, 1913, **156**, 220—222).—The author has measured the potential difference between a gilded electrode and solutions of metallic chlorides with an unpolarisable electrode of mercury coated with calomel, and secondly, solutions of silver salts with a silver electrode. From his results he deduces the following law. There exists the same apparent potential difference between gold and equimolecular solutions of electrolytes containing a common ion and having an electrode corresponding with this ion. W. G.

Theory of the Skinner-Case Electrolytic Thermo-element, $Sn(CrCl_3)Pt$, and on Other Elements of Analogous Type. ROBERT KREMANN and FELIX NOSS (*Monatsh.*, 1913, **34**, 7—67).—The *E.M.F.* of a cell composed of tin or tin amalgam and platinum or carbon in a dilute solution of chromic chloride increases with the temperature, but the observations of Skinner (A., 1896, ii, 3) did not agree with those of Case. Since the action of the cell depends on the reaction $2CrCl_3 + Sn \rightleftharpoons SnCl_2 + 2CrCl_2$, this equilibrium has been studied at the outset. The results show that the dissolution of the tin increases slowly from 22° to 42°, faster from 42° to 62°, and rapidly from 62° to 80°. The constant K from the expression

$$(CrCl_3)^2/\{(SnCl_2)(CrCl_2)^2\}$$

increases with increasing dilution, which is explained by assuming that it is only the green variety of chromic chloride which takes part in the reaction (compare Olie's study of the equilibrium, violet $CrCl_3 \rightleftharpoons$ green $CrCl_3$, A., 1906, ii, 859). For the purpose of the further investigations it was necessary to know the dependence of the amount of tin in solution on the original concentration of the chromium chloride and on the temperature, and therefore the factor $SnCl_2/CrCl_2 + CrCl_3$ has been plotted against chromic chloride (constant temperature) and temperature (constant initial concentration). The stronger the solution, the faster does this factor rise with temperature.

Measurements of *E.M.F.* under different conditions were made; the *E.M.F.* of the system platinum or carbon as +pole, and tin or tin amalgam as −pole, in pure chromic chloride (5 mols. per 100) is independent of temperature, and is about 1 volt, but when the solution is saturated with tin the *E.M.F.* falls off enormously. The potential drop $Pt|CrCl_3$ is also strongly affected by changes in the solution, from which the conclusion is drawn that the tervalent chromium ions are reduced at the anode, a change which is very dependent on temperature. Hence, when an exhausted cell, that is, one which is saturated with tin and chromous chloride, is raised to a higher temperature, more tin dissolves, the reduction of $Cr^{\cdot\cdot\cdot}$-ions to $Cr^{\cdot\cdot}$-ions can proceed farther, and a further current is obtained. When the element has been exhausted at a high tem-

perature (93°), no further current is developed on cooling, since a series of saturations is passed through, but when heated afresh the current is renewed. The quantity of current measured by a copper voltameter is, however, small, but it is about three times as much at 96° as at 18°. It remains constant for some time, then falls, and later on rises again, this change being accompanied by the precipitation of insoluble chromium sesquioxide.

Other equilibria have been studied, and the systems copper–chromic chloride–carbon, tin–vanadic chloride–carbon, and silver–chromic nitrate–carbon, were found to show similar electrical effects, although in the latter case the instability of chromous nitrate soon renders the silver passive, and consequently the potential difference between the electrodes smaller. J. C. W.

The Influence of High Pressures on Faraday's First Law. ERNST COHEN (*Zeitsch. Elektrochem.*, 1913, **19**, 132—133).—The amount of silver deposited in two coulombmeters, one at atmospheric pressure, and the other at pressures of 500, 1000, and 1500 atmospheres, was compared. In most cases the weights are found to be identical; in one case there is a difference of 1 in 15,500. From the results the author draws the conclusion that the ionic charge does not vary 1 in 17,000 on changing the pressure from one atmosphere to 1500 atmospheres. J. F. S.

Anodic Oxidation of Ammonia in an Acid Liquid in the Presence of Silver Salts. GINO SCAGLIARINI and A. CASALI (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 726—729; *Gazzetta*, 1913, **43**, i, 30—36).—When a solution of ammonium sulphate saturated with silver sulphate and contained in a porous pot is used as anodic liquid, and a solution of sulphuric acid (10%) is taken as cathodic liquid, on electrolysis some nitric acid is formed round the anode. From the authors' experiments the production of the acid appears to be favoured by rise of temperature (about 3·5 grams of nitric acid per 100 grams ammonium sulphate at 90°, as compared with 0·13 grams at 0°), but the amount of nitric acid formed is inversely proportional to the concentration of the ammonium sulphate. The production of nitric acid falls off as the experiment is continued, probably owing to migration of the catalyst from the anodic compartment. R. V. S.

The Mechanism of the Chlorination of Benzene in the Electrolytic Cell. RALPH G. VAN NAME and CARLTON H. MARYOTT (*Amer. J. Sci.*, 1913, [iv], **35**, 153—170. Compare Cohen, Dawson, and Crossland, T., 1905, **87**, 1034).—The electrolysis of benzene in a solution of lithium chloride in glacial acetic acid gives chlorinated benzenes, under favourable conditions, to the extent of 50—70% yields. Both addition and substitution products are formed, the latter predominating, but there is nothing to show that the effects are not due to the secondary action of chlorine previously set free by the current and dissolved in the electrolyte. Benzene dissolved in the same solution is readily chlorinated by direct treatment

with chlorine gas in the dark, yielding additive and substitution compounds in proportions which vary with the conditions.

The addition of benzene to the acetic acid–lithium chloride solution during electrolysis raises the anode potential by an amount equal to or greater than that produced by a similar amount of carbon tetrachloride. This indicates that benzene has little or no depolarising action towards chlorine, at least in this case, and therefore that the chlorination of the benzene is not electrolytic in character. Phenol, added under similar conditions, produces a decided lowering of the anode potential, substitution products being formed.

The rate of chlorination of benzene, when dissolved in the same medium saturated with chlorine, was measured at 10·2°, and then the rate under simultaneous electrolysis. In the latter case there was no perceptible acceleration of the rate of chlorination under conditions where a 10% current yield should have been evident. Both additive and substitution products, in the ratio of about 2:3, were formed, this ratio increasing with the progress of the reaction. The reaction velocity calculated on the assumption that monochlorobenzene and benzene hexachloride were the sole products, showed a steady rise, but the rate of chlorination of monochlorobenzene, as determined separately, appeared to be sufficient to account for this effect.

From the above results it follows that there is no positive evidence of strictly electrolytic, that is, anodic, chlorination of benzene.

T. S. P.

Measurement of the Energy of the Ultra-violet Radiation Emitted by an Arc in Mercury Vapour under Different Conditions. MARCEL BOLL (*Compt. rend.*, 1913, **156**, 313—315).—A study of the energy emitted by a mercury-vapour lamp under varying conditions of voltage and current strength. The results show that the energy for $\lambda = 2536$ emitted by the arc in mercury vapour is a parabolic function of the electrical power expended. A formula is given by means of which an approximate calculation can be made for the radiation from such a lamp under any conditions.

W. G.

Selective Absorption of Electromagnetic Waves. W. ROMANOV (*Ann. Physik*, 1913, [iv], **40**, 281—296).—The author has investigated the absorption of electromagnetic waves of wave-length ranging from about 40 to about 100 cm. in methyl, ethyl, *iso*butyl, and amyl alcohols. The curves which are obtained by plotting the absorption coefficient as a function of the wave-length exhibit distinct maxima and minima, indicating that the absorption spectrum for long-waved electromagnetic waves is quite similar to the spectrum obtained in the case of heat rays.

H. M. D.

The Additivity of Diamagnetism in Compounds. PAUL PASCAL (*Compt. rend.*, 1913, **156**, 323—325. Compare A., 1910, ii, 100, 179).—The absolute values of the atomic coefficients of mag-

netisation of a number of non-metallic elements, as calculated by difference from the coefficients of simple organic compounds containing them, the coefficient for water being taken as $-7 \cdot 2 \times 10^{-7}$, show a very close accord with the values obtained directly on the elements. In the case of a diamagnetic metal, the coefficient, similarly calculated by difference, is not a constant value, but diminishes with increase in molecular weight of the organo-metallic compound, the values for a homologous series tending towards a limit figure, which, for the metals studied (tin and mercury), show a striking agreement with the values obtained by direct determination. This method of difference thus affords means of determining the coefficient of magnetisation of diamagnetic elements, which it is difficult to prepare in the pure state, but of which pure organo-derivatives can be prepared. W. G.

Relative Scale of Temperature for Solid Substances. Hans Alterthum (*Ber. Deut. physikal. Ges.*, 1913, **15**, 25—33).—A theoretical paper in which, in reference to the Planck-Einstein formula for the energy content of a solid substance, it is suggested that the temperature of a solid should be expressed on a scale determined by the condition that the energy content is directly proportional to the temperature. This scale will vary from one substance to another, and even in the case of substances of high melting point, the melting points on the relative scale will differ materially from those on the absolute scale. The author considers that Lindemann's formula (*Physikal. Zeitsch.*, 1910, **11**, 609) for the connexion between the melting point and the vibration frequency should be modified in such a way that the melting temperatures are expressed on the relative scale. The modified formula is applied to the data for silver, aluminium, copper, lead, platinum, and zinc. H. M. D.

Specific Heat of Helium and Certain Diatomic Gases between 20° and −180°. Karl Scheel and Wilhelm Heuse (*Sitzungsber. K. Akad. Wiss. Berlin*, 1913, 44—48).—The measurements were made by the method of continuous flow with the apparatus described in a previous paper (A., 1912, ii, 19). From the molecular heat at constant pressure (C_p), that at constant volume (C_v) has been calculated. The following pairs of numbers represent respectively the values of C_p and $k = C_p/C_v$: helium, 18° (4·993, 1·660), −180° (4·934, 1·673); hydrogen, 16° (6·860, 1·407), −76° (6·365, 1·453), −181° (5·330, 1·597); nitrogen, 20° (6·983, 1·400), −181° (7·162, 1·468); oxygen, 20° (6·98, 1·399), −76° (6·86, 1·416), −181° (7·30, 1·447); air, 20° (6·965, 1·401), −76° (7·04, 1·401), −181° (7·23, 1·450); carbon monoxide, 18° (7·006, 1·398), −180°, (7·244, 1·472). The above data are compared with the results of other observers, and evidence adduced which indicates that the probable error attaching to Regnault's numbers is not less than about 1%. In the case of all the diatomic gases examined, it is found that the specific heat ratio increases very considerably when the temperature is lowered from 20° to −180°.

Molecular heat values have also been calculated for the various gases on the assumption that they obey the simple gas laws.

H. M. D.

Influence of the Free Electrons on the Specific Heat of Metals and Alloys. OSKAR RICHTER (*Ann. Physik*, 1912, [iv], **39**, 1590—1608).—The specific heats of complete series of bismuth–tin and bismuth–lead alloys have been determined, with the object of ascertaining whether free electrons contribute in measurable amount to the heat capacity of metals. For both series of alloys the electric and thermal conductivities are much smaller than would be expected according to the mixture rule, and in both series it has been found that the deviations from the straight line relationship are such that the ratio of thermal to electric conductivity remains constant. According to Drude's theory, the diminution in the electric and thermal conductivity observed in a binary alloy of this type is due to a decrease in the number of free electrons, and if these electrons are of any appreciable importance in connexion with the heat capacity of the alloys, it should be possible to detect corresponding deviations from the mixture law in the specific heat values.

The measurements were made in a Bunsen ice calorimeter, and control experiments indicate that the accuracy attained in the specific heats amounts to 0·01 to 0·02%. In the case of the bismuth–tin alloys the observed specific heats are slightly greater than the calculated values if the mixtures close to the tin end of the series are excepted. For the bismuth–lead series the differences between observed and calculated values are in the same direction but of much greater magnitude, a maximum difference being exhibited by the alloy containing equal weights of the two metals.

These experimental measurements afford therefore no evidence in support of the view that the free electrons are responsible for a measurable fraction of the total heat capacity of the metallic alloys. This result is quite consistent with the theory of specific heat put forward by Richarz.

H. M. D.

[Law of Dulong and Petit.] FRANZ RICHARZ (*Ann. Physik*, 1912, [iv], **39**, 1617—1624).—The author discusses the relation between Einstein's theory and the views which he has put forward in reference to the law of Dulong and Petit. It is claimed that the essential difference is to be found in the special assumptions made by Einstein as to the mechanism by which energy transfer takes place between the atoms. These assumptions lead to the conclusion that the atomic heat cannot be greater than the normal value. Since this is not in agreement with experiment, it would appear that these assumptions must be modified, and it is suggested that the electrons responsible for the conductivity are also involved in the process of energy transfer. In addition to this, it would appear to be necessary, in those cases where the normal value of the atomic heat is exceeded, to assume that these electrons are responsible for a portion of the absorbed heat energy. The fact that the

strongly electro-positive alkali metals have abnormally high specific heats at moderate temperatures is regarded as distinctly favourable to this view.

A further factor which may influence the atomic heat is the formation of atomic complexes. This will reduce the degree of freedom of the vibrating atoms, and lead to a diminution in the heat capacity. This may give rise to a variation of the specific heat with the temperature, which is quite independent of that indicated by Einstein's theory. H. M. D.

Internal Pressure in Fluids. ÉMILE H. AMAGAT (*Ann. Chim. Phys.*, 1913, [viii], **28**, 5—48).—A résumé of work already published in A., 1909, ii, 549; 1911, ii, 1061, and 1912, ii, 428. T. A. H.

Melting Curves of Stable and Metastable Crystalline Substances. FRIEDRICH KÖRBER (*Zeitsch. physikal. Chem.*, 1913, **82**, 45—55).—From considerations of the *Z*-function of the thermodynamic potential, it was shown by Tammann (*Göttinger Nachr. math.-phys. Kl.*, 1911, 353) that the melting curves of the stable and metastable forms of a substance would probably not cut one another. The present paper gives an account of the determination of the melting curves of the two forms of acetamide, phthalide, ethyl aminocrotonate, chloroacetic acid, and sodium thiosulphate. These were determined at pressures from 1 to 2875 atmospheres, and although it is the opinion of the author that the pressure applied was not high enough to finally settle the question, yet the results point to the conclusion that the two curves do not cut one another. J. F. S.

Latent Heats of Vaporisation and Maximum Pressures. ANATOLE LEDUC (*Compt. rend.*, 1913, **156**, 225—227).—Combining Clapeyron's formula for the latent heat of vaporisation with his own formula for the specific volume of the saturated vapour (compare A., 1912, ii, 831), and taking previously recorded values for the maximum pressures and specific heats of water, ether, and benzene, the author has calculated the latent heat of vaporisation of these substances at temperatures above their boiling points. His calculated results being at variance, particularly in the case of ether and benzene, with the experimental values recorded by other workers, the author suggests the advisability of redetermining the values of the maximum pressures on the pure substances, the temperatures being converted to the thermodynamic scale. W. G.

Constancy of the Boiling Point of Sulphur. WALTHER MEISSNER (*Ann. Physik*, 1912, [iv], **39**, 1230—1242).—In utilising the boiling point of sulphur as a thermometric fixed point, the mercury or resistance thermometer is usually surrounded by a protecting cylindrical or conical sheath of some material, such as glass, asbestos, iron, or aluminium. With the object of determining the influence, if any, of the nature of the protecting sheath, comparative measurements have been made with sheaths of different

materials. These indicate that aluminium or other good reflectors cannot be satisfactorily employed in the standardisation of thermometers by means of the boiling point of sulphur, for the temperatures indicated are appreciably too low, the difference amounting to as much as 0·2°. If the aluminium sheath is blackened or lined on the inside with asbestos paper, the depression, caused by the reflection from the metal surface, disappears, and the normal boiling point is recorded. H. M. D.

The Vapour-pressure Curve of Nitrogen Tetroxide. FRANZ RUSS [with ERNST EBERWEIN] (*Zeitsch. physikal. Chem.*, 1913, **82**, 217—223).—The present paper is an account of experiments of the same nature as those of Scheffer and Treub (A., 1912, ii, 132). The experimental pressures were obtained by use of a mercury manometer, and despite what is said by Scheffer and Treub against the use of mercury for pressure determinations of this type, they agree very well with those obtained by means of a glass manometer. The vapour pressures were determined from $-80°$ to $-15°$, and are compared with values of Guye and Drouginine (A., 1910, ii, 1056), and found to differ more and more from these values as the temperature is reduced. The vapour pressure is controlled by a calculation of the heat of sublimation of nitrogen tetroxide by the Clausius formula, the value 10,850 cal. being obtained. This agrees well with value of Berthelot and Ogier (*Landolt Börnstein "Tabellen"*) and Ramsay (T., 1890, **57**, 590). The pressure values are also calculated from the Nernst equation, making use of the critical pressure 100 atmospheres as deduced by Scheffer and Treub (*loc. cit.*). The calculated and experimental values agree fairly well. J. F. S.

Simple Demonstration of the Lowering of Vapour Pressure. WALTER W. REED (*Chem. News*, 1913, **107**, 64).—The lowering of the vapour pressure of a solvent by a solute at ordinary temperature is readily demonstrated by using three similar thermometers, two of which are treated as "wet bulbs" in hygrometry, the wick in one case dipping into the pure solvent, in the other case into the solution. It is found that the thermometer with the wick dipping into the solvent has a lower reading than that with the wick dipping into the solution, and that both readings are lower than that indicated by the dry-bulb thermometer. The apparatus is available for organic solvents as well as for water. H. W.

Variation of the Vapour Pressure of Aqueous Sulphuric Acid Solutions with the Temperature. CARL HACKER (*Ann. Physik*, 1912, [iv], **39**, 1338—1349).—According to the relationship known as von Babo's Law, the ratio between the vapour pressure of an aqueous solution (p_s) and that of pure water (p_w) is independent of the temperature. This empirical result is, however, inconsistent with the requirements of thermodynamics, which leads to the relation $d(\log p_s/p_w)/dT = \Delta/RT^2$, where Δ represents the heat of dilution of the solution. In view of this discrepancy, the author has made measurements of the difference between the vapour

pressure of water and a number of aqueous sulphuric acid solutions at temperatures between 30° and 80°. The data show that the ratio $(p_w - p_s)/p_w$ is by no means constant, but diminishes as the temperature rises. In the case of a solution containing 32·59% of sulphuric acid, the value of this ratio was found to fall from 0·277 at 31·3° to 0·252 at 80·3°; for a solution containing 41·54% of acid, the ratio fell from 0·460 at 32·6° to 0·430 at 60·8°.

By reference to Thomsen's data for the heat of dilution of sulphuric acid solutions, it is shown that the observed variation of $(p_w - p_s)/p_w$ with the temperature is in fairly good agreement with that calculated from the above thermodynamic relation. In making this comparison, it has been assumed that the heat of dilution of sulphuric acid solutions may be regarded as independent of the temperature. H. M. D.

Thermochemical Investigations in the Alicyclic Series. WALTER A. ROTH and GUSTAF JIM ÖSTLING (*Ber.*, 1913, **46**, 309—327. Compare T., 1912, **101**, 457; A., 1910, ii, 586; 1911, ii, 1065, etc.). —The following molecular heats of combustion at constant pressure have been determined: Methyl *cyclo*propane-1:1-dicarboxylate, 827·7 Cal.; *cyclo*propanecarboxylic acid, 479·7 Cal.; ethyl *cyclo*butanecarboxylate, 966·0 Cal.; *cyclo*butanecarboxylic acid, 641·6 Cal.; dimethyl*cyclo*butane-1:2-dicarboxylate, 984·5 Cal.; methyl *cyclo*pentane-1:2-dicarboxylate, 1117·7 Cal.; methyl α-tanacetonedicarboxylate, 1452·9 Cal.; keto-α-tanacetonecarboxylic acid, 1328·7 Cal.; *cis*-methyl norpinate, 1288·8 Cal.; methyl pinate, 1441·6 Cal.; methyl pinonate, 1478·8 Cal.; methyl *spiro*heptanedicarboxylate, 1409·1 Cal., β-pinolene or *cyclo*fenchene, 1471·1 Cal.; cyclene, 1469·1 Cal.; thujane, 1508·6 Cal.; thujyl alcohol, 1479·4 Cal.; thujone, 1431·9 Cal.; camphor, 1412·7 Cal. The following dissociation constants in aqueous solution at 25° were also determined: *cyclo*propanecarboxylic acid, 0·0000136; keto-α-tanacetonecarboxylic acid, 0·0000115; *cyclo*butanecarboxylic acid, 0·0000173; pinonic acid, 0·0000215.

From a consideration of the above and other data, the authors come to the conclusion that Stohmann's rule, according to which the molecular heats of combustion and dissociation constants run parallel, holds very well for the simple polymethylene acids, but not for the two keto-acids, keto-α-tanacetonecarboxylic acid and pinonic acid.

The relation between ring-form and energy-content, as put forward by Stohmann-Kleber and Berthelot, is verified for the simpler compounds. The order of the energy-content is: five-ring, six-ring, double linking, three-ring, four-ring. A seven-ring appears to have a somewhat greater energy-content than a six-ring.

The influence of conjugation or non-conjugation, semi-cyclic or endo-cyclic position, of the double linking is discussed, since these secondary influences make comparison very difficult. A marked non-symmetrical structure appears to increase the energy-content.

The results obtained with the one compound so far investigated appear to show that the *spiro*-cyclic arrangement of the carbon

atoms is relatively stable. A di- and tri-cyclic arrangement appears to increase the energy content. For three- and four-rings, which are attached either to or in a six-ring, the energy-content is apparently the same as for the isolated rings. T. S. P.

The Laws of Corresponding States. ÉMILE H. AMAGAT (*Compt. rend.*, 1913, **156**, 271—277).—A theoretical discussion of the above law, which the author considers may hold good for normal substances, deviations from the law being the result of secondary phenomena, particularly those of polymerisation. This is borne out by the fact that, of the organic compounds considered, the alcohols, which exhibit a tendency to polymerise, show the widest deviation from the law. He further replies to some criticisms of Mathias (*Congrès du froid*, 1912). W. G.

The Elements of Energy. JACQUES DUCLAUX (*Compt. rend.*, 1913, **156**, 142—144).—A theoretical discussion of the relationship between the element of energy, as defined by Planck, being the smallest amount of energy which can intervene in a radiation of wave-length λ, expressed by $\epsilon = 19 \cdot 6 \times 10^{-17}/\lambda$, and the element of energy from the Pictet-Trouton law, the smallest amount of energy which can intervene in a chemical transformation or in a change of state at a temperature T, $\epsilon_1 = 9 \cdot 5 \times 10^{-16} T$. Taking the case of a dark body emitting rays entirely of wave-length λ_0 at a temperature T_0, the author finds the ratio ϵ/ϵ_1 is very close to unity. W. G.

The Molecular Association of Liquids. I. ALEXIUS J. BATSCHINSKI (*Zeitsch. physikal. Chem.*, 1913, **82**, 86—89).—Polemical. An answer to the criticism of Tyrer (A., 1912, ii, 739) on the author's calculations of critical temperature (A., 1911, ii, 189). J. F. S.

The Molecular Association of Liquids. II. ALEXIUS J. BATSCHINSKI (*Zeitsch. physikal. Chem.*, 1913, **82**, 90—92).—The author has calculated the metacritical temperature and association factor by means of the formula deduced by him (A., 1902, ii, 444) for propyl, *iso*propyl, butyl, *iso*butyl, amyl and allyl alcohols, and for formic, propionic, butyric, and *iso*butyric acids at a series of temperatures.

He also calculates the metacritical density of water from the atomic critical volumes of hydrogen and oxygen, and thus is able to arrive at the metacritical temperature for water. The result is the same as that previously obtained by him by the method quoted above. J. F. S.

A Method for the Determination of the Density of Solid Substances. J. L. ANDREAE (*Zeitsch. physikal. Chem.*, 1913, **82**, 109—114. See also A., 1911, ii, 469).—A method is given for the determination of the density of solid substances which are either very soluble or lose water of crystallisation very easily. The determinations are effected in a dilatometer, which consists of a bulb *a*

of about 10 c.c. capacity, which is connected by means of a narrow tube *b* with a wider tube *d*. The volume of the bulb is known as well as that of the tube *b*, which is also graduated. The method consists in placing about 20 grams of the carefully dried crystals into *d*; should these contain water of crystallisation, the water content is first of all accurately determined. Then the whole is weighed, the salt is then washed down into the bulb *a*, and sufficient water is added to completely dissolve all the solid. The tube is then placed in an inclined position and heated until the liquid stands in the narrow tube. Then the whole is weighed again; thus the weights of crystals and water are known as well as the sum of the volumes at a given temperature. If then the solubility of the substance at that temperature and the density of the mother liquor is known, it is obvious that the volume of the mother liquor and consequently the volume of the crystals must be known. Hence the density, unaffected by efflorescence or absorbed air, is known. The author has compared the values obtained by this method with the values obtained by other methods for substances which are not easily changed, and comes to the conclusion that by this method the density of a solid can be obtained with the same degree of accuracy as obtains in the case of gases. J. F. S.

Normal and Abnormal Cases of Specific Volume of Binary Liquid Mixtures. H. S. Van Klooster (*J. Amer. Chem. Soc.*, 1913, **35**, 145—150).—It has been shown by Hyde (A., 1912, ii, 1138) that when *p*-nitrotoluene is dissolved in carbon disulphide, the specific gravity of the solution is less than that of carbon disulphide itself, although *p*-nitrotoluene has a higher specific gravity than carbon disulphide. Considerations, based chiefly on Hubbard's work (A., 1910, ii, 809), are now advanced which indicate that this phenomenon cannot be regarded as abnormal, and reference is made to a really abnormal case, that of chloroform and ether, which was recorded by Guthrie (A., 1885, 339). E. G.

A Relation between the Atomic Volumes of the Elements and their Power of Forming Complex Compounds. G. Hirschfeldt Hansen (*Zeitsch. anorg. Chem.*, 1913, **79**, 322—326).—Elements of small atomic volume have the greatest tendency to form stable complex groups. This principle is illustrated by an arrangement of the elements according to atomic volume. C. H. D.

Viscosity and its Significance for the Chemistry of Celluloid in Theory and Practice. H. Schwarz (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 32—42).—An account is given of the application of viscometric methods in the investigation of nitrocellulose, and the changes which it undergoes in solution. From measurements of the viscosity of solutions of nitrocellulose in camphor-alcohol, ether-alcohol, and in acetone, it is found that the viscosity increases very rapidly with increase in concentration, and that the solutions exhibit the phenomena of ageing. The ageing is accompanied by a very considerable increase in the viscosity, which is more pro-

nounced in the case of the more concentrated solutions. The influence of the nitration process, including the washing and bleaching processes, on the viscosity of nitrocellulose solutions is also examined, and the question of the molecular weight of cellulose is discussed in reference to the viscosity data. H. M. D.

Change of the Surface Tension of Mercury on the Addition of Metals. FRIEDRICH SCHMIDT (*Ann. Physik*, 1912, [iv], **39**, 1108—1132).—The influence of small quantities of various metals on the surface tension of mercury has been examined. The surface tension data were obtained by a method involving the measurement of the dimensions of the wave forms which are set up in the jet of liquid which issues from a tube provided with an elliptically shaped aperture. For this purpose the mercury or amalgam jet was photographed, and the required dimensions obtained by measurement of the negatives by means of a micrometer microscope. In addition, the times required for the outflow of equal volumes of mercury and the amalgams were determined, and from these data the ratio of the surface tensions can be calculated.

The observations show that the metals examined can be divided into three groups. Even at the highest concentrations investigated (about 2%), zinc, cadmium, thallium, gold, tin, and lead produce very little change in the surface tension of the mercury. The alkaline earth metals and lithium increase the surface tension to a very considerable extent. Traces are sufficient to produce an appreciable increase, and when the concentration of the added metal amounts to 0·003 to 0·006%, the influence of the addition of a further quantity is relatively small. Sodium, potassium, rubidium, and cæsium reduce the surface tension very markedly. In the case of the first three alkali metals the influence is very small at the lowest concentrations; larger quantities have a relatively very much greater effect, but if the concentration of the alkali metal is still further increased the diminution of the surface tension becomes much less pronounced. The interval of concentration for which the influence of the alkali metal is greatest, varies considerably from one member of the group to another. In the case of cæsium, the initial stage appears to be absent, the smallest traces producing a lowering of the surface tension.

From the observations it is evident that, in general, metals belonging to the same periodic group have a similar action on the surface tension of mercury. When the change in the surface tension is plotted as a function of the atomic weight of the added metal, a periodic curve is obtained.

In the group containing the alkali metals and gold, and in that which contains the alkaline earth metals, lithium and thallium, the surface tension of the amalgam is found to increase with the melting point of the dissolved metal. H. M. D.

Internal Friction of Binary Systems. Characteristics of Definite Compounds. NIKOLAI S. KURNAKOV and S. F. SHEMTSCHUSHNI (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1964—1991).—The

authors have investigated, at various temperatures, the viscosities of the following binary systems, which form definite compounds (thiocarbamides) and at the same time remain liquid and homogeneous: allylthiocarbimide and piperidine; phenylthiocarbimide and diethylamine; [with V. ZEJLIGER] allylthiocarbimide and methylaniline; [with A. ARSENEV] ethylthiocarbimide and piperidine.

The viscosity isotherms if these systems consist of two separate branches, which are convex to the composition axis, and intersect at an angle (increasing in acuteness as the temperature is lowered) in a maximum corresponding with equimolecular proportions of the components. A similar form is exhibited by the curves connecting the temperature-coefficient of viscosity with the composition. This "rational" type of curve represents an addition to the three types given by Dunstan and Wilson (T., 1907, **91**, 83).

The intersection of the branches of the viscosity isotherms in a rational maximum is an example of the break in continuity indicated by Mendeléev on the basis of his views on the nature of solutions. Assuming that the two branches of the viscosity isotherm belong to one and the same curve, the maximum points of diagrams of the rational type may be compared with singular or nodal points of curves of the third and higher orders. These points may be termed "Dalton points," as they characterise phases containing chemical compounds, which are subject to the laws of constant and multiple proportions.

Measurements of the viscosity of liquid systems represent one of the most sensitive methods of investigating the formation of chemical compounds and of determining their purity.

The system consisting of allylthiocarbimide and the tertiary base, pyridine, which form no substituted thiocarbamide, gives a viscosity curve totally different from those described above, the value of η_{25} for a mixture of the constituents in equimolecular proportions being rather less than the arithmetic mean of the values for the pure components. T. H. P.

Influence of Temperature on the Turbulent Flow. CL. SCHAEFER and G. FRANKENBERG (*Physikal. Zeitsch.*, 1913, **14**, 89—93. Compare Sorkau, A., 1912, ii, 900).—The conclusions drawn by Sorkau from his observations on the flow of liquids in the turbulent condition are criticised. The view that the influence of temperature on the rate of flow in the first stage of turbulence is the same for all liquids is shown to be untenable, a theoretical argument being advanced which indicates that the temperature-coefficient is dependent on the specific nature of the liquid. From the hydronamic equations, a formula is deduced for the temperature-coefficient which is in good agreement with the experimental data.

In a similar manner, it is also shown that the supposed lack of a temperature effect in the second and third stages of turbulence is inconsistent with the facts, and that the actual temperature variation may be expressed by formulæ derived in the same way from hydrodynamic equations.

It is further shown that the observed temperature variation of the transition from the first to the second stage of turbulence is determined by the same condition, which has been shown by Reynolds to regulate the influence of temperature on the transition from the condition of steady flow to that of primary turbulent flow.

H. M. D.

Turbulence Viscosity. GUSTAV MIE (*Physikal. Zeitsch.*, 1913, **14**, 93—95. Compare Sorkau, A., 1912, ii, 900, and preceding abstract).—The irregular grouping of the experimental points on the diagram, which is obtained by plotting the rate of flow as a function of the pressure, is considered to be due to the instability of the flow under the conditions which obtain in the second and third stages of turbulence, and not to mere accidental errors of observation. If this is the case, the real influence of pressure on the rate of flow in the turbulent condition will not be obtained by simply drawing a mean curve through the experimental points on the diagram. The probable nature of the true curve is discussed in reference to Sorkau's data for ethyl acetate, chloroform, and acetone.

H. M. D.

Determination of the Degree of Dissociation of Molten Silver Chloride and Silver Bromide. GÜNTHER SCHULTZE (*Zeitsch., El-ktrochem.*, 1913, **19**, 122—126).—The author shows that when sodium glass is dipped into molten silver salts, silver ions diffuse into the glass and sodium ions diffuse into the silver. Under constant conditions the quantity of silver which diffuses is proportional to the concentration of the silver ions for small concentrations. The relation between the quantity of silver diffusing and the concentration of the silver ions is obtained by introducing small quantities of sodium salts of the same anion, and so reducing the silver ion concentration, and then determining the amount of silver which has diffused. From two such experiments, using small but different quantities of the sodium salt, it is possible to calculate the factor which gives the desired relationship by means of the law of mass action. Consequently it is easy to determine the degree of dissociation directly from the amount of diffused silver. From the experiments the values for silver chloride and silver bromide are found to be $AgCl = 1{\cdot}17 \times 10^{-3}$—$1{\cdot}35 \times 10^{-3}$ at 461°, $AgBr = 2{\cdot}35 \times 10^{-4}$ at 450°. These values agree well with those of Abegg obtained from measurements of the decomposition potential (A., 1900, ii, 5).

J. F. S.

Method of Calculation of the Constant of Capillarity. The Eötvös-Ramsay Rule. The Coefficient of Compressibility of Liquids. PETRU BOGDAN (*Zeitsch. physikal. Chem.*, 1913, **82**, 93—108).—A theoretical paper in which it is shown: (1) that the molecular surface energy, calculated from the values $\gamma = \frac{1}{2}grh\rho$, changes in a linear manner with temperature down to the critical point; (2) that in calculating the surface tension of liquids it is unnecessary to subtract the orthobaric density of the vapour from

the density of the liquid; (3) the coefficient of elasticity of a liquid is equal to the internal pressure, and that the product of the internal pressure and the coefficient of compressibility of a liquid is equal to unity; (4) that between the coefficient of elasticity, the internal pressure, and the vapour pressure of a liquid the relationship $E = P + p$ holds. J. F. S.

The Theory of Osmotic Pressure. JOHANNES J. VAN LAAR (*Zeitsch. physikal. Chem.*, 1913, **82**, 223—224).—The author criticises the formulæ derived for osmotic pressure of solutions by Stern (this vol., ii, 28; see also A., 1895, ii, 107; 1906, ii, 526; 1908, ii, 1018; Lewis, A., 1908, ii, 465). J. F. S.

Diffusion through Rubber Membranes. WILLIAM J. GIES, JACOB ROSENBLOOM, WILLIAM H. WELKER, GEORGE D. BEAL, and GEORGE A. GEIGER (*Biochem. Bull.*, 1912, **2**, 55—86).—On the assumption that the diffusion of a solute depends largely on the chemical affinity of the membrane and the materials on each side of it, study was directed to what occurs in membranes made of rubber in relation to substances soluble in ether. The experiments recorded deal with fats, alkaloids, lipoids, proteins, and pigments. W. D. H.

General Characters of the Actions between Molecules. MARCEL BRILLOUIN (*Ann. Chim. Phys.*, 1913, [viii], **28**, 48—77).—A theoretical paper and the first of a series in which the author proposes to consider the mechanical properties of matter, regarded as composed of a large number of identical particles (molecules) which may be isotropic or anisotropic, in equilibrium, in motion due to the action of a homogeneous medium having a mean uniform movement, or undergoing translatory movement in any sense. In this paper the conditions which govern the mutual mechanical action of molecules are discussed, and the views advanced by Schröder, by Sollas, and by Barlow and Pope (T., 1906, **89**, 1723) are examined. The author considers that the form of the neutral zone (in which mutual action between molecules is nil), and therefore crystalline form, may have a direct relationship to the constitution of the molecule, in so far as this depends on valency, but the molecular volume is, in addition to that, dependent on the nature of the atoms. T. A. H.

The Partial Miscibility of Liquids. ÉMILE BAUD (*Compt. rend.*, 1913, **156**, 317—320. Compare A., 1912, ii, 233, 331).—Studying a mixture of acetic acid and *cyclo*hexane the author has determined the temperature of crystallisation of the acid in the solvent at various concentrations, and has plotted a temperature-concentration curve. For conditions of partial miscibility the temperature at which crystallisation commences must be a minimum point on the above curve. W. G.

The Atomistic Theory of Polymorphism. GUSTAV TAMMANN (*Zeitsch. physikal. Chem.*, 1913, **82**, 172—200).—A theoretical paper in

which the following points are discussed: (1) Polymorphism and the molecular composition of the liquids. The conclusion is drawn in this connexion that in liquids which have a value for $-d(\alpha v^{\frac{2}{3}})/dT$ less than 2·00, that is, liquids which are associated, more than one thermodynamic crystal group may separate, whilst for liquids which have a value more than 2·00 only one crystal group can separate. (2) The crystallisation of different crystal groups from associated liquids. (3) The characteristics of association in crystals. (4) The thermal characteristics of the forms of a thermodynamical crystal group. J. F. S.

Jellies. RICHARD ZSIGMONDY and WILHELM BACHMANN (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 16—18. Compare A., 1912, ii, 1149).—Polemical against von Weimarn (this vol., ii, 32). It is pointed out that the observations relating to the morphological structure of gelatinised soap solutions has not been put forward as evidence in support of the crystalline nature of jellies in general. It would appear that von Weimarn and the authors do not agree in respect of the question as to what properties determine whether or not a substance belongs to the group of jellies. H. M. D.

Reversible Coagulation Processes. SVEN ODÉN and E. OHLON (*Zeitsch. physikal. Chem.*, 1913, **82**, 78—85).—Colloidal solutions of silver and sulphur in 1% solutions were placed in a centrifugal machine and treated with a series of different concentrated solutions of electrolytes. In the case of the silver solution, ammonium nitrate was used, whilst with the sulphur solutions, sodium chloride was employed. The addition of the electrolyte caused coagulation, which was completed rapidly by centrifugalising. Then by more rapid centrifugalising the coagulating electrolyte was removed, and the solution made up to its original volume with the pure solvent, when the colloidal substance again passed into solution. The solution was then examined by ultra-microscopic methods, and the number and size of the particles determined. From these experiments the authors state that there is no change in the size of the particles, even after many coagulations and re-solutions, and that the individual particles maintain their identity in the coagulated mass. J. F. S.

Method for the Determination of the Size of Colloidal Particles. A. DUMANSKI, E. ZABOTINSKI, and M. EVSÉEV (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 6—11).—On the assumption that the colloidal particles are spherical in form, it is shown that the radius of the spheres may be obtained from the formula:

$$r = \sqrt[3]{3v(\delta + c - d_S)/4\pi n\delta},$$

in which n is the number of particles in volume v, c the concentration of the colloidal solution, δ the density of the solvent, and d_S that of the solution.

From the data for three colloidal solutions it is found that the value of r given by this equation is from one and a-half to three

times as large as the value obtained from Stokes's equation for the rate of segregation of the particles.

Other formulæ for the radius of the colloidal particles are deduced by combining Einstein's equation, $\eta/\eta_0 = 1/(1-\phi)$, for the relation between the viscosities of the solution (η) and the solvent (η_0) and the volume (ϕ) occupied by the colloidal substance with Stokes's equation. These are applied in the calculation of the dimensions of the particles in colloidal solutions of arsenious sulphide which have been investigated at 0°, 20°, and 50°.

H. M. D.

The Application of the Principles of Colloidal Chemistry to the Considerations of the Question of Specificity. WOLFGANG OSTWALD (*Biochem. Zeitsch.*, 1913, **48**, 225—229).—Michaelis and Davidsohn (this vol., i, 121) have recently shown that the formation of specific agglutins and precipitins is largely independent of the hydrogen ion concentration, and is to a large extent independent of the electrical charge of the particles concerned in the precipitate formation. They draw the conclusion from these results that the cause of precipitation is essentially of a chemical character, and that the general principles of colloidal chemistry are not applicable to these phenomena. To the latter statement the author takes exception, on the ground chiefly that electrical factors are not the only ones to be taken into account as the cause of precipitation from colloidal solutions. He quotes instances to show that adsorptive precipitation can be produced by two substances, both of which have the same kind of electrical charge (toxins and antitoxins), and, furthermore, certain concentrated electolytes which can neutralise and discharge a colloid (gold sols) do not always produce precipitation. Other important factors which determine the precipitability of a colloid, such as the surface tension at the interfaces, are not influenced solely by the electrical charges, but other chemical and physical characters must be taken into account, such as the grade of the dispersion, and the degree of hydration of the colloid.

S. B. S.

Reciprocal Salt Pairs and Double Ternary Salt Mixtures. ERNST JÄNECKE (*Zeitsch. physikal. Chem.*, 1913, **82**, 1—34. See also A., 1908, ii, 808; 1909, ii, 872; 1912, ii, 750).—A theoretical mathematical paper. The relationship between weight % and molecules % curves for reciprocal salt pairs is discussed, and a new method of representing the weight relationships introduced. The solid–liquid relationships of reciprocal salt pairs is discussed, making use of the Z-function of the thermodynamic potential. The Z-function is defined by the equation $Z = E - TS + Pv$, where E is the internal energy, S the entropy, and T, P, and v the absolute temperature, pressure, and volume. The reciprocal pairs are discussed for cases where one, two, three, four, five, and more solid phases are present. Instances are cited of pairs which will probably show the properties theoretically deduced. The equilibrium of double ternary mixtures $(M'M''M''')(S'S'')$ or $(M'M'')(S'S''S''')$, where $M'M''M'''$ represent

metals, $S'S''S'''$ acid radicles, are discussed for the cases where one, two, three, four, five, six, and more than six solid phases are present.
J. F. S.

The Partial Pressures of Ternary Mixtures. FRANS A. H. SCHREINEMAKERS (*Zeitsch. physikal. Chem.*, 1913, **82**, 56—58).—A mathematical paper, in which from Duhem-Margules equation for binary solutions (A., 1901, ii, 227) the author deduces an expression for ternary mixtures which has the form:

$$x_1 dl\pi_1 + y_1 dl\pi_2 + (1 - x_1 - y_1) dl\pi_3 = 0,$$

in which π_1, π_2, and π_3 are the partial pressures of the constituents in the gaseous phase, and x_1, y_1 and $(1 - x_1 - y_1)$ the quantities of the substances in the liquid. This equation is shown to be a special case of the Duhem-Margules equation. J. F. S.

The Quadruple Point and Triple Curves in Binary Systems. FRANS A. H. SCHREINEMAKERS (*Zeitsch. physikal. Chem.*, 1913, **82**, 59—70).—The author considers the relationships, on the basis of the phase rule, of binary systems which can exist in four phases. The changes which occur when pressure, temperature, or concentration is effected at the quadruple point are discussed. The conclusions arrived at are applied to the systems H_2S—H_2O (Scheffer, A., 1911, ii, 264, 870) and iodine–chlorine (Stortenbeker, A., 1889, 102). J. F. S.

The Equilibria in the System Barium Chloride, Sodium Nitrate, Barium Nitrate, Sodium Chloride, and Water. ANGELO COPPADORO (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 842—850. Compare A., 1912, ii, 441).—Of the four ternary systems comprised in this quaternary system, that of sodium chloride, barium chloride, and water has been investigated at 30° by Schreinemakers and de Baat (*Zeitsch. physikal. Chem.* 1909, **65**, 587). The other three systems and the quaternary system have now been investigated at the same temperature, and the present paper gives the results of this work in a number of tables. R. V. S.

Equilibria between Potassium Hydrogen Carbonate and Salts of Magnesium, Nickel, and Cobalt. T. NANTY (*Ann. Chim. Phys.*, 1912, [viii], **27**, 5—89; 1913, [viii], **28**, 77—208).—The results already recorded (A., 1911, ii, 103, 282) for the action of potassium hydrogen carbonate on salts of magnesium are described in greater detail, and a mathematical discussion of the whole subject is given. It is then shown that the action of potassium hydrogen carbonate on nickel salts is strictly analogous to its action on magnesium salts, both actions being reversible in the ordinary sense. These results are therefore at variance with those observed by Engel (A., 1886, 121). Cobalt salts behave differently, no equilibrium being reached in this case.

The conditions prescribed by various authors, and especially Engel (*loc. cit.*) for the preparation of magnesium carbonate, $MgCO_3,3H_2O$, and potassium hydrogen magnesium carbonate,

$KHCO_3,MgCO_3,4H_2O$, are examined, and shown to be inaccurate and incomplete, and experimental data supporting this conclusion are quoted. The conditions under which either or both salts may be formed are then determined by the use of Gibbs' graphic method for ternary mixtures, and it is shown that these conditions can be verified experimentally; thus at temperatures 7—8°, 15°, and 26—27° the composition of the precipitate is independent of the concentration of the magnesium salt, and depends only on the concentration of the potassium hydrogen carbonate in the generating liquid. At 7—8°, 2·2% of the latter salt is the critical value, anything below that giving magnesium carbonate, and anything above it the double carbonate. At 15° the critical value is about 4%, and at 26—27° about 6%. The only secondary reaction is the reversible decomposition of the double carbonate by water, and to this is due the variation of the critical value with temperature.

The second paper begins with a mathematical and experimental investigation of the conditions necessary for the formation of either carbonate, and methods of calculating the composition of solutions which on admixture will give a precipitate of the required composition are given, with experimental verifications.

The equilibrium conditions for the formation of the double carbonate and its decomposition by water are then investigated, and shown to be identical for the same temperature, under atmospheric pressure. The velocity of the reaction in either direction at the same temperature and pressure is proportional to the difference between the initial and final concentration of potassium hydrogen carbonate in the solution; the velocity constant increases with the temperature.

A similar but less detailed study has been made of the formation of nickel carbonate, $NiCO_3,3H_2O$, and of the double carbonate, $NiCO_3,KHCO_3,4H_2O$, and the results are completely analogous to those obtained for the corresponding magnesium salts.

Cobalt salts on precipitation with potassium hydrogen carbonate give a basic carbonate, $CoCO_3,CoO,5H_2O$, and a double carbonate, $CoCO_3,KHCO_3,4H_2O$, the former amorphous, the latter crystalline. No combination takes place between cobalt carbonate and potassium hydrogen carbonate, and no equilibrium is reached in the action of water on the double carbonate, referred to above.

T. A. H.

Displacement of the Primary Amylamines by Gaseous Ammonia. Félix Bidet (*Compt. rend.*, 1913, **156**, 315—317).—A study of the equilibrium pressures of amylamine hydrochloride and its *iso*-isomeride in the presence of gaseous ammonia at different temperatures. The values for the straight-chain compound are considerably lower than those for the *iso*-compound at low temperatures, but the values become practically equal at 50°. The figures indicate the existence of several definite basic hydrochlorides, the state of equilibrium being a function of the concentration of the ammonia.

W. G.

Influence of Temperature on the Velocity of Chemical Reactions. II. B. SCHVECOV (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, Phys. Part, 516—519).—In a previous paper (this vol., ii, 124), the author has suggested the characterisation of the influence of temperature on the velocity of chemical reactions by the logarithmic temperature-coefficient, η, expressed by $(K_2/K_1)^{\frac{\log \rho}{\log T_2 - \log T_1}}$, where K_1 and K_2 are the respective velocity constants determined for the absolute temperature T_1 and T_2, and ρ is a constant. From this expression it follows that constancy of η requires the fulfilment of the condition $d\log K/d\log T = \text{constant}$.

Starting from the assumption that chemical reaction is a consequence of the reacting molecules impinging one on the other with a sufficient degree of violence, the author now shows mathematically that, in the case when molecules of only two kinds react, $d\log K/d\log T$ has the constant value 1·5. The assumptions made in arriving at this result are that the reaction shall be non-reversible, and that it shall take place either in a gaseous medium or in dilute solution. For reversible reactions, constancy of the logarithmic temperature-coefficient is to be expected only when the velocity of the reverse reaction is virtually independent of the temperature. T. H. P.

The Action of Carbonic Acid on Alkalis and Alkaline Earths as a Time Reaction. DANIEL VORLÄNDER and WALTER STRUBE (*Ber.*, 1913, **46**, 172—181).—When a solution of calcium hydroxide, coloured red with phenolphthalein, is rapidly mixed with an aqueous solution of carbon dioxide of slightly more than the equivalent strength, there is no immediate disappearance of the red colour. The time necessary for decolorisation may vary from a few minutes to several days, increasing with the dilution of the solutions. As the excess of carbon dioxide is increased, the time diminishes, but still remains of the order of several seconds when about four times the equivalent of carbonic acid is used. If a precipitate forms, it is deposited before decolorisation occurs. These results were shown not to be due to alkali being dissolved from the glass, or to other such side-reactions.

Similar results were obtained with solutions of barium and sodium hydroxides, but the times necessary for the disappearance of the red colour were very much less, being generally of the order of a few seconds, unless, in the case of barium hydroxide, the dilutions are very great. Lowering the temperature increases the time.

The authors consider that it is probable that the above phenomena are due to the hydration of carbon dioxide to carbonic acid not being complete in aqueous solution, and taking place only slowly during the neutralisation. No other weak acids, such as hydrogen sulphide, acetic acid, etc., gave similar results.

It is found that pure and well-washed calcium carbonate gives an alkaline reaction to water.

The results show that calcium hydroxide cannot be used for the estimation of the free carbonic acid in water. T. S. P.

The Slow Neutralisation of Carbonic Acid. ALFRED THIEL (*Ber.*, 1913, **46**, 241—244).—Polemical against Vorländer and Strube (preceding abstract). The author points out that according to experiments which are to be published later, the hydroxides of the alkaline earths are not suitable for studying the actual time-reaction with carbonic acid, owing to the gradual alteration in condition ("ageing") which takes place of the carbonates formed. The author has previously observed the time reaction between carbonic acid and sodium hydroxide (*Sitzber. Ges. Wiss. Marburg*, Nov., 1912), and given the same interpretation as Vorländer and Strube (compare also MacBain, T., 1912, **101**, 814). T. S. P.

Kinetic Investigation of the Action of Carbon Monoxide on Solutions of Potassium Permanganate. GERHARD JUST and YRJÖ KAUKO (*Zeitsch. physikal. Chem.*, 1913, **82**, 71—77).—The experiments described were carried out in exactly the same way as the previous experiments on the action of hydrogen on potassium permanganate (A., 1911, ii, 494). It is shown that in neutral solutions of potassium permanganate the rate of reaction is proportional to the concentration of the carbon monoxide. It was found necessary, in order to get effective mixing of the gas and solution, to rotate the reaction vessels 5000 times per minute. The concentration variations were brought about by mixing the carbon monoxide with nitrogen. The reaction is shown to take place, in the first place, between one molecule of carbon monoxide and one molecule of potassium permanganate with the probable formation of an unstable quinquevalent manganese derivative. The influence of temperature was investigated, and found to be such that an increase of 10° doubled the velocity of reaction. The reactions were also carried out with a series of hydrogen carbon monoxide mixtures, from which it is evident that both substances react normally without any influence on one another. J. F. S.

The Velocity of the Reaction of Bromine and Aqueous Solutions of Monohydroxy-Aliphatic Alcohols. ELISABETH RÓNA (*Zeitsch. physikal. Chem.*, 1913, **82**, 225—248).—The velocity constants for the reactions between bromine and methyl, propyl, *iso*propyl, butyl, *iso*butyl, and *tert.*-butyl alcohols are determined by the method adopted by Bugarsky (A., 1910, ii, 281) for ethyl alcohol. The reactions were carried out at 25°, and with the exception of those with methyl and *tert.*-butyl alcohols all occurred in two stages, the alcohol being first oxidised to aldehyde or ketone, and this then to acid. The velocity constants were determined for both reactions, as well as the total reaction constant. The constants increased with the molecular weights of the normal alcohol, the value of the first constant increasing less than the constant for the second reaction, the amount of increase slowly increasing as the molecular weight increases. The *iso*-alcohol has in both cases larger velocity constants than the corresponding normal alcohol, and the amount of increase between two consecutive *iso*-alcohols is much greater than that between the corresponding normal alcohols.

J. F. S.

Gradual Hydrolysis. CARL L. WAGNER (*Monatsh.*, 1913, **34**, 95—170).—The hydrolysis of salts of weak bases with strong acids and of strong bases with weak acids can be conveniently studied by the increase in conductivity which is observed when the requisite dilution is reached. In some instances the increase is not sudden, but proceeds at a measurable speed, and three explanations have been offered to account for this phenomenon. In the case of stannic chloride, which is practically a non-conductor, Kovalevski (A., 1900, ii, 256) suggested that the scarcity of ions accounted for the sluggishness of the process. The hydrolysis of ferric chloride has been assumed to proceed through the stages:

$$FeCl_3 \rightarrow FeCl_2{\cdot}OH \rightarrow FeCl(OH)_2 \rightarrow Fe(OH)_3$$

(compare Antony and Giglio, A., 1896, ii, 250; Goodwin, A., 1897, ii, 16; and Malfitano, A., 1912, ii, 337). A third explanation involves hydrate isomerism as exhibited by green and violet chromium chloride. It has therefore been necessary to conclude that just this particular ionic reaction is measurably slow, or to assume purely theoretical ions, or to construct co-ordinate compounds for each case.

It is remarkable, however, that in all the observed cases, either the weak base or the weak acid shows a great tendency to form a colloidal solution, and the author therefore offers a simple explanation of the gradual increase in conductivity which is based on a conception of the changes in superficial magnitude of the colloid. As the result of hydrolysis, the metallic hydroxide (or the acid) is liberated as a highly-dispersed phase, on the enormous surface of which the liberated acid (or base) is at first completely adsorbed. In the process of time the particles become larger, that is, the surface of the dispersed phase rapidly diminishes, and therefore the adsorbed acid or base is able to enter the continuous phase, the solution.

The theory is supported by experiments on the conductivity of ferric alum in various concentrations where, contrary to the experience of Goodwin with ferric chloride (*loc. cit.*), the solutions get turbid, deposit a precipitate, finally become colourless, and the conductivity does not reach a constant, neither does it attain to the value for solutions of sulphuric acid and potassium sulphate containing the equivalent of $\cdot SO_4$ ions. The addition of protective colloids, such as carefully washed agar-agar, or, better still, gelatin, retards the growth of the conductivity. It also prevents the precipitate from settling in a dense form, so that the acid is washed out by the solution to a greater extent, and hydrolysis apparently proceeds farther. When the precipitate begins to form, however, the protective colloid is carried with it, and is thus removed from further action.

Goodwin found that ferric chloride solutions remained perfectly clear, developed the brown colour of ferric hydroxide sols, and attained a conductivity which agreed with the equivalent quantity of hydrochloric acid. This experience is confirmed, and the explanation offered that the requisite diminution in the surface of the dispersed phase takes place within the region of colloidal

solution, that is, without the formation of macroscopic particles, and therefore equilibrium is more quickly reached. The addition of gelatin again retards the growth of the conductivity to a great extent, even when allowance is made for the smaller conductivity of hydrochloric acid in a gelatin solution. The different behaviour of ferric alum is due to the intensive coagulating action of the bivalent $\cdot SO_4$ ions, and the effect of these on a ferric chloride solution is extremely pronounced. The addition of 1/160,000 of an equivalent of potassium sulphate produces a noticeable difference in the conductivity curve (a possible test for traces of $\cdot SO_4$ ions) and more than 1/2000 of an equivalent causes turbidity and precipitation. The final values are not as high as those for the pure solution plus the sulphate, since the coagulating ions are adsorbed on the ferric hydroxide. This is shown by the fact that the addition of $\cdot SO_4$ ions to an already completely hydrolysed ferric chloride solution causes coagulation and a fall in the total conductivity.

The influence of foreign electrolytes also explains some discrepancies which were observed with ferric acetate and aluminium acetate. When these solutions were prepared by double decomposition, or by casual solution of the hydroxide, the conductivities remained constant for a great length of time. A ferric acetate solution made from freshly precipitated hydroxide which had been completely extracted by conductivity water, however, showed the same gradual hydrolysis and rise in conductivity towards the value for acetic acid, and the effect of potassium sulphate was the same as before.

J. C. W.

Saponification in Stages. III. Hydrolysis of Acid Amides and Nitriles. NICOLAS VON PESKOV and JULIUS MEYER (*Zeitsch. physikal. Chem.*, 1913, **82**, 129—171. Compare A., 1907, i, 462, 819; 1909, ii, 391, 803).—In the first part of the paper a general formula is deduced for the velocity constant of a reaction which takes place between two substances in four stages; thus the reaction $RP^1P^2 + MN$ is considered to occur in the stages $RP^1P^2 + MN = RP^1M + NP^2$, $RP^1P^2 + MN = RP^2M + NP^1$, $RP^1M + MN = RM_2 + NP^1$, and

$$RP^2M + MN = RM_2 + NP^2;$$

all four reactions are assumed to have different reaction velocities. The general formula is then simplified to make it adaptable to special cases. The simplified forms are the same as those deduced by Meyer, from other considerations, for the hydrolysis of the normal esters of dibasic acids. In the experimental part of the paper, the hydrolysis of amides and nitriles of monobasic acids and of amides of dibasic acids, are considered. The experiments were carried out with acetamide, formamide, propionamide, butyramide, *iso*butyramide, valeramide, and hexonamide; acetonitrile and propionitrile; malonamide and succinamide. The amides or nitriles were mixed in weighed quantities with known amounts of hydrochloric acid or sodium hydroxide in flasks which were kept at 18° or 25° in a thermostat. At measured intervals of time 10 c.c. of the reaction mixture were withdrawn, and treated with an excess

of sodium hypobromite, and the quantity of nitrogen formed measured. It is shown that the amides of monobasic acids are hydrolysed more rapidly by alkalis than by acid, although here the difference is not so marked as in the case of esters of dibasic acids; in the latter case Meyer (*loc. cit.*) showed that the ratio between the two velocities was about 3500, whilst in the present case it is only about 6. The reaction in every case is strictly bimolecular, and has a temperature-coefficient of about 2·6 for 10° change of temperature. In the experiments with nitriles, it was found that the reactions occurred too slowly with acids, and consequently experiments were only made with alkalis. In this case it was found that equally good reaction constants could be obtained by using the equations for either the two-step reaction (that is, nitrile $\rightarrow$ amide $\rightarrow$ acid) or the one-step reaction (that is, nitrile $\rightarrow$ acid). From this the authors draw the conclusion that the velocity of the first reaction is extremely great when compared with that of the second stage, and consequently the second stage is the only one which conditions the measurement. The temperature-coefficient of these reactions lies in the region of 2·6, as in the case of the amides. An anomalous case is presented by the hydrolysis of the amides of dibasic acids, inasmuch as no reaction constant which is constant can be obtained. The values of k decrease very rapidly, and after some time reach a figure which displays approximate constancy. This is explained by the authors as due to the fact that the first half of the reaction is abnormal, whilst the second half is normal. It is also shown that both amido-groups are not hydrolysed at the same rate. With acids the constant k_1 is smaller than k_2, whilst with alkalis k_2 is smaller than k_1. This is explained by the fact that there will be a repulsion between the negatively charged acid amide radicle, $NH_2 \cdot CO \cdot R \cdot CO \cdot O'$, and the negatively charged OH' group, whilst between the positively charged $H^{\cdot}$ ion and the acid ion there will be an attraction. J. F. S.

The Dynamics of the Change Acetochloroanilide $\rightarrow$ *p*-Chloroacetanilide in the Presence of Acids. ALBERT C. D. RIVETT (*Zeitsch. physikal. Chem.*, 1913, **82**, 201—216).—The velocity of the change of acetochloroanilide into *p*-chloroacetanilide,

$$(C_6H_5 \cdot NAcCl \rightarrow C_6H_4Cl \cdot NHAc)$$

in aqueous solution by hydrochloric acid of various concentrations is investigated. It is found to be a unimolecular reaction, and the velocity increases with the concentration of the acid. The catalytic action is held to be due to the non-ionised acid alone. The relationship between the concentration of the acid and the velocity constant is expressed by the equation $k=(1-\alpha)C(A+B\alpha C)$, in which k is the velocity constant, C is the concentration of the acid, α the degree of ionisation of the acid, and A and B two constants which have values 0·05 and 0·22 respectively. The temperature-coefficient of the reaction is found to be 3·27 for 10° over the range 0—30°. This value agrees with the expression of Harcourt and Esson (A., 1912, ii, 923), that the ratio k/T^m is a constant; using the value $m=34$, the value $k/T^{34} \times 10^{88}=92$ (approx.). The reaction was also

carried out with solutions of acetic, oxalic, trichloroacetic, and sulphuric acids, at 60°, since the reaction was too slow at lower temperatures. Constant values for k could not be obtained in any of these cases, the reactions evidently proceeding in an abnormal manner. It is noticed that a purple coloration of the solution occurs after the reaction has been in progress for some time; 100 to 200 minutes for sulphuric and trichloroacetic acids, 300 minutes with oxalic acid, and 3000 to 4000 minutes with acetic acid. At the end of the reaction a strong reducing agent is present in the solution. J. F. S.

Velocity of Formation of Precipitates. KASIMIR JABŁCZYNSKI (*Zeitsch. physikal. Chem.*, 1913, **82**, 115—121).—The author has studied the rate at which precipitates are formed from dilute solutions. The method consists in mixing measured volumes of solutions of ammonium chloride and silver nitrate of known concentrations, and observing the time required for the formation of a precipitate. The reactions are carried out in test-tubes, which are covered with a paper mantle which has a square hole cut in it. This hole is partly covered with a narrow strip of black paper. The moment at which a precipitate is judged to have been formed is that moment at which the black strip becomes invisible. The reactions were all effected in absence of actinic light. Using a normal solution of silver nitrate and adding to it an equal volume of ammonium chloride of various concentration, it is shown that the velocity diminishes as the concentration of the ammonium chloride increases from 0·01N to 0·016N, at which point it reaches a minimum. Afterwards it increases to an instantaneous precipitation as the concentration increases to normal. Similarly, starting with 5 c.c. of 0·01 ammonium chloride, and adding an equal volume of silver nitrate solution, it is shown that the velocity decreases as the concentration of the silver nitrate increases from 0·01N to 0·02N, after which it increases to an exceedingly high value as the concentration of the silver nitrate is increased to 0·5N. The addition of increasing small quantities of ammonia causes an increase in the velocity as the concentration of the ammonia increases up to 0·006N, whilst on the other hand the addition of sodium thiosulphate causes a retardation of precipitation as the concentration of the sodium thiosulphate increases from 0·000012N to 0·000120N. The addition of alcohol decreases the velocity of precipitation. The velocity of precipitation increases 100% for an increase of 10° in temperature. The velocity of precipitation of silver bromide is only about one-half that of silver chloride, which the author is of the opinion points to the fact that the velocity of precipitation is not conditioned by supersaturation. J. F. S.

Theory of the Efflorescence of Saline Hydrates. Influence of Temperature. CH. BOULANGER and GEORGES URBAIN (*Compt. rend.*, 1913, **156**, 135—137. Compare this vol., ii, 34).—A mathematical discussion of the rate of efflorescence of identical crystals at different temperatures. Coupling this with laws previously deduced (*loc.*

cit.) for the rate of efflorescence of crystals of different sizes and at different stages of efflorescence, the authors have obtained an expression by which it is possible to deduce the heat of hydration from the law governing the efflorescence at two different temperatures.

W. G.

Velocity of Reaction and Catalysis. KURT H. MEYER (*Zeitsch. Elektrochem.*, 1913, **19**, 76).—Polemical. An answer to Trautz (*ibid.*, 1912, **18**, 917) concerning the author's paper (A., 1911, i, 350).

J. F. S.

Outline of a Theory of Homogeneous Catalysis. MARTIN A. ROSANOFF (*J. Amer. Chem. Soc.*, 1913, **35**, 173—177).—Homogeneous catalysis is either direct or indirect. A direct catalyst is a substance which influences the reaction by the formation of intermediate molecular complexes, whilst an indirect catalyst is one which does not take any part in the reaction, but influences its velocity by affecting the particular conditions (such as the association or dissociation of the reacting substances) on which the reaction depends. A direct catalyst obeys the law of mass action, but an indirect catalyst does not. An equation of catalysis has been deduced which is based on the assumption that the relative change of the velocity coefficient of a reaction is proportional to the change in the concentration of the indirect catalyst. It is shown that the number of indirect catalysts possible for any given reaction is indefinitely large, and that all negative catalysts belong to this class. According to this theory, the velocity of chemical reactions is governed both by the law of mass action and a catalysis law. The equation expressing the effect of indirect catalysts has been found of great assistance in enabling the type of catalysis in any given reaction to be characterised and in thereby elucidating the mechanism of the reaction. Experimental evidence of this will be given in subsequent communications.

E. G.

Surface Combustion. WILLIAM A. BONE (*Ber.*, 1913, **46**, 5—28).—An illustrated lecture on the catalytic influence exerted on gaseous combustion by hot surfaces, delivered before the German Chemical Society.

D. F. T.

Catalytic Studies. II. Barium Ion Catalysis. EMIL ABEL (*Monatsh.*, 1913, **34**, 171—191. Compare A., 1912, ii, 927).—The addition of barium salts causes an acceleration in the oxidation of sodium thiosulphate by hydrogen peroxide. This catalytic action is not due to the mere influence of a neutral salt, for alkali salts cause no acceleration, neither is it due to the liberation of hydrogen ions according to the equilibrium, $Ba^{\cdot\cdot} + H_2O_2 \rightleftarrows BaO_2 + 2H^{\cdot}$, for free acids have no effect, and barium peroxide can hardly be expected to behave more powerfully than hydrogen peroxide. The author therefore suggests the possibility of changes in the valency of the barium ion, and since the catalytic action is also observed in the oxidation of potassium iodide with hydrogen peroxide and is therefore due to the action of the peroxide on the barium ion,

the conclusion is drawn that quadrivalent barium ions are formed. Similar results have been obtained in preliminary experiments with calcium and strontium ions. J. C. W.

Catalysis. XIII. Reaction of Ethyl Iodide with Sodium 3-Thio-1-phenylurazole. SIDNEY NIRDLINGER, F. M. ROGERS, and SOLOMON F. ACREE (*Amer. Chem. J.*, 1913, **49**, 116—127. Compare Acree, A., 1912, ii, 1047).—In continuation of the quantitative study of the mechanism of the reactions of alkyl haloids with urazoles by determining the conductivity of urazole salts and the velocity of their reactions with alkyl haloids (Brunel and Acree, A., 1910, i, 520), an investigation has now been made of the sodium salt of 3-thio-1-phenylurazole.

The velocity of the reaction of ethyl iodide and sodium 3-thio-1-phenylurazole has been determined in solutions of concentrations from $0{\cdot}3N$ to $0{\cdot}025N$. The percentage ionisation of the sodium salt has been measured at the same concentrations by means of the conductivity method. By substituting the values obtained in the equation $K_n = K_i\alpha + K_m(1-\alpha)$, satisfactory constants have been found for K_i and K_m. The results indicate that the velocity of the reaction is a function of the concentrations of both the urazole and the non-ionised urazole salt. E. G.

The Periodic System and Atomic Weight. ALOIS BILECKI (*Zeitsch. physikal. Chem.*, 1913, **82**, 249—252).—The author divides the elements into four groups, which end respectively with helium, argon, xenon, and an unknown element. The lengths of these groups are in the ratio of the squares of the uneven numbers. It is shown that if a series of chosen numbers from 21 to 125 are multiplied by the factor 1·86, the atomic weights of some 36 of the elements are obtained with fair approximation. There is also a series of elements the atomic weights of which are whole numbers, and the author states that still a third series must exist the atomic weights of which will be found to be obtained by a combination of multiples of the numbers 1 and 1·86. J. F. S.

The Life and Work of Marcellin Berthelot. ÉMILE JUNGFLEISCH (*Bull. Soc. chim.*, 1913, [iv], **13**, i—cclx).—An obituary notice. T. A. H.

Substitution of Ground Glass Stopper in Combination Barometer and Manometer. ROSS ALLEN BAKER (*J. Amer. Chem. Soc.*, 1913, **35**, 199).—Radulescu (A., 1912, ii, 37) has described a manometer in which a ground-glass stopper is substituted for the usual sealed end. The author points out that he has used a similar device on a combination barometer and manometer. The use of a mercury seal round the ground-glass stopper prevents the risk of leakage. The larger tube, of capacity 10—15 c.c., which forms the mercury cup, may be fused on to the main tube, and is easily stoppered to prevent volatilisation of the mercury. E. G.

New Cover Glass Support. ROSS ALLEN BAKER (*J. Amer. Chem. Soc.*, 1913, **35**, 200).—A convenient cover glass support can be made by fusing three pieces of glass rod together at one end, and afterwards bending them apart at equal angles and downwards to any degree desired. E. G.

A Simple Form of Gas Generator. FRANK SHEDDEN (*J. Soc. Chem. Ind.*, 1913, **32**, 3).—A cylindrical jar, 48—50 cm. high and 18 cm. diameter, and fitted with a stopcock at the bottom, contains an inner tube, 10 cm. in diameter and narrowed at the top to a neck about 6 cm. in diameter, which is closed by a rubber stopper and glass stopcock. About 8—10 cm. from the bottom the inner tube is constricted to a diameter of 1—2 cm. The inner tube rests on a glass triangle, arranged so as to allow free circulation, and is held in place by a wooden cover, which may, if necessary, be weighted with a leaden collar.

When using powdery substances or fine-grained material, a filter plate is placed on the constriction before charging. A generator of the above dimensions will hold 5 litres of liquid and several kilos. of solid. T. S. P.

A New Reflux and Distillation Condenser. FRANZ MICHEL (*Zeitsch. angew. Chem.*, 1913, **26**, 88).—The lower end of the condenser, which is not in the water jacket, is surrounded by a wider tube, into the side of which is sealed a tube connecting it with, and opening into, that part of the condenser tube which is in the lower part of the water jacket. The vapour from the flask, when the condenser is used as a reflux, passes into the annular space between the two tubes, and hence through the side-tube into the condenser, from which it flows back as liquid, through the central tube, into the flask. T. S. P.

Two Lecture Experiments on the Diamond. WILHELM PRANDTL (*Ber.*, 1913, **46**, 216—217).—Moissan's method of making diamonds may be modified as follows: In a cylindrical can of sheet metal, 10 cm. in diameter by 12 cm. high, is placed another cylinder, open at both ends, of less diameter, and the space between the two filled with dry, powdered fluorspar. The inner cylinder is then filled with a mixture of 200 grams of iron thermit and 10—15 grams of powdered coke, after which it is withdrawn, so that the thermit mixture is surrounded at the sides by the fluorspar, but is in direct contact with the bottom of the sheet metal can. The can is fixed on an iron ring placed above a vessel containing mercury covered with a layer of 15—20 cm. of water, and the thermit mixture fired. The liquid iron dissolves the carbon, melts through the bottom of the can, and is quenched in the water and mercury. The iron is then treated in the usual way to obtain the microscopic crystals of diamond, which are accompanied by some doubly refracting, hexagonal plates, probably of carborundum.

The combustion of a diamond in oxygen can be conveniently shown by heating it in a quartz test-tube, fitted with a cork through

which pass inlet and exit tubes for the oxygen and products of combustion respectively. The combustion of the diamond is started by heating that part of the quartz tube on which the diamond rests with a blowpipe flame. T. S. P.

Reaction between Calcium Permanganate and Ethyl Alcohol. F. ALEX. McDERMOTT (*J. Amer. Chem. Soc.*, 1913, **35**, 219).—The following is recommended as a lecture experiment for demonstrating the oxidation of alcohol to aldehyde. A few fragments of calcium permanganate are dropped on a porous plate moistened with ethyl alcohol. The permanganate first scintillates and then glows for a few minutes, and irritating fumes, suggestive of formaldehyde, acetaldehyde, and acraldehyde, are produced, which, if drawn through a warm ammoniacal solution of silver nitrate, effect a marked reduction.

*iso*Amyl alcohol reacts similarly, but somewhat more slowly, but methyl alcohol and acetone do not behave in this way. E. G.

Lecture Experiments Showing the Formation of Binary Liquid Eutectics. NIKOLAI S. KURNAKOV and N. N. EFREMOV (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1992—2000).—Camphene and methylthiocarbimide readily form a liquid eutectic when mixed at the ordinary temperature, the change taking place in a few seconds. Also, owing to the appreciable vapour pressures of the two components, if these are placed in separate vessels in a closed space, the liquid eutectic makes its appearance in the vessel containing the camphene after the lapse of about twenty-four hours.

The authors have investigated this system, the specimen of camphene used having b. p. 158—158·5°, m. p. 49·3°, and $[\alpha]_D$ + 57·4°. The eutectic mixture is found to contain 73 mol. % of camphene, and to solidify at −8°. The limits of existence of the liquid phase at 15° are represented by 14% and 76·5% of methylthiocarbimide. The system forms no solid solutions of marked concentration, the two components separating in the pure state.

Other systems forming liquid eutectics at the ordinary temperature are: camphene–naphthalene; camphene–benzene; camphene–phenanthrene, and methylthiocarbimide–naphthalene, but in these cases this occurs only within much narrower concentration limits than with camphene–methylthiocarbimide. The following compositions (mol. %) and solidifying points of the liquid eutectic were determined: (1) 86 camphene + 14 naphthalene, +7·5°; (2) 90·5 camphene + 9·5 phenanthrene, +13·5°; (3) 65 methylthiocarbimide + 35 naphthalene, +4·0°. T. H. P.

Inorganic Chemistry.

A New Hydrogen Table. LUDWIG VANINO and A. SCHINNER (*Zeitsch. angew. Chem.*, 1913, **26**, 55—56).—The authors have con-

structed a table showing the weight of 1 c.c. of hydrogen for each degree between the temperatures 10° and 30° and for pressures of from 700 to 770 mm. The weight of 1 c.c. of hydrogen at 0° and 760 mm. is taken as 0·08995 mg.

Optical Investigation of Solidified Gases. II. Crystallographic Properties of Hydrogen and Oxygen. WALTER WAHL (*Proc. Roy. Soc.*, 1913, *A*, **88**, 61—69. Compare A., 1912, ii, 1044).—The apparatus described previously has been modified so as to facilitate the investigation of the crystalline form of hydrogen and oxygen. In spite of the low temperature of crystallisation, the velocity with which hydrogen crystallises is very large. The growth-structures are isotropic, and from the fact that the needle-shaped branches usually grow at right angles to a crystal face of the fully developed crystal, it is inferred that the hydrogen crystals, when fully developed, belong to one of the forms of the regular system rich in crystal faces, that is, the trisoctahedron or the hexoctahedron.

In the case of oxygen, the liquid becomes very viscous before crystallisation sets in, and the crystals which appear are badly developed, and grow very slowly. In order to obtain a homogeneous crystallised product, the cooling must take place slowly, and this condition is difficult of attainment. When the crystalline substance is further cooled it is converted into a strongly doubly-refracting, fine-grained mass of crystals, and from this it appears that oxygen is polymorphous. The transition from one form to the other takes place quite sharply, but the temperature in question has not been determined. It is, however, quite close to the melting point.

Since the physical constants of oxygen have been determined for the most part at the boiling point of hydrogen, these constants must refer to the second crystalline modification. H. M. D.

Condensation of Water Vapour in Presence of Oxides of Nitrogen and of Hydrogen Peroxide. Evidence of the Formation of Hydrogen Peroxide by Oxidation of Water Vapour. Action of Ultra-violet Sunlight on the Earth's Atmosphere. WILLIE BIEBER (*Ann. Physik*, 1912, [iv], **39**, 1313—1337).—The condensation of water vapour from dust-free gases has been examined with the view of determining the nature of the nuclei which act as condensation centres. Ozonised oxygen, which preliminary observations had shown to be free from condensation nuclei, was found to remain inactive when nitrogen was mixed with it. The admission of a small quantity of nitrogen peroxide, on the other hand, gave rise to spontaneous condensation of the water vapour, and subsequent expansion experiments showed that the nuclei formed persist for a considerable time. These observations indicate that Pringal's statement (A., 1908, ii, 798) that nitrogen is acted on by ozone in presence of water vapour, cannot be accepted.

In reference to the activity of the oxides of nitrogen, it has been supposed that nuclei are formed consisting of a higher oxide of unknown composition. Experiments with electrolytic oxygen and

oxygen prepared from hydrogen peroxide indicate that the same blue-coloured cloud is formed in oxygen which is free from nitrogen. The search for the substance which is active under these circumstances indicates that it is probably hydrogen peroxide. This is formed when ultra-violet light acts on moist oxygen, as a result of the oxidation of water vapour by the atomic oxygen, which is supposed to be produced by the action of the short-waved rays on the oxygen molecules.

The formation of hydrogen peroxide by ultra-violet sunlight is considered to be chiefly responsible for the atmospheric condensation of water vapour, although nuclei resulting from the action of atomic oxygen on other constituents of the atmosphere, such as ammonia, are probably responsible for some portion of the effect.

H. M. D.

The Preparation of Anhydrous Hydrofluoric Acid and the Isolation of Fluorine. FREDERICK D. CHATTAWAY (*Chem News*, 1913, **107**, 37—39).—Historical.

Chemical Reactions at Very Low Pressures. I. The Clean-up of Oxygen in a Tungsten Lamp. IRVING LANGMUIR (*J. Amer. Chem. Soc.*, 1913, **35**, 105—127).—On heating a tungsten wire in a vacuum, a steady evolution of gas was observed. This was found to be due to water vapour given off by the glass of the bulb, which, on coming into contact with the hot wire, produced hydrogen and oxidised the tungsten. It was found that in order to avoid the formation of the gas it was necessary to heat the bulb at 360° for an hour or more after it had been exhausted, and to absorb the water vapour by means of phosphoric oxide or liquid air. By this means about 300 cubic mm. of water-vapour, 20 cubic mm. of carbon dioxide, and 4 cubic mm. of nitrogen were withdrawn from a 40-watt lamp bulb.

When a tungsten wire is heated in oxygen at a low pressure it oxidises to WO_3 at about 800° (abs.), but on raising the temperature to 1200° (abs.) the oxide volatilises, and leaves the metal clean and bright. At temperatures above 1200° (abs.) oxygen at pressures below 0·02 mm. acts on a tungsten wire at a rate which is proportional to the pressure of the oxygen and the surface of metal exposed, and increases rapidly with the temperature. No fatigue effect can be observed. The velocity is not affected by varying the temperature of the bulb. The mechanism of the reaction is discussed.

E. G.

The Presence of Selenium in Hydrochloric Acid. ENRIQUE MOLES and S. PIÑA DE RUBIES (*Anal. Fis. Quim.*, 1913, **11**, 73—77) —It is shown that selenium probably exists in some commercial acids in the form of the dichloride, produced when seleniferous sulphuric acid is heated with salt. The presence of ferric chloride aids the formation of the selenium dichloride, although oxidising agents, such as chlorates and nitrates, do not have this effect. On diluting a seleniferous hydrochloric acid, selenium is separated as an impalpable scarlet powder.

G. D. L.

The "Chemically Active Modification" of Nitrogen. F. COMTE (*Physikal. Zeitsch.*, 1913, **14**, 74—76. Compare Strutt, A., 1912, ii, 935).—Experiments are described which seem to show that the after-luminosity effect, which is observed when a Leyden jar discharge is passed through a discharge tube containing nitrogen, is dependent on the presence of small quantities of oxygen. The apparatus used by the author was very similar to that employed by Strutt (*loc. cit.*). With nitrogen containing 0·6% oxygen, an intense orange-yellow after-luminosity was observed when the dry gas was passed through the discharge tube at a pressure of 0·5—1 mm. It is essential that the gas should be freed from water vapour, for traces of this inhibit the phenomenon. When the dry gas, before entering the discharge tube, was passed through a long tube containing copper gauze and reduced copper oxide, heated at 550°, and then over phosphoric oxide, the after-luminosity was found to disappear almost entirely when the gas had been passing through the apparatus for some time. When a small quantity of air was allowed to mix with the oxygen-free nitrogen, the luminescent effect was again obtained. The observations indicate that there is a certain small proportion of admixed oxygen which gives the maximum after-luminosity effect.

It is also shown that the passage of dry air through a discharge tube is accompanied by a similar after-luminosity if the pressure in the tube is maintained at 6 to 10 mm. of mercury. H. M. D.

Active Nitrogen. ERICH TIEDE (*Ber.*, 1913, **46**, 340).—When pure nitrogen is used the active nitrogen of Strutt cannot be obtained. It is probable that the nitrogen used by Strutt contained oxygen, the presence of which gave rise to the observed phenomena. The matter is being further investigated in order to find the true explanation (compare also Comte, preceding abstract). T. S. P.

Catalytic Oxidation of Ammonia. II. D. MENEGHINI (*Gazzetta*, 1913, **43**, i, 81—90. Compare A., 1912, ii, 344).—The experiments have been continued for the purpose of comparing the efficacy of different catalysts. From the results (which are shown in tables and curves) it appears that the best catalysts are roasted pyrites, chromic oxide, and a mixture of oxides of the rare earths (Nd, Pr, La); Fe_2O_3, MnO_2, and CeO_2 are less active. R. V. S.

Chemistry of the Formation of Nitric Oxide in the High Tension Arc. ADOLF KOENIG (*Ber.*, 1913, **46**, 132—134).—The author criticises adversely the conclusions which Fischer and Hene (this vol., ii, 132) draw from their experiments. Since active nitrogen does not react with oxygen, and ordinary nitrogen is not oxidised by ozone, it is possible that both the nitrogen and ozone are made active before combining to form nitric oxide. T. S. P.

Chemical Reactions in Compressed Gases. Decomposition of Nitric Oxide. EMIL BRINER and BOUBNOFF (*Compt. rend.*, 1913, **156**, 228—230. Compare A., 1909, ii, 557; 1910, ii, 707; 1912, ii, 544).—A study of the decomposition of nitric oxide over wide

ranges of pressure (50 to 700 atmos.) and temperature ($-80°$ to $300°$). Nitrogen, nitrous and nitric oxides, and nitrogen trioxide and peroxide were found in the products of the reaction. The authors consider that two reactions take place simultaneously, namely:

$$(1)\ 2NO = N_2 + O_2 \quad \text{and} \quad (2)\ 4NO = 2N_2O + O_2,$$

the second predominating, the higher oxides of nitrogen being produced by the secondary action of the oxygen on the untransformed nitric oxide. At constant pressure, rise of temperature accelerates the transformation and favours reaction (2) and the secondary formation of nitrogen peroxide. Increase in pressure accelerates the decomposition of the nitric oxide into more stable substances. W. G.

The Luminescence and Ionising Action of Inactive Gases Saturated with Phosphorus Vapour. HANS SCHMIDT (*Physikal. Zeitsch.*, 1913, **14**, 120—123).—When a current of purified hydrogen, carbon dioxide, or nitrous oxide is passed through an emulsion of phosphorus in water or through a solution in benzaldehyde, the luminosity and cloud formation, which are observed in the early stages, gradually diminish in intensity, and disappear when the oxygen has been completely removed from the apparatus. With a current of coal gas these effects vanish before the oxygen has been entirely displaced, and in this respect coal gas behaves like small quantities of ethyl ether, chloroform, ethyl alcohol, and other substances. On passing pure oxygen through the emulsion or solution, the luminosity and cloud formation disappear as the partial pressure of the oxygen rises in consequence of the removal of air.

When the inactive gases charged with phosphorus vapour are passed into the chamber of an electroscope, ionisation currents are obtained, which are very much larger than the currents obtained when air similarly saturated with phosphorus vapour is passed into the chamber. H. M. D.

The Formation of Hypophosphoric Acid in Corne's Reaction. FRITZ TAUCHERT (*Zeitsch. anorg. Chem.*, 1913, **79**, 350—354).—The action of yellow phosphorus on copper nitrate (Corne, A., 1882, 1264) has been investigated by Rosenheim and Pinsker (A., 1910, ii, 708), who attributed the formation of hypophosphoric acid to the action of the copper ion, and not of the nitrate ion. A comparison of other copper salts confirms this result, copper sulphate, chloride, formate, oxide, and phosphate also giving hypophosphoric acid. When phosphorus acts on copper hypophosphate, the quantity of hypophosphoric acid is also increased.

The reactions occurring are:

$$(1)\ 5Cu(NO_3)_2 + P_4 + 8H_2O = 2H_3PO_4 + Cu_3P_2 + 2Cu + 10HNO_3.$$

$$(2)\ 4Cu(NO_3)_2 + P_4 + 6H_2O = H_4P_2O_6 + Cu_3P_2 + Cu + 8HNO_3.$$

The nitric acid then reacts with the copper phosphide and excess of phosphorus, forming phosphoric and phosphorous acids and nitric oxide. Not more than 7% of the phosphorus is obtained as hypo-

phosphoric acid, whilst as much as 20% may be obtained from a hot solution of copper sulphate. C. H. D.

The Synthesis of a Silicalcyanide and of a Felspar. J. EMERSON REYNOLDS (*Proc. Roy. Soc.*, 1913, *A*, **88**, 37—48).—In various papers (compare T., 1906, **89**, 397; 1909, **95**, 505, 508, 513, etc.) the author has given an account of organic compounds containing the silicocyanogen group, SiN, in combination, the existence of such compounds affording complete proof that silicon has a marked affinity for tervalent nitrogen. In the mineral kingdom, no definite compounds of silicon with nitrogen have been met with, but the existence of the great group of "alumino-silicates" affords clear evidence of the strong attraction of silicon for aluminium. The question therefore arises as to whether some of the alumino-silicates may not be regarded as fully oxidised products of silicides of tervalent aluminium, somewhat analogous to SiN, which have been formed at high temperatures in the first instance below the oxidised crust of the earth. Such "nuclear" silicides should be obtained either by the complete deoxidation of the corresponding native silicates, or by direct synthesis from the suitable elements. The first method has been found to be impracticable, but the second method has given satisfactory results.

The compound of silicon and aluminium analogous to cyanogen would have the formula Si_2Al_2, the name suggested for it being silicalcyanogen. Attempts to prepare this compound by synthesis from the elements were not satisfactory, combination to any material extent not taking place when a liquid mixture in atomic proportions is heated to full redness for more than two hours. It is well known that carbon and nitrogen behave similarly, but in the presence of a third element, such as an alkali metal, combination takes place with the formation of a cyanide. A mixture of silicon (103 grams), aluminium (100 grams), and calcium (74 grams), that is, in the proportion of Ca : 2Si : 2Al, behaves in an analogous manner. The silicon and aluminium are fused together, and then the calcium added in small portions at a time, the mass being stirred with a steel rod. After cooling, a dark grey, crystalline mass is obtained, the brilliant crystalline faces of a fracture apparently belonging to octahedral forms. The substance is analysed by decomposing it in a current of dry chlorine, and found to have the formula $CaSi_2Al_2$, that is, it is a *calcium silicalcyanide*, analogous to CaC_2N_2. It is readily attacked by hydrochloric acid, slowly by boiling nitric acid, and hardly at all by hot sulphuric acid. Sodium and potassium hydroxides readily decompose it. It is only very slightly attacked by oxygen until the temperature of the oxyhydrogen flame is reached, but if heated to low redness in a stream of moist oxygen, it is converted into a white mass having a composition agreeing with that of the mineral anorthite, namely, $CaAl_2Si_2O_8$, with which mineral its physical properties are also in agreement.

Experiments in which the alkali metals were used instead of calcium gave indications of the formation of a (sodium) silicalcyanide, but pure products could not be obtained. T. S. P.

Tschermak's Method for the Isolation of Silicic Acids. ENNIO BASCHIERI (*Jahrb. Min.*, 1912, ii, Ref. 323 ; from *Proc.-verb. Soc. Toscana Sci. Nat.*, 1910, **19**, 84—87. Compare A., 1911, ii, 502).—The following percentages of water were determined in the silicic acids isolated from apophyllite and datolite by the use of various acids of definite concentration. (The numbers given in parentheses are those in which the transformation point had been passed.)

	HCl (D 1·2).	H_2SO_4 (D 1·2).	HNO_3 (D 1·5).
Apophyllite	12·39, 12·69	12·03, (10·01)	11·33, (10·63)
Datolite...........	(11·66)	12·67	13·55, 13·98

These results, as well as those obtained with some other silicates, are in close agreement with those obtained by other observers, and the correspondence can scarcely be accidental. The method is therefore of value in indicating the constitution of silicates (compare Mügge, A., 1908, ii, 277). L. J. S.

Tendency of Haloids and Phosphates of the Same Metal to Combine. II. Alkali Fluorides and Phosphates. MARIO AMADORI (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 688—695. Compare A., 1912, ii, 940).—The present paper deals with the systems formed by the fluoride and phosphates of potassium. The melting point of potassium fluoride was found to be 855°.

In the system $KF-KPO_3$ there is evidence of the formation of the compound $2KF,KPO_3$ at 793°, and of the formation of the compound KF,KPO_3 at 880°. Mixtures containing from 0—20 mol. % of phosphate show a eutectic point corresponding with 742° and 20 mol. % of KPO_3, whilst those containing from 50—100 mol. % KPO_3 have a eutectic at 604° (82 mol. % of KPO_3). Mixtures with 0—45 mol. % of KPO_3 show a slight pause at 540°, which probably corresponds with the transformation point of the compound $2KF,KPO_3$. The transformation point (450°) of the metaphosphate is observed in all the mixtures up to 60 mol. % of potassium fluoride.

In the system $KF-K_4P_2O_7$ there is a eutectic at 730° and 20 mol. % of $K_4P_2O_7$. The transformation point (278°) of the pyrophosphate is shown by all mixtures down to 10 mol. % of $K_4P_2O_7$.

The system $KF-K_3PO_4$ has a eutectic at 766° (20 mol. % of K_3PO_4), and there is a further development of heat in the solid mass at 700°, probably due to the decomposition of a compound. R. V. S.

Borates. The System $(NH_4)_2O-B_2O_3-H_2O$ at 30°. U. SBORGI (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 855—859).—The experiments were carried out by keeping mixtures of the three substances in a closed vessel in a thermostat at 30° until equilibrium was reached. Of the eleven ammonium borates which have been described, only one, namely, $(NH_4)_2O,5B_2O_3,8H_2O$, was obtained, and in addition a new *borate*, $2(NH_4)_2O,4B_2O_3,5H_2O$.

A new form of stirrer and shaker is described. A vertical axis bearing the pulley carries also a crank, and the crank-rod is a

rack, which engages with a pinion borne on a second vertical axis. The lower end of the second axis dips below the water of the thermostat, and to it the vessels to be shaken are attached symmetrically. When the pulley is revolving, the rack is moved to and fro, so that axis of the pinion makes revolutions in opposite directions alternately; this motion shakes the vessels and stirs the water of the thermostat at the same time. R. V. S.

Silver Thioaluminates. LIVIO CAMBI (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 837—842).—The author has investigated the system Ag_2S–Al_2S_3 by the method of thermal analysis. The thermal analysis was effected in graphite crucibles in a current of hydrogen sulphide, and the composition of the mixtures was deduced by subsequent analysis. Mixtures containing more than 40 mol. % of Al_2S_3 do not yield satisfactory results. Evidence was obtained of the existence of a *compound*, $4Ag_2S,5Al_2S_3$, which melts unchanged at 1035°, and probably another compound decomposing at 825° (which is very near a eutectic point) and containing 60—70 mol. % of Ag_2S. The compound $4Ag_2S,5Al_2S_3$ forms homogeneous, flesh-coloured, birefringent crystals. R. V. S.

Hydrates of Calcium Oxide and their Molecular Compounds. I. F. SELIVANOV (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1797—1813).—The author has studied, first, the composition of hydrates of calcium oxide prepared by slaking lime obtained by heating marble or calcium nitrate or oxalate, or by precipitating calcium chloride solution with sodium hydroxide, and, secondly, the action on these hydrates of dry water vapour.

The hydrates obtained by slaking specimens of calcium oxide of different origins all agree closely in composition with the formula $Ca(OH)_2$, whilst the precipitated hydrate contains an appreciable excess of water.

These hydrates absorb water vapour, but hold it only loosely, change of temperature from 14·5—16° to 21° resulting in a loss of almost one-third of the absorbed water. This absorbed water is largely lost in a desiccator containing heptahydrated zinc sulphate or hexahydrated calcium chloride, and is almost completely given up in presence of sulphuric acid or on heating at 60°; the last traces of the water are given up only with difficulty. Considerable differences in the proportion of absorbed water held by the hydrate are virtually without influence on the solubility in water.

From the results of his experiments the author draws the conclusion that the amorphous hydrate of calcium oxide and water behave one to the other in the same way as two liquids exhibiting slight mutual solubilities, a solution of the hydrate in water and one of water in the hydrate being formed when the two are shaken together. T. H. P.

Solubility of the Nitrates of the Alkaline Earths in Mixtures of Alcohol and Water at 25°. JOH. D'ANS and R. SIEGLER (*Zeitsch. physikal. Chem.*, 1913, **82**, 35—44).—Mixtures of

alcohol and water of known composition are shaken with the various nitrates until equilibrium is attained, and then analysed. Three types of solubility isothermals are obtained: (1) with barium nitrate, which does not form compounds with either water or alcohol, a straight line curve is obtained, showing decreasing solubility with increasing alcohol concentration. (2) With strontium nitrate, which forms the compound $Sr(NO_3)_2,4H_2O$ with water, but does not form a compound with alcohol, a curve which is divided into two branches is obtained owing to the fact that the hydrated salt is stable in the dilute alcohol solutions, whilst the anhydrous salt is stable in the concentrated alcohol solutions. (3) With calcium nitrate, which forms $Ca(NO_3)_2,4H_2O$ with water and $Ca(NO_3)_2,2C_2H_5{\cdot}OH$ with alcohol, a curve of three branches is obtained. It is found that between the areas in which the hydrate and alcoholate are stable there is a small meta-stable region, in which anhydrous calcium nitrate constitutes the solid phase. The solubility of the three nitrates was also determined at 25° in methyl alcohol, ethyl alcohol, propyl alcohol, *iso*butyl alcohol, amyl alcohol, acetone, ether, and paracetaldehyde. Barium nitrate is found to dissolve to a slight extent only in all the solvents. Strontium nitrate is very slightly more soluble, whilst calcium nitrate is very soluble except in the cases of ether and paracetaldehyde, in which it is not more soluble than the other nitrates. J. F. S.

Action of Aqueous Barium Hydroxide on Certain Kinds of Glass. CURT BUNGE (*Zeitsch. anal. Chem.*, 1913, **52**, 15—17).—An insoluble coating observed in a burette in which *N*/4-barium hydroxide had been kept was found to consist of barium sulphate.

Further investigation proved the sulphate to be derived from the glass, and evidently owing to the use of sodium sulphate in glass manufacture. L. DE K.

The Solubility of Glucinum Sulphate in Water and Sulphuric Acid. FRITZ WIRTH (*Zeitsch. anorg. Chem.*, 1913, **79**, 357—359. Compare Parsons, A., 1904, ii, 658; 1905, ii, 34; Levi-Malvano, A., 1906, ii, 165).—The solubility of glucinum sulphate hexahydrate in water at 25° is much less than that previously recorded, being only 0·07857 mol. in 100 grams of solution. Sulphuric acid at first only slightly lowers the solubility, but beyond 12·5*N* the hexahydrate passes into the tetrahydrate, the solubility of which is much further diminished by sulphuric acid. As the solubility curve of aluminium sulphate in sulphuric acid has an entirely different form, this property may be used for the purification of glucinum salts.

C. H. D.

Glucinum Chromates. N. A. ORLOV (*Zeitsch. anorg. Chem.*, 1913, **79**, 365—367. Compare Bleyer and Moormann, A., 1912, ii, 762).—The following compounds have been obtained: from glucinum sulphate and potassium chromate, $9GlO,GlCrO_4,16H_2O$ and $20H_2O$ and $14GlO,GlCrO_4,31H_2O$; from a solution of glucinum hydroxide in chromic acid and potassium chromate, $12GlO,GlCrO_4,16H_2O$; and

by precipitating a solution of glucinum hydroxide in chromic acid with alcohol, $5GlO,GlCrO_4,14H_2O$. Glucinum and aluminium chromates are gradually hydrolysed by water, without the formation of any definite basic salt. C. H. D.

The Thermal Dissociation of Amorphous Magnesite. O. KALLAUNER (*Chem. Zeit.*, 1913, **37**, 182).—Amorphous magnesite begins to lose carbon dioxide at 500°, but the temperature at which the evolution takes place almost momentarily is 620—625°. T. S. P.

Action of Hydrogen Peroxide on Alkaline Solutions of Lead Oxide. V. ZOTIER (*Bull. Soc. chim.*, 1913, [iv], **13**, 61—66). —In this reaction lead peroxide is first formed, which then reacts with some hydrogen peroxide, giving rise to oxygen and some lead oxide, so that the precipitate produced usually consists of both oxides.

With increasing quantities of hydrogen peroxide, the quantity of lead peroxide rises to a maximum, and then remains constant. For the quantity of hydrogen peroxide necessary to produce this maximum quantity of lead peroxide, the reaction is expressed by the equation $10PbO + 10H_2O_2 = 10H_2O + 4PbO_2 + 6PbO + 3O_2$.

The amount of lead peroxide formed diminishes with rise of temperature, slightly up to 30°, considerably from 30° to 60°, and very rapidly above 60°. About 90—95°, lead peroxide is formed, but disappears immediately, due to the second phase of the reaction.

Water has little influence on the reaction, and considerable quantities must be introduced before differences greater than those due to experimental error are noticeable.

The quantity of lead peroxide formed diminishes as the ratio NaOH : PbO increases, and with sufficient sodium hydroxide the lead peroxide formed is immediately decomposed. T. A. H.

Tendency of Haloids and Phosphates of the Same Metal to Combine. III. Fluoride, Chloride, and Phosphate of Lead. MARIO AMADORI (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 768—774. Compare this vol., ii, 213).—Lead orthophosphate has m. p. 1006°, and its cooling curve shows a transformation point at 782°. Mixtures of lead orthophosphate and lead fluoride, containing from 0 to 10 mol. % of phosphate, show a eutectic corresponding with 678° and 7·5 mol. % of phosphate. The curve also shows a maximum at 1046° and 75 mol. % of phosphate, and at this temperature the compound of the same composition, $PbF_2,3Pb_3(PO_4)_2$, crystallises. The eutectic pause is not seen in mixtures containing more than 10 mol. % of phosphate. The curve of the compound $PbF_2,3Pb_3(PO_4)_2$ shows a transformation point at 696°, and it probably exists also in a third modification. There is complete miscibility between the α-form of the compound and the α-form of the phosphate, and there is extensive solubility in the solid state between the α-form of the compound and the fluoride. Between the presumed β-form of the compound and the β-form of the phosphate there is also probably complete miscibility, whilst this

modification of the compound and the fluoride probably form a series of mixed crystals. The γ-form of the compound is not miscible (or is miscible only to a very limited extent) with the β-form of the phosphate, and it is not miscible with the fluoride.

Owing to the volatility of the chloride, the experiments with lead chloride and lead orthophosphate were mainly qualitative, but it is probable that a compound is formed analogous to that above described; its m. p. lies above 1100°.

The compound of fluoride and phosphate corresponds with calcium salts (apatite) occurring in nature, and that between chloride and phosphate would correspond with pyromorphite.

R. V. S.

Double Salts of Thallous Chloride with Ferric Chloride and with Bismuth Chloride. G. SCARPA (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 719—725).—The paper gives an account of the thermal analysis of the systems $TlCl-FeCl_3$ and $TlCl-BiCl_3$.

In the case of the former system the volatility of ferric chloride causes some experimental difficulties, and it is necessary to determine the composition of the mixtures by actual analysis of the separated solid. For the same reason, it is not possible to deal with mixtures containing more than 62 mol. % of ferric chloride. There is a eutectic corresponding with 266° and 26 mol. % of ferric chloride, and a maximum at about 33 mol. % of ferric chloride and 290°. This indicates the formation of a compound $2TlCl,FeCl_3$, stable on fusion. Mixtures containing more ferric chloride show a eutectic point at about 220°, and the initiation of crystallisation is very high; for instance, the mixture with 62% of ferric chloride begins to crystallise at 299°, which is almost the m. p. of ferric chloride. It is therefore legitimate to suppose that the curve would show another maximum above this point.

In the system $TlCl-BiCl_3$, there is a eutectic corresponding with 360° and 12·5 mol. % of bismuth chloride, and a maximum at 413° (25 mol. % of bismuth chloride). A pause occurs at 330° (about 40 mol. % of bismuth chloride), and a more evident pause at about 225° (52 mol. % of bismuth chloride). The curve then descends to a eutectic at 150° (67 mol. % of bismuth chloride), and finally rises to the m. p. of this salt. Mixtures containing 0—25 mol. % of bismuth chloride show a pause at 360°, which vanishes for the 25% mixture; this indicates the existence of the compound $3TlCl,BiCl_3$. Mixtures from 25% to 40% of bismuth chloride exhibit a slight pause at 330°, probably due to the formation of a compound $2TlCl,BiCl_3$, which decomposes on fusion. Mixtures containing 35—50 mol. % of bismuth chloride show a pause at 224°, which demonstrates the existence of a compound $3TlCl,2BiCl_3$, decomposing on fusion. Above 70% of $BiCl_3$, the mixtures deposit mixed crystals.

R. V. S.

Molecular Complexity of Metals in the Solid Phase. MAURIZIO PADOA and F. BOVINI (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 708—713).—From the diagram of the system copper–bismuth, which is known, the authors calculate the cryoscopic constant of

copper (874·5) in good agreement with the value obtained from the heat of fusion of copper (855). Mixtures of copper and silicon containing little silicon are simple solutions of the silicon in the copper, and applying the above constant, the authors calculate (from published data of this binary system) the molecular weight of silicon dissolved in liquid copper. The values obtained vary from 32·7 to 24·5, indicating that in these circumstances silicon is monatomic. It is probable that its state of aggregation is the same also in solution in solid copper.

[With CARLO MARANI.]—The authors have also determined the molecular complexity of cadmium in solution in solid tin. In the system Sn–Cd–Bi, bismuth does not form solid solutions with either of the other constituents, whilst cadmium gives a solid solution with tin. Analysis of the crystals separating from the solution of cadmium in tin (bismuth being also present) shows that the solid solution has very nearly the same composition as the liquid solution, the partition coefficient being sensibly constant, and therefore the cadmium has the same degree of molecular complexity in both, that is, it is monatomic also in the solid solution. R. V. S.

Electrical Conductivity of Alloys of Copper and Zinc. NIKOLAI A. PUSCHIN and V. N. RJASHSKI (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1905—1918).—Investigation of the electrical resistance and of its temperature-coefficient for alloys of copper and zinc gives results in general agreement with Shepherd's conclusions based on the melting-point diagram and on the microstructure (A., 1904, ii, 662). The system forms (1) the solid solutions: α, 0—36 atom %; γ, 59—67 atom %; ϵ, 80—85·7 atom %; and η, 91—100 atom % of zinc; (2) the mixed crystals: $\alpha+\beta$, 36—50; $\beta+\gamma$, 50—59; $\gamma+\epsilon$, 67—80; and $\epsilon+\eta$, 85·7—91 atom % of zinc. The existence of the solid solution, β, within narrow limits is regarded as a sign of the existence of the definite compound ZnCu, which is slightly dissociated at the ordinary temperature. The results also indicate the probable existence of the two compounds, Zn_2Cu and Zn_6Cu (compare also Norsa, A., 1912, ii, 890). T. H. P.

The Tensile Strength of the Copper–Zinc Alloys. J. M. LOHR (*J. Physical Chem.*, 1913, **17**, 1—25).—The brasses examined covered the whole range of useful mixtures, namely, from 47·5% to 100% of copper. The metals were melted under coal gas and poured from a plug hole in the bottom of the crucible in order to avoid dross. The pouring temperatures by thermocouple were from 50° to 250° above the liquidus points. The mould consisted of a split Acheson graphite block arranged to cast a test-bar 6 in. long by 0·40 in. diameter, with an **S**-shaped gate termed a "centrifugal sprew" and a very substantial riser, the test-bar being slightly inclined so as to sweep forward and upward into the riser any floating zinc oxide. The mould was preheated by external gas burners. With these precautions test-bars were usually obtained free from blow holes and dross. Any bar which showed signs under a lens of pipe formation or pinholing after fracture was rejected.

After casting, the bars were quickly removed from the mould

and chilled in water from a temperature of 700—800°, and were subjected to no other heat treatment before testing. Consequently they consisted of pure α-phase down to 66% of copper, mixed α- and β-crystals from 66% to 57% of copper, pure β-crystals from 57% to 50%, and mixed β- and γ-crystals below 50%. Owing to the high temperature of quenching, α- and γ-mixtures were not present, and in the range of compositions studied, pure γ-, as well as the δ-, ϵ-, and η-phases do not exist.

The α-brasses have a tensile strength which is almost constant at about 33,000 lb. per sq. in. from 95% to 66% of copper. When the β-phase appears, the strength rises and attains a maximum at 55% in the pure β-phase of about 71,000 lb., or when calculated on the reduced area, 100,000 lb. per sq. in., with an elongation of 14·8%. The strength falls off rapidly when the γ-phase appears, the 47·5% copper alloy, which appeared to contain about three-fourths β-crystals with one-fourth γ-crystals, giving 23,000 lb. only.

The maximum elongation of 36% was observed in the α-phase at 62% to 70% of copper, the corresponding tensile strength being 36,000 lb. Occasional specimens gave higher results; for example, in one case, the elongation was 60%, and in another the tensile strength 137,000 lb. per sq. in.

It was noticed in casting that alloys between 100% and 80% of copper and between 65% and 47·5% of copper usually gave homogeneous test-pieces, whereas between 80% and 65% of copper (maximum ductility), it was difficult to obtain castings free from porosity. The best pouring temperature was from 100° to 200° above the liquidus. Below this the metal was usually too viscous, and above this it often contained black spots of porous material.

R. J. C.

Some Basic Copper Sulphates. GEORGE FOWLES (*J. Soc. Chem. Ind.*, 1913, **32**, 9).—The author points out that some of the results published by Ermen (A., 1912, ii, 453) have been obtained previously by other investigators.

T. S. P.

Blue Gelatin Copper. WILDER D. BANCROFT and T. R. BRIGGS (*J. Ind. Eng. Chem.*, 1913, **5**, 9—11).—One gram of gelatin is dissolved in 325 c.c. of a 1% solution of cupric acetate, and the solution electrolysed for five minutes between carefully cleaned and burnished electrodes of sheet copper, using a current density of 0·15—0·45 amps. per sq. dcm. at the cathode. The cathode becomes covered with a thin, pale brown deposit, possessing a peculiar, slippery surface, owing to the gelatin deposited with the copper. If the cathode is washed, and then immersed in a 5% solution of copper acetate containing no gelatin, a series of remarkable colour changes takes place until the surface has acquired a magnificent deep blue coloration. The process of the formation of this blue colour is called "development" by the authors.

Gelatin, in concentrations varying from 0·25 to 0·66%, must be present for development to occur. The copper acetate may be replaced by copper propionate or formate (not so good), but not by

the sulphate, nitrate, or chloride The most satisfactory temperatures lie between 20° and 40°; at 50° or higher temperatures, red or golden films are produced, which will not develop, but may be preserved by lacquering. The copper acetate or propionate solution should contain 1 or 2 parts of the crystallised salt to 100 parts of water; the limits of current density are given above. Anodes of nickel, brass, or platinum may be used.

Experiments with various solutions showed that development takes place successfully only in solutions of copper acetate or propionate, so that this phenomenon must be a function of the copper contained in the developing solutions. If the developed electrode is placed in a solution of hydrazine hydrate, the colour slowly disappears, with evolution of nitrogen; it may then be re-developed, but not to such a good colour as before, in copper acetate solution. If the deposited film is left undeveloped for several hours, it completely loses its power of developing in copper acetate, probably because of oxidation.

The deposited film of metal is probably an irreversible gel of colloidal copper, and the process of development is an adsorption of hydrated copper oxide by the surface of the colloid film. This hydrated copper oxide is present as a suspension in very appreciable quantities in the acetate or propionate solutions. T. S. P.

Action of Distilled Water on Impure Aluminium. ALBERTO SCALA (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 43—49) —When ordinary aluminium (Kahlbaum) is kept in contact with carefully prepared distilled water at the ordinary temperature it eventually shows signs of chemical action, for the surface becomes black, and bubbles of gas appear. The time elapsing before this action is evident varies from months to days in different experiments, but when once started it proceeds somewhat rapidly. Suspended in the water are then to be found aluminium hydroxide and a chestnut-coloured substance, which is a compound containing aluminium, iron, and perhaps silicon. During the reaction hydrogen is evolved.

R. V. S.

Alloys of Aluminium and Vanadium. NICOLAS CZAKO (*Compt. rend.*, 1913, **156**, 140—142. Compare Moissan, A., 1896, ii, 608; Matignon and Monnet, A., 1902, ii, 326).—By fusing vanadic acid with aluminium in the necessary proportions, the author has prepared alloys of aluminium and vanadium, containing from 1 to 80% of vanadium, and has examined them micrographically. He has isolated crystals having the definite constitution Al_3V and AlV, and obtained indications of a compound AlV_2. The hardness of the alloys increases with the vanadium content up to 60%, when it is from 6 to 7, after which it diminishes. The alloy containing 53% vanadium is full of cavities, and in consequence difficult to examine micrographically. W. G.

The Crystallisation of Pure Aluminium Salts from Solutions containing Iron, and the Artificial Preparation of Halotrichite. FRITZ WIRTH (*Zeitsch. angew. Chem.*, 1913, **26**, 81—83).—The author has determined the solubilities at 25° of

ferrous sulphate, aluminium sulphate, and of each of these salts in the presence of varying proportions of the other, in order to determine the region of the existence of the double salt, halotrichite, $FeSO_4,Al_2(SO_4)_3,24H_2O$. The solubilities of the pure components are respectively 0·8124 mol. of aluminium sulphate, and 1·503 mols. of ferrous sulphate in 1000 grams of solution. The double salt exists over the region between the two solutions containing respectively 0·723 mol. of aluminium sulphate and 0·38 mol. of ferrous sulphate, and 0·7045 mol. of aluminium sulphate and 0·6827 mol. of ferrous sulphate. It follows that from a solution containing equimolecular quantities of the two salts, ferrous sulphate first crystallises, and then the double salt. The preparation of the double salt is best carried out by shaking a solution, saturated with respect to the two components, with the solid sulphates contained in a silk bag. Strongly supersaturated solutions are thus obtained, from which the double salt separates after a few hours.

The solubility curve gives the conditions of relative concentrations under which pure aluminium sulphate can be crystallised out from a solution containing ferrous sulphate, and experiments made by the author show that complete separation of aluminium from iron can thus be carried out. If the iron is in the ferric condition, separation is impossible, owing to the formation of mixed crystals; the iron must first be reduced to the ferrous state. A method is thus given, which is applicable commercially, for the preparation of pure aluminium sulphate from bauxite. T. S. P.

The Solubility of Aluminium and Iron Sulphates in Sulphuric Acid. FRITZ WIRTH (*Zeitsch. anorg. Chem.*, 1913, **79**, 360—364).—The presence of sulphuric acid at first increases the solubility of aluminium sulphate in water, but a further addition of acid produces an enormous depression. From 20*N* onwards there is again a slight increase, without any change in the solid phase. This has already been observed with other sulphates. With concentrated sulphuric acid, aluminium sulphate forms the compound $Al_2(SO_4)_3,H_2SO_4,3H_2O$, the mixture solidifying after a few hours.

Ferrous sulphate is converted into the monohydrate by sulphuric acid of greater concentration than 12·5*N* at 25°. The solubility curve of ferrous sulphate in sulphuric acid is nearly parallel to that of aluminium sulphate as far as 40% H_2SO_4. Ferric sulphate is somewhat less soluble. C. H. D.

Ultramarine Compounds. II. L. WUNDER (*Zeitsch. anorg Chem.*, 1913, **79**, 343—349. Compare this vol., ii, 54).—When ultramarine red is heated out of contact with air, it is converted into a blue product, the loss of weight which occurs being due to loss of water. The constitution is, however, changed, as the new blue evolves hydrogen sulphide with acids, whilst the red yields sulphur dioxide. It differs from commercial ultramarine blue in not being converted into violet by heating in chlorine and hydrogen chloride at 170—250°, and in not being reduced to white by the action of phosphorus in carbon tetrachloride. In accordance with

its higher proportion of silica, the new blue is more stable towards acids and alum than ordinary ultramarine.

The presence of the sodium is necessary for the blue colour, complete replacement by mercury yielding a yellow product. The violet ultramarine yields a yellow silver derivative, which again becomes violet when heated with lithium chloride. The silver derivative of ultramarine red is brown, and is free from sodium. Alkali haloids convert it into blue.

The blue colour is considered to depend on (1) the presence of an alkali metal, (2) the direct union of a part of the sulphur with metal, (3) the presence of a part of the sulphur in a lower state of oxidation. Neither aluminium nor silicic acid is essential, as the former may be replaced by boron, and the latter by a polyboric acid. Boron-ultramarine, however, fulfils the conditions mentioned above (compare Hoffmann, A., 1906, ii, 545). The colloidal theory of the blue colour is rejected. C. H. D.

The Heusler Ferromagnetic Manganese Alloys. EDGAR WEDEKIND (*Zeitsch. angew. Chem.*, 1913, **26**, 72).—Polemical. A reply to Heusler (this vol., ii, 139). L. DE K.

The Reactions which Accompany the Osmosis of Hydrogen through Iron. GEORGES CHARPY and S. BONNEROT (*Compt. rend.*, 1913, **156**, 394—396. Compare A., 1912, ii, 336).—A study of the change in iron and steel when submitted to the prolonged diffusion of hydrogen through it at 600—900°. Iron thus traversed for a long time by a current of hydrogen does not absorb any of the gas, since the amount of hydrogen obtainable on heating the iron in a vacuum is generally slightly less after than before the osmosis. The physical properties of the metal are modified, it being softened by prolonged diffusion of the gas, which exercises a reducing action, removing such constituents as sulphur, phosphorus, and carbon in the form of their hydrides, the desulphurisation being particularly rapid. In an experiment on a steel tube, 3·5 mm. thick, containing 0·9% carbon, at 900°, 2·3 c.c. of gas diffused through, and was found to contain 4% of hydrocarbons. The iron thus undergoes a process of purification by the passage of the hydrogen, and this may possibly explain certain of the anomalies in the metallurgy of iron and steel, the hydrogen arising from the contact of water vapour with the hot metal. W. G.

The Transformations of Iron and Steel at High Temperatures. KÔTARÔ HONDA and HIROMU TAKAGI (*Sci. Reports, Tôhoku Imp. Univ.*, 1912, **1**, 207—217).—A series of specimens ranging from pure iron to steel containing 1·50% of carbon have been examined in an electric furnace by a magnetometric method, simultaneous observations of time, temperature and magnetic deflection being made.

The β–α magnetic transformation extends over a small interval of temperature. The interval β–α or γ–α increases with increasing carbon in steels, as measured magnetically, whilst the thermal

change is not recognisable. The eutectoid point is marked by an increase in the magnetic properties on cooling. C. H. D.

The System Iron–Carbon. OTTO RUFF (*Zeitsch. Elektrochem.*, 1913, **19**, 133).—Polemical. An answer to Smits (this vol., ii, 56). The author states that Smits bases his calculations on experiments which are only to be regarded as preliminary. J. F. S.

Complete Solubility of Chromium Hydroxide in Ammonia. MILORAD Z. JOVITSCHITSCH (*Monatsh.*, 1913, **34**, 225—242).—Chromium may be precipitated with small quantities of ammonium hydroxide as a light grey hydroxide which dissolves in excess with ruby-red colour, the solubility being influenced by salts of ammonium. From the solution substances may be obtained which contain hydroxyl groups, ammonia, and, according to circumstances, acid radicles. They are not to be considered as derivatives of normal chromium hydroxide, $Cr_2(OH)_6,4H_2O$, as, for example, $(NH_3)_3Cr_2(OH)_2Cl,4H_2O$, but rather as based on Colson's hypothetical oxyhydroxide (A., 1908, ii, 45), with which the analyses and properties are most in accordance.

The solution of chromium hydroxide may be effected in different ways, but the best consists in dissolving 1 gram of the substance in just sufficient mineral acid, diluting to about 25 c.c., and adding the same volume of ammonia. A grey precipitate is formed, which redissolves in the course of an hour or so. *Tetrachromiumoxidehexamminodisulphate*, $\begin{matrix}(NH_3)_2\vdots Cr\cdot O\cdot NH_3\cdot Cr\vdots SO_4 \\ | \qquad\qquad | \\ (NH_3)_2\vdots Cr\cdot O\cdot NH_3\cdot Cr\vdots SO_4\end{matrix},10H_2O$, is precipitated by alcohol from such a solution as a red oil which, when freed from ammonium sulphate, solidifies to a red mass. When dried over sulphuric acid, it loses $4H_2O$, but when left in contact with water, it gradually suffers hydrolysis and becomes paler, the acid radicles being partly replaced by hydroxyl groups. It is stable in absolute alcohol, but absorbs carbon dioxide when exposed to the air. The addition of alcohol to the solution made with nitric acid at first causes the precipitation of a pale pink amminochromium hydroxide, but later on, *tetrachromiumoxideheptamminotrinitrate*, $\begin{matrix}(NH_3)_2Cr\cdot O\cdot NH_3\cdot Cr(NO_3)_2 \\ | \qquad\qquad | \\ (NH_3)_2Cr\cdot O\cdot NH_3\cdot Cr<^{NO_3}_{NH_3}\end{matrix},10H_2O$, separates as a scarlet, dense mass, which is soluble in water, but is speedily hydrolysed. The preparation of *tetrachromiumoxidehexamminodichloride*, $\begin{matrix}(NH_3)_2Cr\cdot O\cdot Cr(NH_3)_2 \\ | \qquad | \\ (NH_3)_2Cr\cdot O\cdot CrCl_2\end{matrix},10H_2O$, as a violet-red precipitate is even more difficult. It is soluble in water, but only after some hours does silver nitrate form a precipitate. No change is observed when the ruby-red solutions are neutralised, but when they are kept, *diamminochromium hydroxide*,

$$Cr(OH)_6(NH_3)_2,10H_2O,$$

is precipitated as a violet-blue mass which absorbs carbon dioxide. J. C. W.

Diffusion of Molybdenum in the Coalfield of Liege. ARMAND JORISSEN (*Bull. Soc. chim. Belg.*, 1913, **27**, 21—25. Compare A., 1897, ii, 265).—The author has examined samples of soot and fine dust resulting from the combustion of coal from this district, and has succeeded in isolating molybdenum in small quantities therefrom in the form of its sulphide, and has further identified it by the characteristic tests. A portion of the molybdenum is present in a form soluble in and extracted by water. W. G.

Iso- and Hetero-Poly-salts. VII. Molybdic Acid Hydrates and Some Polymolybdates. ARTHUR ROSENHEIM and JOSUA FELIX [with JACOB PINSKER] (*Zeitsch. anorg. Chem.*, 1913, **79**, 292—304. Compare A., 1911, ii, 116; Wempe, this vol., ii, 58).—Octomolybdates are prepared by adding the calculated quantity of hydrochloric acid to normal molybdates, or by saturating solutions of the latter with molybdic acid dihydrate. The salts have the formula $M'_2Mo_8O_{25}$, the calcium and barium salts having $18H_2O$, the sodium salt $17H_2O$, the ammonium salt $16H_2O$, and the potassium salt $13H_2O$. Sodium octamolybdate passes at the ordinary temperature into a decamolybdate, $Na_2Mo_{10}O_{31},6H_2O$.

The electrical conductivity of the aqueous solutions shows that the octamolybdates contain ionisable hydrogen. They are therefore hydrogen tetramolybdates, such as $NaHMo_4O_{13}$, and when neutralised yield normal tetramolybdates, such as $Na_2Mo_4O_{13}$, the electrical conductivity of which shows that they are entirely similar to the metatungstates.

The tetramolybdates are thus 12-molybdic acid hydrates, $M'_6H_4[H_2(Mo_2O_7)_6]$, and the octamolybdates are hydrogen salts with the same complex anion, $M'_3H_7[H_2(Mo_2O_7)_6]$.

Sodium tetramolybdate, $Na_6H_4[H_2(Mo_2O_7)_6],21H_2O$, forms microscopic, yellow crystals. The *potassium* salt has $18H_2O$, the *barium* salt $12H_2O$, the *guanidinium* salt, like the corresponding metatungstate is anhydrous. The octamolybdates already known are formulated afresh in accordance with this view of their constitution.

Two series of decamolybdates exist, one readily, and the other sparingly, soluble, and either isomeric or polymeric. When a soluble salt is added to hot water, it dissolves immediately, but if warmed with an insufficient quantity of water, it passes into the sparingly soluble modification. The following salts have been prepared: (soluble) $(NH_4)_2Mo_{10}O_{31},19H_2O$; $K_2Mo_{10}O_{31},15H_2O$; $Na_2Mo_{10}O_{31},22H_2O$; (sparingly soluble) $(NH_4)_2Mo_{10}O_{31},3H_2O$; $K_2Mo_{10}O_{31},9H_2O$.

It has not been found practicable to prepare the free acid. C. H. D.

Uranyl Iodates. PAUL ARTMANN (*Zeitsch. anorg. Chem.*, 1913, **79**, 327—342).—Uranyl iodate has been described with $5H_2O$, with H_2O, and anhydrous. It is now found that the precipitation of uranyl nitrate solution with sodium iodate yields a salt with H_2O or $2H_2O$, according to the conditions. The monohydrate forms

rhombic prisms when precipitated from cold solution, or pyramids from hot solution. The two modifications have D^{18} 5·220 and D^{18} 5·052 respectively. The first is converted into the second by boiling, whilst the reverse transformation occurs slowly at the ordinary temperature.

The dihydrate has a lighter yellow colour, and forms irregular aggregates.

Uranyl potassium iodate, $UO_2K(IO_3)_3,3H_2O$, is a very sparingly soluble yellow powder, and is obtained by precipitation with an excess of potassium iodate. It is hydrolysed by water, and is converted into uranyl iodate by an excess of uranyl nitrate.

Uranyl iodate does not give up its last mol. of water when heated. It is assumed to have the constitution:

$$OH\cdot UO_2\cdot O\cdot IO{<}^{O}_{O}{>}IO\cdot OH,$$

the anhydrous potassium salt being $IO_3\cdot UO_2\cdot O\cdot IO{<}^{O}_{O}{>}IO\cdot OK$.

C. H. D.

Zirconium. II. EDGAR WEDEKIND (*Annalen*, 1913, **395**, 149—194. Compare A., 1910, ii, 302).—[With HANS KUŽEL.]—The preparation of the metal by the reduction of the oxide by the Goldschmidt process fails in the case of zirconium, as also of other highly infusible metals. Reduction of the oxide by magnesium also is unsatisfactory. The following process of reduction by calcium, however, is convenient, and gives good results.

An intimate mixture of zirconium oxide and an excess of the finest calcium shavings is heated in an iron tube under a pressure of 0·1—0·5 mm., the heating being discontinued as soon as the reaction commences. When quite cold, the contents of the tube are powdered, and are treated successively with cold water, acetic acid, dilute hydrochloric acid, and water (until the washings do not contain calcium chloride), all of these operations being performed in the absence of air. The residual powder is finally washed with acetone and dried at first at the ordinary temperature, then in a high vacuum at 250—300°, and finally in a completely evacuated porcelain tube at 800—1000°. At the last temperature, which is far below the m. p. of zirconium, the powder sinters to lumps, which exhibit the brilliancy of a mirror by polishing. The metal obtained in this manner contains 99·09% of zirconium. An attempt to remove the small quantity of oxygen still present, by heating again with calcium in a nickel tube, resulted in the isolation of a less pure product. The yield of the powder is 97·5%; it has D^{18} 5·98, the sintered modification having D^{11} 6·280 and $D^{17\cdot5}$ 6·204. When pressed into rods and fused electrically in a vacuum (compare Weiss and Neumann, A., 1910, ii, 217), the powder is converted into globules, D^{16} 6·40, containing 98·5% of zirconium, being therefore less pure than the globules obtained by Weiss and Neumann (*loc. cit.*).

Titanium, thorium, uranium, vanadium, and tantalum have also been prepared by the calcium method.

The m. p. of zirconium is given as about 2350° by Wedekind and Bolton (A., 1910, ii, 302). Estimations by Burgess's platinum method (A., 1909, ii, 41) give a mean value, 1530°, of the m. p. The latter value is probably more correct, since zirconium cannot be employed for the manufacture of metal filament lamps.

Weiss and Neumann (*loc. cit.*) have described a zirconium hydride, ZrH_2. If this is a chemical individual, it is of great interest as being the first authentic example of a derivative of bivalent zirconium. The authors have also prepared this substance by heating zirconium powder in hydrogen at 700° and 1·5 atmospheres, and are of opinion that it is a chemical individual of the formula ZrH_2; its dissociation pressure at temperatures up to 1100° has been measured. Evidence of the existence of a volatile zirconium hydride has not been obtained.

In contrast to titanium, zirconium and nitrogen do not react much at temperatures below 1000°, but at 1000—1050°, a *nitride*, Zr_3N_2, D^{15} 6·75, a microcrystalline, tombac-coloured, glistening powder, is formed. The nitride is more stable than zirconium towards oxygen or chlorine, dissolves readily only in hydrofluoric acid, and is stable to aqueous alkalis. Fused potassium hydroxide or sodium carbonate causes an incomplete evolution of the nitrogen as ammonia. The nitride has no measurable dissociation pressure at 1100°, and in the compressed state is a conductor of electricity. The nitride, which is also produced by heating zirconium in ammonia at 1000°, partly loses its nitrogen by heating in hydrogen at 1050°; a partial formation of the nitride is also observed when zirconium hydride is heated in nitrogen at 1050°.

[With S. JUDD LEWIS.]—According to the literature, zirconium has been prepared in crystalline, graphitic, and amorphous modifications. It has already been shown that "crystalline zirconium" is an aluminium zirconide. The existence of Troost's graphitic zirconium, prepared by heating iron and sodium zirconate, is more than doubtful, since a reduction of zirconium oxide by iron is impossible. The black, amorphous zirconium prepared by Berzelius by heating potassium zirconium fluoride and potassium, has also been prepared by the authors (a better result is attained by using sodium instead of potassium), and found not to be an individual substance. It has the characteristics of a gel, and retains water most pertinaciously. By treatment with acids, it is converted into the hydrosol, from which the gel is recovered by coagulation or by evaporation after dialysis.

Amorphous zirconium and its gel are very closely related. The latter contains more oxygen and an appreciable amount of nitrogen. It has D^{16} 3·75, but the higher the temperature at which the amorphous zirconium or its gel is dried, the greater is the density, until, after drying at about 1000° in a high vacuum, it has D^{21} 5·79. Compressed amorphous zirconium or its gel is a non-conductor of electricity at low voltages, but becomes a conductor after being heated at 1000° in a vacuum. In its chemical properties, amorphous zirconium or its gel behaves very like metallic zirconium. It burns brilliantly when gently heated, is very stable

towards dilute acids, and is slowly attacked by chlorine. It inflames when heated with sulphur, and yields a mixture of the oxide and sulphide; with selenium a greyish-black *selenide* is produced. Reasons are given for the belief that amorphous zirconium is not a mixture of finely divided metal and the dioxide, or of the metal and the monoxide.

The authors are of opinion that amorphous zirconium is the colloidal modification of the metal. By treatment with acids, it yields the hydrosol. The gel recovered from the latter by coagulation agrees in its properties with the amorphous zirconium prepared directly by Berzelius's method. The two modifications of zirconium bear to one another the same relation as do amorphous and crystalline silicon.

[With J. TELETOW.]—Zirconium dioxide has been reduced by magnesium in hydrogen at high temperatures, whereby about one-third of the oxide escapes reduction. By a second and a third repetition of the reduction, the product becomes more and more pyrophoric and unmanageable, but in no case has the amount of zirconium corresponded with that required by a zirconium oxide, ZrO, the existence of which has been assumed by Winkler and by Dennis and Spencer (*J. Amer. Chem. Soc.*, 1896, **18**, 651). C. S.

The Subhaloid Compounds of Some Elements. I. The So-called Bismuth Subiodide. LUIGI MARINO and R. BECARELLI (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 695—701).—The authors have investigated the system Bi–I by the method of thermal analysis, and find no indication of the existence of any compound of the two elements other than BiI_3. The heating and subsequent cooling of the mixture of the two elements were effected in a sealed glass tube, precautions being taken to exclude all traces of water. The eutectic of Bi and BiI_3 lies at 284°. When mixtures containing 5—43% of iodine are cooled, two layers are formed, of which the upper contains excess of BiI_3, and the lower excess of Bi. At 340° the upper layer begins to deposit solid BiI_3, and as an invariant system is thus formed, this crystallisation continues until all the upper has solidified; during this process the upper layer contains 66·5% of BiI_3, and the lower 7·73%. Mixtures with 43—64·63% of iodine deposit BiI_3 until the temperature 340° is reached; two layers are then formed as before. After the upper layer has crystallised, the temperature falls until the eutectic 284° is reached, but there is a thermal effect at 294°, possibly due to a transformation product of bismuth. Mixtures containing more than 64·63% of iodine deposit BiI_3, and show a eutectic at 117°, but mixtures with more than 90% of iodine could not be investigated, owing to the breakage of the tubes in consequence of the pressure of the iodine vapour.

R. V. S.

History of Colloidal Gold. I. Gold Ruby Glass. ALFONSO CORNEJO (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 1—6).—The view that Kunckel (1679) was the original discoverer of ruby gold glass is erroneous, for Libavius (1595), Neri (1614), Glauber (1648),

Cassius, and Tachenius (1668) not only employed gold as a colouring agent, but gave exact directions for the preparation of ruby gold glass. H. M. D.

Disintegration of Metals at High Temperatures. Condensation Nuclei from Hot Wires. JOSEPH H. T. ROBERTS (*Phil. Mag.*, 1913, [vi], **25**, 270—296. Compare Crookes, A., 1912, ii, 563).—The disintegration of the platinum metals at high temperatures has been investigated, the formation of clouds in a Wilson expansion apparatus being employed as a delicate means of detecting the presence of disintegrated particles in the gaseous atmosphere surrounding the electrically heated metal wires. As evidence of the superiority of this method of investigating the disintegration, it is stated that no loss of weight could be detected on heating a platinum wire for thirteen hours at 650°, whereas a dense cloud was obtained in the expansion apparatus when the wire was heated by the passage of the same current for two seconds.

From observations in an atmosphere of hydrogen, oxygen, nitrogen, and air and in a vacuum, it has been found that the disintegration process is characterised by the emission of two sets of nuclei. The first set, which are got rid of after continuous experimenting, depends on the presence of hydrogen and other gases in the metal. The emission of the second set is conditioned by the presence of oxygen in the neighbourhood of the heated metal, and also on the attainment of a certain definite temperature.

In regard to the first set of nuclei, it has been found that they are emitted at comparatively low temperatures, the minimum temperature at which they can be detected falling as the pressure of the surrounding gas is diminished. The power of emitting these nuclei is temporarily lost when emission has been taking place for some time, but is gradually regained when the metal is allowed to remain unheated. The emissive power is immediately regained when hydrogen is brought into contact with the metal, whereas air, oxygen, and nitrogen do not produce this effect. If, however, the metal has been kept at a white heat in a vacuum for a long time, hydrogen also fails to restore the power of emitting the first type of nuclei. The fact that the nuclei diminish in size and disappear soon after their liberation indicates that these nuclei are not of the nature of solid particles, and it is suggested that they may be either minute drops of water or traces of compound gases produced by the union of hydrogen with other occluded gases.

The second set of nuclei are probably particles of an unstable oxide of the metal, this view being in agreement with the fact that oxygen is necessary for their production, that they begin to be formed at a fairly definite temperature, are very persistent, do not alter in size, and are unaffected by light or by an electric field.

At temperatures where the rate of loss of weight of platinum, rhodium, and iridium is immeasurably small in nitrogen, hydrogen, or a vacuum, the rate is very considerable in oxygen. At a given temperature, the rate of loss for platinum and rhodium is approximately proportional to the oxygen pressure, and in the case of

iridium it increases much more rapidly than the pressure. From experiments with platinum, in which the loss of weight of the metal was compared with the diminution in the quantity of oxygen in the surrounding gas, it was found that in pure oxygen the ratio corresponded approximately with the formation of the oxide PtO_2. In air, the ratio of oxygen absorbed to platinum disintegrated was much smaller, but this would be readily accounted for on the very probable view that the oxide PtO_2 dissociates on cooling. Similar experiments with iridium gave numbers in close agreement with those required for the formation of the oxide IrO_2.

From these facts the author draws the conclusion that the disintegration of platinum, rhodium, and iridium in air at high temperatures is conditioned entirely by the formation of volatile oxides of the formulæ PtO_2, RhO_2, and IrO_2.

Palladium behaves quite differently from the above three metals, and the disintegration in this case appears to be due to simple volatilisation of the metal. The fact that palladium does not yield nuclei of the second type is quite consistent with this view.

The deposits which are obtained on the walls of the vessel containing the electrically heated metals have also been examined, and these observations are consistent with the above views relative to the disintegration process. H. M. D.

Mineralogical Chemistry.

Asphalt Veins in Quartz-Porphyry near Heidelberg WILHELM SALOMON (*Zeitsch. Kryst. Min.*, 1913, **51**, 634; from *Ber. Oberrhein. Geol. Ver.*, 1909, **42**, 116—123).—A black asphalt with conchoidal fracture occurs with minute quartz crystals in crevices in the porphyry of Dossenheim. Analyses by Ebler gave: C, 77·8—79·8; H, 7·7—8·0; N, 0—2·7; S, 2·2—2·8; ash, 1·0%. Optically active substances being absent, there is no evidence of organic origin; and it is not improbable that the material has been deposited by thermal waters. L. J. S.

[Minerals from Sierra Mojada, Coahuila, Mexico.] FRANK R. VAN HORN (*Amer. J. Sci.*, 1913, [iv], **35**, 23—30).—A description is given of 21 mineral species found in the Veta Rica mine. The ores of silver, lead, and copper occur in a gangue of gypsum and barytes near the contact of Cretaceous limestone with rhyolite. The following analyses, by N. A. Dubois, are given: I, of argentite; II, of proustite:

	Ag.	Cu.	As.	Sb.	S.	Total.	Sp. gr.
I.	86·18	0·70	—	—	13·18	100·06	7·40
II.	64·65	0·70	15·25	trace	0·18	100·78	5·60

L. J. S.

The Bauxite Question. FRAN TUCAN (*Centr. Min.*, 1913, 65—68).—A discussion of previous papers (A., 1912, ii, 357; this vol., ii, 64, 69).—Bauxite is a mixture of minerals, and cannot be regarded as a definite aluminium hydroxide. Adsorption combinations of colloidal aluminium hydroxide and hydrated silica cannot always be distinguished by chemical and microscopical means from homogeneous materials. L. J. S.

Some Minerals from Tuscany. ERNESTO MANASSE (*Jahrb. Min.*, 1912, ii, Ref. 343—346; from *Mem. Soc. Toscana Sci. Nat*, 1911, **27**, 19 pp.).—Millerite, a species not before recorded from Tuscany, occurs sparingly as fine needles with marcasite in a calcite vein intersecting black clay-slate in the antimony mine of Cetine di Cotorniano.

Turgite occurs in the Rio Marino mine at Rosseto, Elba, as thin crusts and stalactites on limonite. It is fibrous, steel-grey, and lustrous, and has previously been mistaken for goethite. Analyses I—III (I, fibrous-lamellar; II, fibrous-radiated; III, stalactitic). Formula $H_2Fe_4O_7$.

Goethite is found in an iron mine at Capo d'Arco, Elba, as thin, fibrous crusts on limonite. Analysis IV. Formula $HFeO_2$:

	SiO_2.	Fe_2O_3.	H_2O.	Total.	Sp. gr.
I.	2·65	92·60	5·56	100·81	—
II.	2·11	92·04	5·58	99·73	4·34
III.	1·18	93 54	4·95	99·67	—
IV.	3·21	87·10	10·11	100·42	4·17

Zinciferous rhodochrosite ("zincorhodochrosite") as imperfect crystals and rounded masses of a rose-red colour and vitreous lustre on the turgite (see above) from Rosseto, Elba. Analysis V, corresponding with 50% $MnCO_3$, 45% $ZnCO_3$:

	CO_2.	FeO.	MnO.	ZnO.	CaO.	MgO.	Total.	Sp. gr.
V.	36·60	0·66	30·17	31·03	2·10	0·05	100·61	3·86

Jarosite occurs at Capo d'Arco, Elba, as a thin encrustation on, and as small nodules in, limonite. It is brown with an adamantine lustre, and under the microscope the minute, rhombohedral crystals are transparent and gold-yellow. Analysis VI corresponds with 91·17% jarosite, the remainder being admixed quartz and limonite. Jarosite [natrojarosite, A., 1902, ii, 666] occurs also at Capo Calamita, Elba, as a thin encrustation on limonitic ores. Analysis VII corresponds with 95·33% jarosite:

	SiO_2.	SO_3.	Fe_2O_3.	K_2O.	Na_2O.	H_2O.	Total.
VI.	2·16	28·71	48·68	7·82	1·77	[10·86]	100·00
VII.	1·20	31·61	50·28	0·98	5·55	[10·38]	100·00

Alunogen from Vigneria, Elba, is white when pure, but frequently green from admixed melanterite and ihleite; it also encloses small crystals of iron-pyrites. Analysis VIII corresponds with 88·37% of alunogen, $Al_2(SO_4)_3,16H_2O$.

Fibroferrite from Capo Calamita, Elba, is finely fibrous with yellowish-green colour and silky lustre, D 2·08—2·09. Analysis IX corresponds with $Fe_2O(SO_4)_2,10H_2O$. At 98—100° 23·02% water

is expelled, and at 285° 35·60%, with a gradual change in the optical characters. All the water is re-absorbed from a moist atmosphere, and it is therefore regarded as water of crystallisation. Fibroferrite also occurs at Vigneria and at Capo d'Arco, in Elba:

	SO_3.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	K_2O.	Na_2O.	H_2O.	Insol. in water.	Total.
VIII.	37·80	14·30	0·42	2·16	trace	0·45	0·21	44·31	0·24	99·89
IX.	32·03	—	30·58	1·50	—	—	—	36·40	—	100·51

L. J. S.

The Stassfurt Deposits. MICHAEL RÓZSA (*Zeitsch. Elektrochem.*, 1913, **19**, 109—115).—This paper is divided into two parts, the first of which is theoretical and shows that the nature of the Stassfurt deposits is not in accord with the theory "that the area over which the deposits were formed was separated from the ocean by a bar," but rather that irregular floods took place, and that these with the evaporation periods are capable of explaining the peculiarities of the deposits. The layers of hard salt are held to be the product of changed deposits. The second part of the paper gives a comparative table of the layers found in the Kieserite-Carnallite region and the hard salt region. The relative thicknesses of the various layers are indicated. J. F. S.

Question of the Identity of Podolite and Dahllite. VLADIMIR TSCHIRVINSKI (*Centr. Min.*, 1913, 97—102).—Podolite, described as a new mineral by Tschirvinski (A., 1907, ii, 481), has been suggested by Schaller (A., 1910, ii, 1076) to be identical with dahllite. The following new analysis of a podolite concretion from the village of Krutoborodinzy, govt. Podolia, Russia, agrees with the formula previously given, with the addition of a little water, namely, $3Ca_3(PO_4)_2,CaCO_3,\frac{3}{4}H_2O$:

CaO.	P_2O_5.	CO_2.	F.	SiO_2.	Organic matter.	Water of crystallisation.	Hygroscopic water.	Undetermined (Al_2O_3, Fe_2O_3, alkalis, etc.)
50·72	37·08	4·32	0·29	4·18	0·52	1·16	0·37	[1·36]

Analyses of dahllite, on the other hand, lead to the formula $2Ca_3(PO_4)_2,CaCO_3,nH_2O$, where $n=\frac{1}{2}$—1. The two minerals are therefore regarded as being chemically distinct. In physical characters they, however, show little difference; but here podolite approaches francolite and staffelite more nearly than dahllite.

L. J. S.

Mineralogy of the [Russian] Phosphorite Deposits. JAKOV SAMOILOV (*Jahrb. Min.*, 1912, ii, Ref. 338—339; from *Arb. Komm. Moskauer Landw. Inst. Erforschung der Phosphorite*, 1911, **3**, 671—690).—The following analysis is of an unweathered phosphatic nodule of Jurassic age from a boring at Moscow, corresponding with $Ca_3(PO_4)_2$ 46·96, CaF_2 3·74, $CaCO_3$ 10·41, $MgCO_3$ 1·71%:

CaO.	MgO.	Al_2O_3.	Fe_2O_3.	Mn_2O_3.	K_2O.	Na_2O.	P_2O_5.	CO_2.	F.
39·08	0·82	1·70	1·67	trace	0·92	0·99	21·51	5·47	1·82

SiO_2.	FeS_2.	Loss on ignition.	Organic matter.	Insoluble.	Total (less O for F).
0·47	2·52	3·91	0·61	19·43	100·16

According to their external appearance, Russian phosphorites are divisible into two classes: (1) Nodules with a dark, lacquer-like surface, either polished or dull. These show an increasing amount of phosphate from the interior to the exterior; for example, a nodule from the village Wopilowka, govt. Pensa, contained in the interior portion: P_2O_5, 23·89, and insoluble material, 18·22%, and in the exterior portion P_2O_5, 26·81, and insoluble, 4·5%. (2) Nodules with a light-coloured, grey, earthy exterior, due to chemical alteration; here in the exterior portion the phosphate is reduced in amount, and the insoluble material increased. L. J. S.

Occurrence of Scorodite in Rhodesia. A. E. V. Zealley (*South African J. Sci.*, 1911, **8**, 133—134).—Compact or crystallised scorodite occurs together with mispickel, limonite, and quartz in several auriferous districts in Rhodesia. A mixed sample of amorphous and finely crystallised green scorodite from Gwanda gave on analysis by J. B. Bull:

As_2O_5.	Fe_2O_3.	H_2O.	Total.
50·53	33·49	15·98	100·00

L. J. S.

Uranium Minerals from Prov. Itasy, Madagascar. Alfred Lacroix (*Bull. Soc. franç. Min.*, 1912 [*i.e.*, 1913], **35**, 233—235).—The new species betafite (A., 1912, ii, 567) has been found as fine crystals (octahedron with rhombic dodecahedron) at some other localities in Madagascar. Analysis I, by Pisani, is of betafite, D 3·75, from Ambalahazo. The mineral is readily attacked by acids, giving a yellow solution, the uranium being present as UO_3 (not as UO_2, as previously stated):

	Cb_2O_5.	Ta_2O_5.	TiO_2.	SnO_2.	ThO_2.	UO_3.	$(Ce,La,Di)_2O_3$.	Al_2O_3.	Fe_2O_3.	MgO.	CaO.	PbO.	H_2O.	Total.
I.	34·80	1·00	16·20	0·37	1·12	27·15	1·00	1·50	0·50	trace	3·12	0·38	12·50	99·64

Euxenite, occurring as crystals in association with betafite and green apatite in pegmatite at Andibakely, gave analysis II, by Pisani:

	Cb_2O_5.	TiO_2.	ThO_2.	UO_2.	$(Y,Er)_2O_3$.	Ce_2O_3.	$(La,Di)_2O_3$.	Al_2O_3.	Fe_2O_3.	CaO.	H_2O.	Total.
II.	35·50	23·60	3·70	3·00	20·80	0·40	1·70	1·31	1·09	4·01	4·35	99·46

L. J. S.

The Chemical Constitution of the Kaolinite Molecule. II. Joseph W. Mellor and A. D. Holdcroft (*Trans. Eng. Ceramic Soc.*, 1911–12, **11**, 169—172. Compare A., 1911, ii, 607).—The composition of a specimen of crystalline kaolinite is as follows:

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	MgO.	CaO.	K_2O.	Na_2O.	Loss on ignition.
45·04	—	38·58	0·14	0·01	0·38	0·18	0·13	15·94

The loss on ignition included: H_2O, 14·44, and C, 0·80%.

The heating curve was determined, and also the loss of water occurring at different temperatures, the results showing that there is no definite temperature of dehydration, even with well-defined crystals.

The kaolinite used was obtained from the coalfield of Glamorganshire, and has been described by Butler (*Min. Mag.*, **16**, No. 73).

T. S. P.

Mineralogy of Renfrewshire. ROBERT S. HOUSTON (*Trans. Paisley Nat. Soc.*, 1912, **1**, 1—88).—A review is given of the literature relating to the seventy-six species of minerals that have been found in Renfrewshire, and several new analyses are given (compare A., 1909, ii, 63). Analysis I is of native copper from Boylestone:

Cu.	Fe.	CuO.	Fe_2O_3.	CaO.	MgO.	Insol.	Total.
95·61	0·56	1·02	0·80	0·58	0·28	1·20	100·06

II, olivine from Gleniffer; III, ferrite from Gleniffer; IV—VI, prehnite from Boylestone; VII—IX, analcite from Boylestone; X, analcite from Bardrain; XI—XII, thomsonite from Boylestone; XIII—XV, saponite from Boylestone; XVI, saponite from Kilbarchan; XVII, saponite from Bridge of Weir; XVIII, saponite (variety bowlingite) from Boylestone. Analyses are also given of impure samples of chalcocite, iron-pyrites, quartz, wad, and chalybite:

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	Na_2O.	H_2O.	Total.	Sp. gr.
II.	43·31	15·46	6·72	5·54	—	17·82	8·87	0·84	1·86	100·42	—
III.	15·68	5·40	61·47	—	trace	2·03	10·41	—	5·04	100·03	—
IV.	42·02	27·92	trace	—	—	23·82	1·23	—	5·40	100·39	2·858
V.	40·22	24·64	4·22	—	—	25·02	—	1·16	5·20	100·46	2·918
VI.	42·25	27·40	trace	—	—	25·99	—	—	3·87	99·51	—
VII.	54·42	23·02	—	—	—	0·95	0·26	13·36	8·20	100·21	—
VIII.	52·83	24·69	trace	—	—	0·39	—	12·92	8·60	99·43	2·168
IX.	54·22	23·42	trace	—	—	0·42	0·38	13·68	8·20	100·32	—
X.	55·31	22·89	—	—	—	0·63	0·13	13·49	8·40	100·85	2·252
XI.	33·86	32·24	—	—	—	16·22	trace	3·63	14·20	100·15	—
XII.	41·45	27·71	—	trace	—	13·61	0·51	3·81	12·80	99·89	—
XIII.*	33·96	16·14	8·00	8·93	—	7·10	7·49	0·98	13·62	99·39	—
XIV.†	36·65	5·61	4·69	5·33	—	4·01	17·29	2·55	20·44	99·72	2·224
XV.	32·62	17·82	3·70	8·21	0·62	—	21·26	2·41	13·91	100·55	2·426
XVI.	35·02	22·82	4·16	3·55	—	1·22	23·99	0·40	9·14	100·30	—
XVII.	40·43	9·33	1·12	3·74	—	2·06	23·36	2·87	17·10	100·01	2·239
XVIII.‡	29·71	22·01	1·60	15·41	trace	4·19	15·39	—	11·49	99·80	—

* Also CO_2 3·17. † Also CO_2 3·15. ‡ Also CO_2 trace.

L. J. S.

Origin of Moldavites and similar Sporadic Glasses. GEORGE P. MERRILL (*Jahrb. Min.*, 1912, ii, Ref. 351; from *Proc. U.S. Nat. Mus.*, 1911, **40**, 481—486).—A meteoric origin having been ascribed to the so-called tektites (a general term to include moldavites, billitonites, and australites), the author has examined a series of obsidian pebbles from various localities in North and South America and from Iceland. These are of undoubted terrestrial origin, and they show the same peculiarities of surface markings as the typical tektites. The following analysis of an obsidian pebble from Cali, dep. Cauca, Colombia, is compared with published analyses of tektites, from which it does not appreciably differ:

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	MgO.	CaO.	Na_2O.	K_2O.	H_2O.	SO_3.	Total.
75·87	trace	14·35	0·22	0·29	nil	3·96	4·65	0·33	0·23	99·90

L. J. S.

Chloritoid (Ottrelite) from the Apuan Alps, Tuscany. ERNESTO MANASSE (*Jahrb. Min*, 1912, ii, Ref. 329—330; from *Mem. Soc. Toscana Sci. Nat.*, 1910, **26**, 23 pp.)—The ottrelite of the ottrelite-schists of the Apuan Alps is proved on optical and chemical grounds to be identical with chloritoid. Those analyses of ottrelite which show an excess of silica may be explained by the presence of admixed quartz. The optical characters are stated in detail, and the following analyses are given of ottrelite from: I, Stazzema; II, Camporaghena, near Fivizzano; III, Corchia. These agree with the chloritoid formula $H_2O,(Fe,Mg)O,(Al,Fe)_2O_3,SiO_2$. The ratios of Fe_2O_3 : Al_2O_3 range from 1 : 10·81 to 1 : 23·99, and of MgO : FeO from 1 : 2·85 to 1 : 7·31:

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	H_2O.	Total.	Sp. gr.
I.	24·37	trace	37·03	5·36	21·91	0·52	0·16	4·32	7·16	100·83	3·44
II.	26·07	trace	37·01	3·97	24·76	trace	0·12	1·90	7·03	100·86	3·51
III.	25·36	trace	38·99	2·54	23·06	trace	0·24	3·16	7·28	100·63	3·56

L. J. S.

Composition of Some Minerals of the Chloritoid Group. ERNESTO MANASSE (*Jahrb. Min.*, 1912, ii, Ref. 330—333; from *Proc.-verb. Soc. Toscana Sci. Nat.*, 1911, **20**, 29—42).—Previous analyses are quoted and discussed; the variations shown by them may be explained by the impurity of the materials analysed. The following new analyses are given of carefully selected material: I, Masonite from Natick, Rhode Island. II, Sismondine from Champ de Praz, Aosta, Piedmont. These two analyses agree closely with the formula $H_2R''R'''_2SiO_7$. Associated with the sismondine is a chloritic mineral, which gave analysis III, corresponding with $H_{20}Mg_{10}Fe_2Al_6Si_7O_{45}$. IV, Ottrelite from Ottrez, Ardennes. Under the microscope this material is seen to contain a considerable amount of quartz, together with small quantities of magnetite and ilmenite. Deducting 24·38% of admixed quartz, the formula agrees with that given above; corrected D 3·44. V, Ottrelite from a quartz-phyllite on Mt. Fenouillet, near Hyères (Var), contains an excess of 7·65% silica as admixed quartz; corrected D 3·68. VI, Venasquite from Vénasque, Pyrenees, contains 17·98% admixed quartz; corrected D 3·56:

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	H_2O.	Total.	Sp. gr.
I.	24·56	34·57	5·93	27·20	1·14	—	0·36	6·64	100·40	3·54
II.	25·36	42·58	0·72	18·02	0·53	0·18	5·96	7·50	100·85	3·45
III.*	28·06	21·25	—	9·75	—	—	27·46	11·78	99·15	—
IV.	42·93	29·60	0·86	15·43	3·75	—	2·12	5·48	100·17	3·25
V.†	29·71	34·35	4·71	20·33	1·41	1·16	1·69	6·64	100·00	3·60
VI.	37·87	31·12	3·25	20·48	0·62	trace	1·44	5·80	100·58	3·40

* Also Na_2O, 0·55; K_2O, 0·30. † Also TiO_2, trace.

L. J. S.

Minerals from Ambatofotsikely, Madagascar. ALFRED LACROIX (*Bull. Soc. franç. Min.*, 1912 [*i.e.* 1913], **35**, 231—233).—The pegmatites at this locality, situated 27 km. west of Miandrarivo, contain abundance of ampangabeite (A., 1912, ii, 567), fine crystals

of monazite (A., 1913, ii, 69), and fragments of orthite. This orthite, D 3·43, is rich in thoria; the following analysis by Pisani corresponds with the formula

$$[(Si,Th)O_4]_{11}(Al,Ce,La,Di,Fe)_8(Ca,Fe,H_2)_{10}:$$

SiO_2.	ThO_2.	Al_2O_3.	Ce_2O_3.	$(La,Di)_2O_3$.	$(Y,Er)_2O_3$.	Fe_2O_3.	FeO.	MnO.	CaO.	H_2O.	Total.
32·00	5·60	12·40	9·08	7·38	0·40	4·50	11·60	0·54	15·58	1·24	100·82

L. J. S.

Lavas from Central Madagascar. ALFRED LACROIX (*Compt. rend.*, 1913, **156**, 175—180).—Twenty-seven detailed analyses, by Boiteau, are given of rocks from the volcanic districts of Ankaratra and Itasy. They range from rhyolite, with 71·45% silica, to nephelinite, with 38·74% silica. L. J. S.

Ilmenite from the Quarries of Potstone at Sasso di Chiesa (Val Malenco). L. MAGISTRETTI (*Atti R. Accad. Lincei*, 1912, [v] **21**, ii, 761—767).—A crystallographic study of this mineral, which has D 4·55, and the following composition:

[With A. MORESCHI]:

SiO_2.	TiO_2.	Fe_2O_3.	FeO.	MnO.	Al_2O_3.	MgO.	Total.
0·65	47·20	33·50	15·00	1·34	1·00	0·90	99·59

R. V. S.

Meteorite of Gumoschnik, Bulgaria. G. BONTSCHEW (*Jahrb. Min.*, 1912, ii, Ref. 354—355; from *Period·česko. spisanie, Sofia*, 1910, **71**, 373—390).—A meteoric fall was observed on April 28th, 1904, near the village of Gumoschnik, in the Trojan district. Five or six stones, with a total weight of 5669 grams (the largest 3815 grams), were picked up. The material consists of olivine, enstatite, augite, iron, pyrrhotite, chromite, and a fine-grained to compact mass of undetermined nature. Chondrules of olivine and enstatite are set in a brecciated groundmass. The following analyses are of: I, the magnetic portion; II, the non-magnetic portion; and III, the bulk analysis. The amount of nickel is unusually low:

	Fe.	Ni.	Fe_7S_8.	SiO_2.	Cr_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	Lost on ign.	Total.
I.	67·141	2·135	2·028				28·310					99·614
II.	—	—	—	45·980	0·062	22·834	4·082	0·190	2·460	24·470	—	100·078
III.	15·012	0·467	0·453	42·363	0·048	17·872	3·295	0·147	1·916	18·998	0·163	100·734

L. J. S.

Existence of Natural Ozonised Waters and Probable Theories of the Phenomenon. The "Acqua Forte" of the Bagnore of Monte Amiata. RAFFAELE NASINI and C. PORLEZZA (*Atti R. Accad. Lincei*, 1912, [v], **21**, ii, 740—750, 803—811; *Chem. Zeit.*, 1913, **37**, 129.—The authors have discovered two natural waters which contain ozone as a normal constituent, and in such quantity as to smell plainly of the gas. The acid waters of the Bagnore of Monte Amiata are highly ozonised, and those of the springs of the Bagnoli in the same region in smaller degree. The

data in the present paper refer to the former water. In one litre of it at 21·5°, the following gases are dissolved: carbon dioxide, 543·72 c.c.; oxygen, 1·26 c.c.; ozone, 0·135 c.c.; the inert gases were not determined. The gases arising from the water at the source have the following composition (per 100 c.c.): carbon dioxide, 93·45 c.c.; oxygen and ozone, 0·15 c.c.; residue unabsorbed, 6·40 c.c.; the ozone amounted to 0·00064 c.c. Dispersion experiments showed that the air above the well contained 1838 ions per c.c., whilst the number in the ordinary air of the locality did not exceed 1000 per c.c. From experiments with water in which known amounts of ozone had been dissolved, it was found that the odour is still perceptible when 0·037 c.c. of ozone is dissolved in one litre of water, and the limit of sensibility of the iodide starch reaction is not reached at 0·02 c.c. per litre. For this and other reasons the authors are sceptical concerning the few other alleged ozonised waters mentioned in the literature. As possible explanations, the authors suggest the autoxidation of ferrous salts, either alone or in conjunction with ferruginous micro-organisms. The water contains 0·001565 gram of iron per litre, probably in the form of ferrous hydrogen carbonate, which is known to be an autoxidisable substance. Attention is drawn to the possible therapeutic value of the waters. R. V. S.

Analytical Chemistry.

Hempel Double Pipette Modified to Facilitate Filling. ALEXANDER CHARLES CUMMING (*J. Soc. Chem. Ind.*, 1913, **32**, 9).—A side-tube, opening vertically, is fitted to the second bulb from the burette, and this enables the pipette to be filled as easily as a simple pipette. The pipette is first filled with an indifferent gas by passing it through, whilst the additional side-tube is closed with a cork. The reagent is then introduced through the side-tube, and water is poured into the two last bulbs, through the exit-tube from the last bulb, to form a water seal. The side-tube is then closed with a well-fitting rubber cork. T. S. P.

Micro-chemical Reagents. WILHELM LENZ (*Zeitsch. anal. Chem.*, 1913, **52**, 90—99).—Directions are given for preparing absolutely pure reagents (acids, ammonia, alcohol, platinum chloride, ammonium uranyl acetate, ammonium cobalt thiocyanate, metallic tin and zinc) for use in micro-chemical testing.

Glass utensils and slides should not be used. The reagents should be kept in flasks made of fused silica; the distilled water should be stored in a, preferably gilded, silver flask. L. DE K.

Apparatus for Electrolytic Estimations. FELIX CHANCEL (*Bull. Soc. chim.*, 1913, [iv], **13**, 74—76).—The bottom of a test-tube, 30 × 125 mm., made of thin Jena glass, is pierced by a

platinum-iridium wire 1 mm. in diameter and 50 mm. long, of which 40 mm. are inside the tube and 10 mm. outside. This serves as an anode, and is connected by a clip with a silver or copper wire bent twice at right angles, and then brought parallel to the length of the tube and secured to the upper portion of the latter, where, when the apparatus is in use, it is connected to the positive pole of the battery. The cathode consists of a cylinder of platinum gauze, 20×30 mm., hung inside the tube by a platinum wire 110 to 120 mm. long, which is attached to a support in the usual way. In use the tube is closed by a watch glass suitably pierced to take the suspending wire. T. A. H.

The Use of an Extract of Red Cabbage as an Indicator for the Measurement of the Hydrogen Ion Concentration. L. E. WALBUM (*Biochem. Zeitsch.*, 1913, **48**, 291—296).—The alcoholic extract of red cabbage can be used as an indicator for concentrations between $p_H = 2{\cdot}0$ and $p_H = 4{\cdot}5$, within which limits results agreeing closely with those by the electrometric method can be obtained. Good results are obtained even in the presence of relatively large amounts of proteins, which are not affected by the presence of salts (even $\frac{1}{2}M$-sodium chloride), toluene, or chloroform. S. B. S.

Estimation of Moisture. GEORGE N. HUNTLY and JOHN H. COSTE (*J. Soc. Chem. Ind.*, 1913, **32**, 62—67).—In considering the question of the estimation of moisture in commercial products, the authors mention in some detail the various methods which are employed for the purpose. These methods are divided into three groups, namely: *Direct methods.* 1. Water driven off by ignition, condensed in part of the ignition tube and weighed directly. 2. Substance heated in a current of dry gas, or in a vacuum, water vapour collected in calcium chloride or sulphuric acid, and weighed. 3. Substance mixed with an excess of a volatile, non-miscible liquid, such as xylene, distilled, and the water measured under the hydrocarbon layer. 4. The substance is heated directly to 130° by a vapour (high pressure steam) jacket, the steam given off condensed, and measured. *Gasometric methods.* 5. The substance is mixed with calcium carbide; acetylene measured. 6. The substance is mixed with magnesium methyl haloid in the presence of a suitable dry solvent; methane measured. 7. The substance is treated with sodium; hydrogen measured. *Indirect methods.* 8. Estimation of the loss of weight by heating to a definite or indefinite temperature (the usual method). 9. Prolonged exposure in a vacuum in the presence of sulphuric acid, either at ordinary or at a higher temperature. Most of the methods are trustworthy under particular conditions and when they are applied to suitable substances. Special attention is given to the last two methods mentioned, and it is recommended that care should be taken to have the temperature inside the ordinary drying oven as nearly as possible 100°; for general work a few degrees higher will be found to be more satisfactory. In the method where the substance is dried in a vacuum,

the pressure should be as low as possible, and the exposed surface of the sulphuric acid large. When applied to coals, this method yields results which are invariably higher than those obtained by drying the coal in a water-oven. W. P. S.

Estimation of Moisture in Organic Substances. F. H. CAMPBELL (*J. Soc. Chem. Ind.*, 1913, **32**, 67—70).—The calcium carbide method is recommended for the estimation of moisture in such substances as coal, coffee, cocoa, tea, butter, etc.; in the process employed by the author, the amount of acetylene evolved is estimated gravimetrically, and an apparatus is described for this purpose. The results obtained agree closely with those found by drying the substances under reduced pressure over sulphuric acid. W. P. S.

Estimation of Moisture in Foods and Other Organic Substances. WILLIAM P. SKERTCHLY (*J. Soc. Chem. Ind.*, 1913, **32**, 70).—Results are recorded which show that many organic substances yield more moisture when dried under reduced pressure in the presence of sulphuric acid than when they are heated to constant weight in the ordinary steam-oven. The difference was most marked in the case of farinaceous substances, amounting in one instance (arrowroot starch) to 2%. It was also found that flours, meals, etc., increased in weight when heated for more than two hours at 100°. W. P. S.

Colour Reaction of Chlorates. JOSEPH PIERAERTS (*Bull. Soc. chim.*, 1913, [iv], **13**, 104—109; *Bull. Assoc. chim. Sucr. Dist.*, 1913, **30**, 401—406).—When 1 c.c. of a 0·5% potassium chlorate solution is treated with 5 c.c. of a 2·5% aqueous aniline solution and 6 c.c. of concentrated hydrochloric acid, a red coloration is obtained which changes in a few minutes to blue. The test is not to be trusted when the potassium chlorate solution contains less than 0·1% of the salt, but 0·05% solutions yield a coloration when the aniline solution is prepared with 50% alcohol. The blue coloration may be extracted from the mixture by shaking with chloroform, ether, or amyl alcohol. The test is useless in the presence of iodates, as these yield a similar coloration to that obtained with chlorates. W. P. S.

Disturbing Influence of Alcohol on Various Reactions. ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1913, **83**, 164—165).—When half a volume of alcohol is added to a potassium iodide solution to which chloroform, a few drops of sulphuric acid, and a solution of nitrite are also added, instead of the characteristic violet colour being formed in the chloroform layer after shaking, an orange or reddish-yellow coloration is obtained. Methyl or amyl alcohol, ethyl acetate, and acetone have a similar disturbing influence.

The characteristic colour reaction of phenol with ferric chloride is also entirely altered by the presence of alcohol, a dirty green or yellow coloration being obtained instead of the characteristic blue. E. F. A.

Estimation of Hydriodic Acid in Tincture of Iodine. ANDRÉ LECLÈRE (*J. Pharm. Chim.*, 1913, [vii], **7**, 68—69).—In general, iodine is estimated in tincture of iodine by titration with sodium thiosulphate, and then the hydriodic acid is determined by adding potassium iodate solution and titrating the iodine set free. It is pointed out that this last estimation is subject to two sources of error. If the iodate solution used is not exactly neutral, an excess of iodine is liberated. Further, the amount of hydriodic acid is frequently calculated from the equation $HIO_3 + 5HI = 6I + 3H_2O$ instead of from the relation $KIO_3 + 6HI = KI + 3H_2O + 6I$, which correctly represents what takes place. T. A. H.

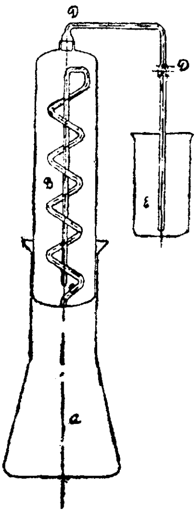
A New and Delicate Test for Oxygen. KARL BINDER and RUDOLF F. WEINLAND (*Ber.*, 1913, **46**, 255—259).—The authors have previously shown that the deep red solutions formed when ferric salts and catechol are mixed in alkaline solution contain the salts of an acid $H_3[Fe(C_6H_4O_2)_3]$ (compare A., 1912, i, 184, 445). They have now found that if ferrous sulphate is used instead of ferric salts, no colour is produced, but that oxygen is very rapidly absorbed from the air, giving the red colour. The formation of this red colour is an exceedingly delicate test for oxygen, and the authors have devised a special apparatus in which the respective solutions can be prepared and mixed in an atmosphere of oxygen-free hydrogen and then brought into contact with the gas which is to be tested for oxygen. The authors were able to detect oxygen in the Tübingen coal gas, and in carbon dioxide used in the estimation of nitrogen by Dumas's method.

The alkaline solution of ferrous sulphate and catechol can be used in the Hempel pipette for the absorption of oxygen in gas analysis. For quantitative absorption, it is necessary to shake vigorously for five minutes. T. S. P.

Estimation of Available Oxygen in Persalts and Washing Powders with Titanium Trichloride. LUDWIG MOSER and F. SEELING (*Zeitsch. anal. Chem.*, 1913, **52**, 70—85).—Perborates may be titrated by dissolving about 0·25 gram of the salt (or about 3 grams of washing powder) in water, 25 c.c. of dilute sulphuric acid are added, and while passing a current of carbon dioxide the liquid is titrated with standard titanium trichloride, the end point being shown by the disappearance of the yellow pertitanic colour. Two mols. of titanium trichloride = 1 mol. of sodium perborate. In the case of washing powders it is advisable to add, before titration, some carbon tetrachloride to dissolve the separated fatty matter; or a definite volume of titanium trichloride may be added, and the excess titrated as usual by means of ferric chloride.

Percarbonates may be tested similarly, but as the direct titration is attended with loss of oxygen, the solution should be delivered from a pipette which dips into a known volume of titanium trichloride in an atmosphere of carbon dioxide. The excess of titanium is then titrated with ferric chloride. Two mols. of titanium trichloride = 1 mol. of potassium percarbonate. Persulphates are treated like percarbonates. L. DE K.

Apparatus for the Estimation of Sulphur in Steel and Iron. GEORG PREUSS (*Chem. Zeit.*, 1913, **37**, 82).—After the material to be tested has been placed in the flask *A*, the cooler *B* is filled half way with cold water; this serves for the purpose of cooling and also for the absorption of hydrogen chloride. The cooler *B* is closed with the bent tube *D*. Immediately after introducing the acid, the cooler *B* is placed on the flask *A* in such a manner that the tube *D* dips into the beaker *E*, containing 40 c.c. of cadmium solution. An escape of hydrogen sulphide during this momentary opening is not to be feared. On warming with a small flame, the gases evolved pass through the serpentine tube *C*, penetrate the water column in cooler *B*, and then pass through the beaker *E*, where every trace of hydrogen sulphide is absorbed. The sulphur may then be estimated either gravimetrically or volumetrically.



L. DE K.

A Source of Error in the Kjeldahl-Gunning Process. EM. CARPIAUX (*Bull. Soc. Chim. Belg.*, 1913, **27**, 13—14).—The Gunning modification of Kjeldahl's process (heating with addition of potassium sulphate) does not work well in the case of several vegetable products (alkaloids, for instance). The relation between potassium sulphate and free sulphuric acid towards the end of the operation is also a matter of importance, because a loss of ammonia is to be feared when an insufficiency of free acid is present.

When working as follows these sources of error disappear: 1·5 grams of the sample (sesame cake, for instance) are heated with 30 c.c. of sulphuric acid, and after a while 15 grams of potassium sulphate are added. To make sure of the complete conversion of the nitrogen into ammonia, 1 gram of mercury and 1 gram of dry copper sulphate should also be added. The heating should not be continued longer than necessary, so as to prevent undue loss of acid.

L. DE K.

Estimation of Ammoniacal Nitrogen by means of Formaldehyde. GAILLOT (*Ann. Chim. anal.*, 1913, **18**, 15—17).—When an ammonium salt is treated with formaldehyde, the ammonia combines with the aldehyde to form hexamethylenetetramine, and the acid radicle of the salt is set free; the amount of this free acid, as estimated by titration, is a measure of the ammonia present. For the estimation, a weighed quantity of the ammonium salt is dissolved in water, the solution neutralised, an excess of neutral formaldehyde added, and the resulting acidity of the mixture is titrated, phenolphthalein being used as indicator. W. P. S.

Estimation of Nitric Acid by Schloesing's Method. MAURICE CANET (*Bull. Soc. chim. Belg.*, 1913, **27**, 10—11).—This

process, based on the liberation of nitric oxide when a nitrate is boiled with hydrochloric acid and ferrous chloride, does not always give a pure gas, since the author finds that, when treated with pure oxygen and then with alkaline pyrogallol, it leaves an appreciable volume of unabsorbed gas.

One of the sources of error must no doubt be attributed to the use of an indiarubber cork on the distilling flask, which at a high temperature does not completely prevent the entrance of atmospheric air. The error is somewhat counterbalanced, but not removed, when making a check experiment with a known amount of nitrate. If in the testing of nitrocellulose, this is dissolved first in sulphuric acid, the nitric oxide is contaminated with traces of carbon monoxide. L. DE K.

The Reaction between Formaldehyde and Nitrous Acid. LUDWIG VANINO and A. SCHINNER (*Zeitsch. anal. Chem.*, 1913, **52**, 21—28).—About 0·25 gram of sodium nitrite is dissolved in water, and boiled in a suitable apparatus until the air has been completely expelled. A sufficiency of formaldehyde is then introduced, followed by hydrochloric acid, when carbon dioxide and nitrogen are evolved. The former is absorbed by aqueous potassium hydroxide, and the latter is then measured with the usual precautions. One atom of nitrogen = 1 mol. of nitrous acid. L. DE K.

Estimation of Nitric Oxide. KOEHLER and M. MARQUEYROL (*Bull. Soc. chim.*, 1913, [iv], **13**, 69—72).—The method described by Baudisch and Klinger (this vol., ii, 74) is not applicable to mixtures containing, in addition to nitric oxide, nitrous oxide, nitrogen, carbon dioxide, and carbon monoxide. In such cases the authors absorb the nitrogen trioxide formed by means of ethylaniline. In the residue, carbon dioxide is estimated by means of potassium hydroxide and the excess of oxygen added is absorbed by alkaline pyrogallol; the rest of the analysis is carried out in the ordinary way. Ethylaniline dissolves a little more than its own volume of carbon dioxide at 15° to 20° under atmospheric pressure, so that when only one-sixth or one-seventh of the total pressure is due to this gas, the volume dissolved by the small amount of ethylaniline used is negligible. T. A. H.

Estimation of Phosphoric Acid Soluble in Citric Acid in Thomas Slag. W. SIMMERMACHER (*Chem. Zeit.*, 1913, **37**, 145—146. Compare A., 1907, ii, 577; 1912, ii, 992, 993).—When ferric chloride is added to the citric acid solution of the phosphoric acid in order to prevent precipitation of silica, the subsequent addition of the mixture of ammonium citrate solution and magnesia mixture must be made in small quantities at a time, otherwise ferric hydroxide is precipitated and does not re-dissolve in the reagent. Ferrous chloride does not prevent the precipitation of the silica. The mixture of ammonium citrate solution and magnesia mixture must be freshly made. W. P. S.

Some Factors Influencing the Quantitative Estimation of Arsenic in Soils. J. E. GREAVES (*J. Amer. Chem. Soc.*, 1913, **35**, 150—156).—The methods which have hitherto been recommended for the estimation of arsenic in soils are liable to give inaccurate results, as they do not take into account the effect produced by the presence of iron. A study has now been made of the influence of iron on the estimation of arsenic by Marsh's method and of the effect of stannous chloride in overcoming the retention of arsenic by iron.

The following method has been found to give the best results. To 10 grams of the soil are added 25 c.c. of concentrated nitric acid, and the mixture is heated for thirty minutes. While still fairly hot, 10 c.c. of concentrated sulphuric acid are added, and the mixture is again heated for thirty minutes. The mixture is then filtered, and the soil washed with hot water; the filtrate is evaporated to dryness and heated until free from nitrates. The residue is treated with dilute sulphuric acid and 20 c.c. of 10% solution of stannous chloride, and then slowly introduced into the Marsh apparatus. This method enables very small quantities of arsenic to be estimated accurately. E. G.

Estimation of Arsenic in Urine and Blood. FRANZ LEHMANN (*Arch. Pharm.*, 1913, **251**, 1—4).—A method described previously in detail by the author and E. Rupp (A., 1912, ii, 866) may be used for the estimation of arsenic in urine and in blood. In the case of urine, 500 c.c. of the sample are treated with 2·5 grams of powdered potassium permanganate and evaporated almost to dryness, a small quantity of solid paraffin being added to prevent frothing. This preliminary treatment with permanganate is essential in order to avoid loss of traces of arsenic during the evaporation. The estimation is then proceeded with as described. Blood (50 grams) is shaken for ten minutes with 2·5 grams of permanganate before the sulphuric acid and the main quantity of permanganate are added. W. P. S.

The Separation of Arsenic and Tungsten. SIEGFRIED HILPERT and THEODOR DIECKMANN (*Ber.*, 1913, **46**, 152—155).—Owing to the formation of very stable complexes between arsenic and tungstic acids, precipitation methods do not give a satisfactory separation. The authors make use of the distillation method for separating the arsenic, using cuprous chloride as the reducing agent. To the mixture containing the complex of arsenic and tungsten (0·0646 gram of arsenic and 0·1313 to 0·2626 gram of tungstic acid), 15 grams of cuprous chloride are added and 150 c.c. of hydrochloric acid (D = 1·16), and the distillation carried out until only a small residue is left. The distillation is again repeated with another 150 c.c. of hydrochloric acid, after which no more arsenic will pass over. It is found, however, that arsenic still remains in the residue, although there is no definite molecular ratio between the arsenic and the tungsten. It is probable that it is adsorbed by the tungstic acid, since if the residue is made alkaline with potassium hydroxide,

heated, cooled, and then again distilled twice with 150 c.c. of hydrochloric acid, the remainder of the arsenic distils over, and a quantitative separation is attained. The arsenic in the distillate is determined by titration with iodine.

The quantity of tungstic acid should not exceed the amount given above. T. S. P.

Estimation of Carbon and Carbon Dioxide. ACH. GRÉGOIRE, JAMES HENDRICK, EM. CARPIAUX, and E. GERMAIN (*Ann. Chim. anal.*, 1913, **18**, 1—8).—In the method proposed, the substance containing carbon is ignited in a current of oxygen, and the carbon dioxide (after the gases have been passed over copper oxide) is absorbed in barium hydroxide solution. The latter is contained in a Pettenkofer absorption tube, and the resulting barium carbonate is then collected on a filter, precautions being taken to prevent absorption of carbon dioxide from the atmosphere during the filtration. The barium carbonate is next decomposed in a modified Scheibler's apparatus, and the volume of the liberated carbon dioxide is measured. Particular attention is paid to the volume of carbon dioxide which dissolves in the nitric acid employed for the decomposition, and a table is given showing the corrections to be applied on this account. For instance, 10 c.c. of nitric acid, D 1·20 at 16°, absorb 10·67 c.c. of carbon dioxide (calculated to normal temperature and pressure). W. P. S.

Portable Pettersson-Palmqvist Apparatus. R. P. ANDERSON (*J. Amer. Chem. Soc.*, 1913, **35**, 162—168).—A modification of the Pettersson-Palmqvist apparatus for estimating carbon dioxide in air is described, which has the advantages of being more readily and conveniently manipulated than the original form, and of being more easily portable. By means of a coil of copper tubing submerged in the water in the glass cell, the sample of air can be rapidly adjusted to the temperature of the apparatus. Carbon dioxide can be quickly and accurately estimated when present in quantities not exceeding 0·5% by volume. E. G.

The Use of Phenolphthalein and of Rosolic Acid for the Estimation of Free Carbonic Acid in Water. HERMANN NOLL (*Zeitsch. angew. Chem.*, 1913, **26**, 85—87).—Chiefly a reply to Tillmans and Heublein (A., 1912, ii, 685). Further experiments made by the author indicate that in the titration of the free carbonic acid in water, the hydrogen carbonates behave differently towards phenolphthalein from what they do towards rosolic acid. With the latter indicator, a definite portion of the free carbonic acid is not accounted for, which portion is always proportional to the hydrogen carbonates present. Thus, using a rosolic acid solution of the strength 1 : 1000, 1 mg. of carbonic acid present as hydrogen carbonate masks the presence of 0·25 mg. of free carbonic acid, whereas with a strength of 1 : 1500, 0·15 mg. is masked. These results verify those of Tillmans and Heublein with respect to rosolic acid. T. S. P.

Microchemical Reaction for Carbonates in Rock Sections. W. HEEGER (*Centr. Min.*, 1913, 44—51).—The reagent used consists of 2—3 c.c. $N/10$-hydrochloric acid, to which a few drops of potassium ferricyanide solution have been added. From the velocity of the reaction and the intensity of the blue coloration produced, conclusions can be drawn as to the presence of various carbonates—calcite, dolomite, ankerite, etc. Only in very exceptional cases is calcite so free from iron that no colour is obtained. This method has the advantage over other colouring methods in being applicable when the rock constituents are in a finely divided state. L. J. S.

Qualitative Organic Analysis by means of Magnesium. JOSÉ GIRAL PEREIRA (*Anal. Fis. Quim.*, 1913, **11**, 68—73).—When organic compounds are ignited with magnesium or, better, with magnalium, carbon may be detected in the residue by treatment with ammoniacal cuprous chloride and acidification, nitrogen by the generation of ammonia on warming with water, and oxygen by means of the feeble alkalinity of the magnesium oxide. The oxygen test is not trustworthy, and magnalium gives better results than magnesium. G. D. L.

Detection of Silicic Acid in Urine without Incineration. ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1913, **83**, 143—152).—The urine is partly evaporated and precipitated with alcohol. The sticky precipitate is stirred with alcohol, brought on to a filter, washed with alcohol, and dried after washing with ether. It is then shaken out of the filter, stirred with dilute hydrochloric acid, and finally returned to the filter, and the insoluble portion well washed. On incineration, almost pure silicic acid is obtained.

The daily urine contains on the average about 0·1 gram SiO_2. E. F. A.

Decomposition of Silicates. WALTHER HEMPEL (*Zeitsch. anal. Chem.*, 1913, **52**, 86—90).—If an electric oven is at disposal by means of which a temperature of 1360° can be obtained, the best way for rendering silicates soluble is to heat 1 gram of the powdered sample with 3 grams of pure barium carbonate for ten minutes.

The chief advantage of the process lies in the fact that the barium is readily removed from the resulting solution by means of sulphuric acid; also, the platinum crucible does not suffer. L. DE K.

General Method for the Analysis of the Ashes of Body Fluids. W. MESTREZAT (*J. Pharm. Chim.*, 1913, [vii], **7**, 60—65).—A general method is described for the determinations successively of phosphoric acid, iron, aluminium, lime, and magnesia on the same specimen of ash prepared from a body fluid. Estimations of sodium and potassium are best made on a second specimen of the ash. The method is particularly applicable to ash from the cerebro-spinal fluid. T. A. H.

Evaulation of Barium Sulphide. JULIUS F. SACHER (*Zeitsch. anal. Chem.*, 1913, **52**, 28—31).—To the solution of the sulphide is

added a definite number of c.c. of a solution of lead nitrate (16 grams per litre), a little acetic acid is added, and the lead sulphide is filtered off and washed with cold water. The excess of lead is then titrated with ammonium molybdate (8·526 grams per litre; 1 c.c. = 1 c.c. of the lead solution), using a 0·5% solution of tannin as external indicator, 1 c.c. of lead solution = 0·0081814 gram of barium sulphide. L. DE K.

Estimation of Magnesium Chloride in Water. EMIL BOSSHARD and W. BURAWZOW (*Zeitsch. angew. Chem.*, 1913, **26**, 70—72).—A known volume of the sample is evaporated on the water-bath, and the residue extracted with a mixture of equal volumes of absolute alcohol and ether, which dissolves any magnesium (and calcium) chloride present. The filtrate is then diluted with water to a definite volume, and in an aliquot part of this the chlorine is estimated volumetrically. In another part, the calcium is estimated gravimetrically, and after allowing for this, the remaining chlorine is calculated to magnesium chloride. L. DE K.

Behaviour of Uric Acid towards Ammonia and Magnesium Salts and the Estimation of Magnesium in Urine. ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1913, **83**, 152—159).—When urine is precipitated by magnesia mixture and the precipitate filtered immediately, there is no separation of uric acid. When the filtrate is left for a day or more, in addition to a little ammonium magnesium phosphate, there is a characteristic yellow separation. This substance contains uric acid, ammonia, and magnesia, and represents perhaps a compound of the structure

$$Mg(NH_4)_2(C_5H_2O_3N_4)_2.$$

Various unsuccessful attempts to synthesise such a compound are described.

The influence of these observations on the direct estimation of magnesium in urine without incinerating is investigated and proved to be without moment. E. F. A.

Rapid Estimation of Zinc. KURT VOIGT (*Zeitsch. angew. Chem.*, 1913, **26**, 47—48. Compare Abstr., 1912, ii, 298).—The author again proves by a number of experiments that in the presence of sufficient ammonium chloride no insoluble zinc silicate is regenerated on adding ammonia. L. DE K.

Influence of Lead on the Titration of Zinc with Ferrocyanide. VICTOR LENHER and C. C. MELOCHE (*J. Amer. Chem. Soc.*, 1913, **35**, 134—138).—The most satisfactory volumetric method for estimating zinc in ores is the modified Waring method. Conflicting statements have been made with reference to the influence of lead on the titration with ferrocyanide, and this question has therefore been investigated.

The results show that when the titration is carried out in the usual way, the presence of lead is immaterial. In estimating lead by the ferrocyanide method. an acetic acid solution should be used, and mineral acids must not be present.

In the estimation of zinc in ores in which lead and iron are the only heavy metals present in any considerable quantity, such as the Wisconsin zinc ores, the lead need not be removed before carrying out the ferrocyanide titration. The ore (0·5 gram) is dissolved in 10 c.c. of concentrated hydrochloric acid and a little nitric acid. After dilution, the solution is treated with ammonia and afterwards filtered. The precipitate is dissolved in dilute hydrochloric acid and reprecipitated with ammonia. The filtrate is added to that from the earlier precipitation, is acidified with hydrochloric acid, and, after being concentrated by evaporation, is ready to be titrated. The solution should be hot when titrated, should have a volume of 200 c.c., and should contain 6—10 c.c. of concentrated hydrochloric acid and 10 grams of ammonium chloride. The ferrocyanide solution should be of such strength that 1 c.c. is equivalent to 0·005 gram of zinc. Solution of uranium nitrate (5%) is the best indicator. E. G.

Colorimetric Determination of Traces of Zinc. ANGEL DEL CAMPO CERDAN and JOSÉ DE LA PUENTE (*Anal. Fis. Quim.*, 1913, **11**, 98—108).—The formation of a blue colour on the addition of aqueous ammonia and resorcinol to zinc solutions may be made the basis of a colorimetric method for the recognition of zinc down to 1^{-7} gram. For every 100 c.c. of liquid, 2 c.c. of 0·92 ammonia and 2 c.c. of 5% resorcinol are added. The liquid is covered with paraffin to exclude oxygen, and after twenty-four hours examined in the colorimeter. The maximum error observed was 6·6%. G. D. L.

Detection and Colorimetric Estimation of Lead, Copper, and Zinc in Potable Water. LUDWIG W. WINKLER (*Zeitsch. angew. Chem.*, 1913, **36**, 38—44).—In the usual colorimetric estimation of lead it is necessary to add to the sample and to the comparison fluid a certain amount of ammonium chloride, otherwise the result will be deceptive.

It is pointed out that in the presence of even traces of suspended ferric hydroxide, the lead will pass into the deposit, so that the water may appear lead-free. Instead of hydrogen sulphide water, the author prefers a solution of sodium monosulphide; both acetic acid or ammoniacal liquids may be used. If copper is also present, the following process is recommended. The copper is estimated colorimetrically by means of ferrocyanide in the presence of potassium hydrogen carbonate, potassium cyanide is added (which causes a green coloration), then an ammoniacal solution of ammonium chloride, and finally sodium sulphide, which will react with the lead only.

A new process is given for the estimation of zinc. The oxide obtained by the usual process is converted by way of a check into chloride, and the chlorine is then titrated with silver in the usual manner after adding a little potassium hydrogen carbonate. Minute traces of zinc are judged from the turbidity caused by the reagents. L. DE K.

Detection of Traces of Copper. WESLEY B. PRITZ, A. GUILLAUDEU, and JAMES R. WITHROW (*J. Amer. Chem. Soc.*, 1913, **35**, 168—173).—In the course of certain work on the electrolytic precipitation of copper, it was desired to ascertain the sensitiveness of the various reagents which are usually employed to determine whether the metal has been removed completely from the solution. It has been found that, if the volume of the electrolyte is 100 c.c., and 1 gram of copper is originally present and other metals are absent, the end-point can be detected by ammonium hydroxide within 0·105%, by ammonium sulphide within 0·015%, and by potassium ferrocyanide within 0·009%.

The following method is recommended for detecting traces of copper in the solution after electrolytic precipitation has been effected. One c.c. of the sample is introduced into a glass tube, 3—5 mm. in internal diameter, 15 cm. long, and with a capacity of nearly 3 c.c. The solution is rendered alkaline with ammonia, acidified with glacial acetic acid, and then treated with two drops of 2% potassium ferrocyanide solution. If more than 1 mg. of copper is present, a pronounced red coloration is produced, but if there is not more than 0·1 mg. of copper in 100 c.c. of the solution, the colour is practically identical with that of a blank experiment made in a similar tube. E. G.

Estimation of Copper with Sodium Hypophosphite. RICHARD WINDISCH (*Zeitsch. anal. Chem.*, 1913, **52**, 1—13).—The process, previously recommended by Dallimore (A., 1909, ii, 833), is intended more particularly for commercial copper sulphate. One hundred grams of the sample are dissolved in water, 60 c.c. of dilute sulphuric acid (1 : 7) are added, and the whole diluted to one litre; 50 c.c. are then heated to boiling in a deep porcelain dish with addition of 20 c.c. of commercially pure sodium hypophosphite (200 grams per litre). After fifteen minutes' action, the precipitate, consisting of metallic copper, is collected, washed first with hot water, then with alcohol, and finally converted by ignition into oxide. L. DE K.

Estimation of Copper in Preserved Vegetables by means of the Spectrophotometer. EUGÈNE TASSILLY (*Bull. Soc. chim.*, 1913, [iv], **13**, 72—74).—The method depends on the complete extraction of the copper from the charred vegetables and its conversion into copper ferrocyanide, which is then estimated by means of a spectrophotometer, previously graduated by means of a similar copper ferrocyanide solution of known strength.

From 10 to 15 grams of the product are ignited gently to produce a charred mass retaining the shape of the original. This is extracted at 100° with 2 to 5 c.c. of sulphuric acid, water added, the solution filtered, and the residue washed. The copper in the filtrate and washings is precipitated by sodium hyposulphite and the precipitate washed and carefully ignited as usual. The residue is dissolved in 1 to 1·5 c.c. of sulphuric acid, a few drops of nitric acid added, and the excess of acid evaporated. The cupric sulphate

is dissolved in water, 2 c.c. of potassium ferrocyanide solution (0·07 gram per c.c.) added, and the liquid diluted to 100 c.c. and examined in the spectrophotometer, using the portion 115—125 of the micrometer when the *D*-ray is at 80°. T. A. H.

The Mercury Content in the Air, Dust, etc., of Places where Metallic Mercury is in Use. ARVID BLOMQUIST (*Ber. Deut. pharm. Ges.*, 1913, **23**, 29—46).—The mercury vapour contained in the air of rooms where mercury or its preparations are constantly being used is estimated by evolving chlorine, and so converting the mercury into the chloride. Four thousand litres of the air are then drawn through a series of absorbers, two of which contain 100 c.c. of 5% hydrochloric acid, containing 1% of stannous chloride; the third contains 100 c.c. of 5% aqueous potassium hydroxide. The mercury is then estimated by means of a slight modification of Farup's method (intended for urines). A large number of experiments are communicated showing the quantity of mercury found in the air and dust of laboratories and in the urine of the persons employed there, mostly fractions of a milligram. L. DE K.

New Method for the Estimation of Mercury in Urine and in the Tissues. HANS BUCHTALA (*Zeitsch. physiol. Chem.*, 1913, **83**, 249—303).—See this vol., i, 318.

Comparison of Farup's and Schumacher-Jung's Methods for the Estimation of Mercury in Urine. WILHELM BECKERS (*Arch. Pharm.*, 1913, **251**, 4—7).—Farup's method (collecting and weighing the mercury on a gilt asbestos filter after it has been reduced to the metallic state) yields results which agree closely with those obtained by the Schumacher-Jung method (A., 1903, ii, 44), and the methods are equally trustworthy. W. P. S.

Application of Diphenylcarbazide as Indicator in the Titration of Iron with Dichromate. O. L. BARNEBEY and S. R. WILSON (*J. Amer. Chem. Soc.*, 1913, **35**, 156—162).—Brandt (A., 1906, ii, 309) has suggested the use of diphenylcarbazide as an indicator in the titration of iron. On applying this method, concordant results could not be obtained, and the present investigation was therefore undertaken.

It has been found that the variation in the results is due to the indicator itself, which is oxidised by the dichromate during the titration, 3 mols. of diphenylcarbazide requiring 2 mols. of potassium dichromate for their oxidation.

If a blank experiment is carried out to ascertain the reducing power of the indicator, the method is rendered applicable to the estimation of iron in ores. The end-point is excellent, and small quantities of iron can be estimated as accurately as by the more common methods. E. G.

Estimation of Iron in Presence of Organic Substances. ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1913, **83**, 159—164).—A critical study of the difficulties experienced in estimating iron in

association with proteins or other organic substances. The iron is converted by fusion with a mixture of alkali nitrate and carbonate into oxide, the fused mass dissolved in water, and the iron oxide collected on an ash-free filter. It is advantageous to carry out the washing with a 10—15% solution of ammonium nitrate, and finally to fill the filter with alcohol. A further difficulty is often experienced in removing all traces of iron oxide from the platinum dish.

The method of estimation of iron as ferric phosphate is examined and found to be very unsatisfactory. Washing the ferric phosphate precipitate with ammonium acetate does not remove the difficulties.

E. F. A.

The Separation of Iron and Manganese. F. H. CAMPBELL (*J. Soc. Chem. Ind.*, 1912, **32**, 3—4).—The cold solution of iron and manganese salts, preferably the sulphates, is almost neutralised with ammonia, and a mixture of equal volumes of a 25% potassium iodide solution and a saturated solution of potassium iodate then added. Ferric hydroxide is precipitated by the hydrolysis of the ferric salt, the hydrolysis being made complete because of the removal of the acid formed by the mixture of iodide and iodate, with liberation of iodine. After allowing the precipitate to settle, the liberated iodine is removed by a slight excess of 20% sodium thiosulphate solution. The precipitate is collected, washed first with cold and finally with boiling water, and the manganese determined directly in the filtrate as pyrophosphate (compare Gooch and Austin, A., 1899, ii, 128). When metals such as calcium and magnesium are present, the manganese should be separated as sulphide, re-dissolved in acid, and then precipitated as the phosphate. Nickel, cobalt, and zinc do not interfere on account of the solubility of their phosphates in ammonia.

So long as the conditions given above are observed, the results for manganese are accurate, one precipitation only being necessary. Hot solutions cannot be used, since manganese is then precipitated with the iron. If the precipitate of ferric hydroxide is ignited and weighed, the results, for some unknown reason, are high; the precipitate should be dissolved, the ferric salt reduced, and then titrated with permanganate or dichromate.

In the tests carried out, the mixtures contained 0·0287—0·2300 gram of iron, and 0·0328—0·2628 gram of manganese. T. S. P.

Analysis of Ferro-Zirconium. MAX WUNDER and B. JEANNERET (*Zeitsch. anal. Chem.*, 1913, **52**, 99—101).—A reply to the criticism of Weiss and Trautmann (A., 1912, ii, 495). The authors uphold the accuracy of their process (*ibid.*, ii, 96), which is now used exclusively by many works chemists. L. DE K.

The Direct Volumetric Estimation of Tin. HENRY J. B. RAWLINS (*Chem. News*, 1913, **107**, 53—55).—The author recommends the well-known titration with iodine or with ferric chloride in the assay of commercial tin. The titanium chloride process (estimation of excess of iron added) may also be used. The standard solutions

should be checked against a known weight of pure tin dissolved in hydrochloric acid in a current of carbon dioxide. The presence of antimony causes the results to be slightly in excess of the truth and, in delicate assays, it should be determined and allowed for.

The author thinks the titration results are more trustworthy than a gravimetric assay based on an estimation of the impurities.

L. DE K.

New Colorimetric Method for Titanium. VICTOR LENHER and W. G. CRAWFORD (*J. Amer. Chem. Soc.*, 1913, **35**, 138—145).—The most generally applicable method hitherto proposed for the estimation of small quantities of titanium is Weller's colorimetric method (A., 1883, 381), in which hydrogen peroxide is employed.

A study of the behaviour of a large number of organic compounds with titanium in concentrated sulphuric acid has shown that distinctive colorations are produced by thymol, phenol, quinol, salicylic acid, and chromotropic acid. Of these, thymol has proved to be the most satisfactory for detecting and estimating small amounts of the metal. The intensity of the coloration is at least 25 times as great as that produced by the hydrogen peroxide method. The colour is not affected by diluting the solution with water until the strength of the sulphuric acid is reduced to 79·4%, and beyond this point it fades in a regular manner. When the solution is heated, the colour disappears, but returns on cooling, and is not permanently discharged until the solution is heated to 100°. The colour is bleached by fluorides or hydrofluoric acid. Chlorides, phosphates, and tin do not affect the intensity, but tungstic acid reduces it in direct proportion to the amount of tungsten present.

In order to apply the test, the substance containing titanium is fused with potassium hydrogen sulphate; the product is dissolved in concentrated sulphuric acid, an excess of thymol in sulphuric acid is added, the solution diluted to a definite volume, and the colour compared in a colorimeter with that given by a standard titanium solution. The method is simple and rapid, and can be applied to smaller quantities of titanium than can be estimated by Weller's method.

E. G.

Use of Cupferron in Quantitative Analysis [of Titanium] ITALO BELLUCCI and L. GRASSI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 30—34. Compare Baudisch, A., 1911., ii, 939).—When an aqueous solution of cupferron is added to an acid solution of titanium chloride or titanium sulphate, the canary-yellow salt, $(NO\cdot NPh\cdot O)_4Ti$, is precipitated quantitatively. If the precipitate is filtered off, dried and ignited (TiO_2 being formed), the process forms a very accurate and convenient means of estimating titanium. Very good results have also been obtained in the application of the method to the separation of titanium from aluminium. R. V. S.

Estimation of Bismuth by Titration of the Hydrochloric Acid Solution of Bismuth Oxyiodide by Means of Alkalis. C. REICHARD (*Pharm. Zentr.-h.*, 1913, **54**, 103—104).—The process is

intended for the evaluation of bismuth oxynitrate. 0·4 Gram of the powder is dissolved in 10 c.c. of 25% hydrochloric acid, 2 grams of potassium iodide are added, and the liquid diluted to 100 c.c. Twenty-five c.c. of the solution are then titrated with *N*/2-sodium hydroxide until the yellow colour has disappeared. The difference between the alkali used and that required to neutralise the acid represents the bismuth; 2 mols. of sodium hydroxide = 1 mol. of bismuth oxide. L. DE K.

The Reaction between Formaldehyde and Bismuth or Copper in the Presence of Strong Alkali. FRANZ HARTWAGNER (*Zeitsch. anal. Chem.*, 1913, **52**, 17—20).—Bismuth chloride may be reduced to metal by heating with a large excess of both formaldehyde and aqueous sodium hydroxide. If only theoretical quantities are used, or when the liquid is too much diluted, the reduction is very imperfect. Copper, however, is more readily reduced to metal. In the presence of a large excess of alkali, hydrogen is also evolved.

The author also investigated the action of chloral hydrate and acetaldehyde on some metals. In alkaline solution, gold is completely reduced, and should it become colloidal, it may be precipitated by boiling with excess of dilute sulphuric acid. Acetaldehyde also reduces gold in acid solutions. Copper salts are reduced to metal by chloral hydrate in presence of alkali; the metal, however, is very liable to oxidation; acetaldehyde causes no reduction, but, on boiling, copper oxide separates. Bismuth chloride in the presence of alkali is reduced very slowly and incompletely by chloral hydrate, but not by acetaldehyde. Silver salts are completely reduced in alkaline solutions both by chloral hydrate and acetaldehyde; here the latter is to be preferred in practice. L. DE K.

Estimation of Tantalic Acid and Columbic Acid in Tantalites, Columbites, Yttrotantalites and Fergusonites, and the Colorimetric Estimation of Columbium. E. MEIMBERG (*Zeitsch. angew. Chem.*, 1913, **26**, 83—85).—The principle of the method is as follows. The mineral is decomposed by fusion with potassium hydrogen sulphate. The fusion is digested with hydrochloric acid, the residue of mineral acids neutralised with ammonia, and then digested with ammonium sulphide at a gentle heat for twenty-four hours. The residue is collected, washed successively with hot water and boiling, dilute hydrochloric acid, and then dissolved in excess of hydrofluoric acid. The tantalum is then precipitated as potassium tantalum fluoride, K_2TaF_7, by the addition of a concentrated solution of potassium hydrogen fluoride, the columbium remaining in solution. The filtrate from the precipitate is evaporated to dryness, digested with strong sulphuric acid, boiled with water to remove the sulphuric acid, dissolved in hydrofluoric acid, and again precipitated with potassium hydrogen fluoride in order to remove any tantalum still remaining. This process is repeated until the tantalum is completely separated from the

columbium. The potassium tantalum fluoride is then converted into the pentoxide and weighed as such. It generally contains some titanium, which must be estimated colorimetrically.

For the estimation of the columbium, all the hydrofluoric acid filtrates are evaporated to dryness, and then again taken down with strong sulphuric acid. The residue is treated successively with boiling water, ammonia, ammonium sulphide, and very dilute hydrochloric acid, and weighed as columbium pentoxide.

Gallotannic acid has hitherto been used in testing colorimetrically for columbic acid, but the colour is affected considerably by the presence of tantalum. The author makes use of the fact that the columbates, especially the fluoride compounds, are reduced by tin and hydrochloric acid to coloured products, whereas the tantalates are not affected. The potassium tantalum fluoride, which is to be tested for columbium, is dissolved in dilute hydrochloric acid containing some hydrofluoric acid, and the solution evaporated down until a copious precipitation of potassium tantalum fluoride has occurred. After cooling, the crystals are collected and washed with cold dilute hydrofluoric acid. The columbium, together with some tantalum, is in the filtrate, which is evaporated to dryness on the sand-bath. The residue is dissolved in concentrated hydrochloric acid, the solution placed in a colorimeter tube, and reduced with tin. The reduction is complete in about fifteen minutes, and the colour is then compared with that of a standard, which must be freshly made for each determination. The solutions to be estimated, as also the standard, should not contain more than 0·1% of columbium. By this method 0·01—0·005% of columbium can readily be estimated. T. S. P.

Delicate Colour Reactions of Gold Salts. JOHN EDWARD SAUL (*Analyst*, 1903, **38**, 54).—If a 0·1% solution of either of the following substances, quinol, pyrogallol, gallotannic acid, *p*-hydroxyphenylaminoacetic acid, salts of phenylhydrazine, 3:4-diaminophenol (amidol), the monomethyl derivatives of *m*- and *p*- (metol) and *o*-aminophenol, associated with quinol in (ortol) and *m*-phenylenediamine, is added to ten volumes of a 0·002% solution of gold chloride, a colloidal solution of gold is formed, presenting a beautiful violet colour varying in intensity and shade with the reagent used. Gallotannic acid gradually produces a rose colour. The author recommends *p*-phenylenediamine as a suitable test for traces of gold. The coloration is at first of a dark green, and still shows with a 0·0001% solution. After some time the colour undergoes changes. L. DE K.

Estimation of Palladium and its Separation from Copper and Iron. MAX WUNDER and V. THÜRINGER (*Zeitsch. anal. Chem.*, 1913, **52**, 101—104).—To the solution is added a 1% solution of dimethylglyoxime in dilute hydrochloric acid; should ferric chloride be present, a large excess should be added, owing to reduction taking place. The precipitation of the palladium compound is favoured by gentle boiling, and the precipitate is then converted into metal by ignition, with the usual precautions.

From the filtrate the copper is precipitated as thiocyanate by addition of sulphur dioxide and potassium thiocyanate, and weighed as such. The filtrate contains the iron, which is first precipitated with ammonium sulphide and finally weighed as oxide.

L. DE K.

A Source of Error in the Determination of "Permanganate Absorbed" by Drinking Waters by Schulze's Method. LEO GRÜNHUT (*Zeitsch. anal. Chem.*, 1913, **52**, 36–40).—This method (boiling with alkaline permanganate and titrating the excess) is affected when the water itself contains manganese. This, however, may be remedied as follows: To 120—150 c.c. of the sample is added 0·6—0·75 c.c. of 33% aqueous sodium hydroxide, and after shaking a few times and waiting for a few minutes, the precipitate, which also contains the manganese, is filtered off through a Gooch crucible, and 100·5 c.c. of the clear filtrate are then boiled with permanganate as usual.

L. DE K.

A Method of Analysing Mixtures of Hydrogen and the Gaseous Saturated Hydrocarbons, Hydrogen, Methane, Ethane, and Propane. PAUL LEBEAU and A. DAMIENS (*Compt. rend.*, 1913, **156**, 144—147; 325—327).—Taking advantage of the fact that, of the four gases under consideration, only hydrogen and methane have any appreciable vapour tension at $-190°$, the authors first liquefied the gaseous mixture, and then submitted it to fractional distillation, by means of a mercury pump, at $-190°$. The volatile portion contained the hydrogen and methane, and was analysed eudiometrically, the ethane and propane being pumped off at higher temperatures. By an examination of more complex mixtures, the authors have determined conditions of temperature favourable for a practical separation of other gaseous hydrocarbons from hydrogen.

In the second paper, the mixture studied contained ethane, propane, and *iso*butane, and it was found that by maintaining the mixture at $-127°$ and pumping off all the gas possible, all the ethane and a portion of the propane were removed and could be analysed eudiometrically, the residual liquid containing the remainder of the propane, and all the *iso*butane being pumped off at a higher temperature and similarly analysed. In general, by a study of the vapour tension of the hydrocarbons when liquefied, it is possible, by suitable choice of temperatures, to separate mixtures into fractions containing only two of the hydrocarbons, the fractions then being analysed eudiometrically.

W. G.

Estimation of Glyceryl Acetate in Essential Oils. S. GODFREY HALL and ARTHUR J. HARVEY (*J. Soc. Chem. Ind.*, 1912, **32**, 61—62).—The method depends on the separation of the glycerol and its estimation by the triacetin method. A quantity of not less than 10 grams of the essential oil is saponified by heating with alcoholic potassium hydroxide solution, and the solution is then neutralised with hydrochloric acid. After the alcohol has been

removed by evaporation to dryness, the residue is dissolved in a small quantity of water, and the oily portion is separated by extraction with ether. The aqueous solution is then evaporated to a syrupy condition, and the glycerol in it is estimated in the usual way by the triacetin method. W. P. S.

Detection of Pentoses in Urines containing Dextrose. ADOLF JOLLES (*Zeitsch. anal. Chem.*, 1913, **52**, 104—108).—To 100 c.c. of diabetic urine (containing up to 5% of dextrose) are added 4 grams of phenylhydrazine hydrochloride and 8 grams of sodium acetate (sugar-free urine is mixed with 1% of dextrose). The whole is heated for an hour in the boiling water-bath and then rapidly cooled. The deposit is collected on a filter and well drained. It is then removed from the filter into a beaker, 15 c.c. of hot water are added, and the whole heated for five minutes on a boiling water-bath. After filtering rapidly, the liquid, which contains the pentosazone, is distilled with addition of 6 c.c. of fuming hydrochloric acid, and 6 c.c. are collected in a test-tube. Three c.c. of the distillate are then mixed with 5 c.c. of Bial's reagent (1 gram of orcinol, 500 c.c. of 30% hydrochloric acid, 30 drops of officinal ferric chloride), and boiled for a short time. In the presence of as little as 0·05% of pentoses, a distinct green coloration is noticed.

When testing urines with more than 5% of dextrose, the amount of the reagents should be doubled. L. DE K.

Estimation of Dextrose in Urine. K. K. JÄRVINEN (*Zeitsch. anal. Chem.*, 1913, **52**, 14—15).—The dark colour obtained with diabetic urines on heating with alkaline bismuth solution (Almen-Nylander's process) is matched by means of a series of tubes containing increasing quantities of dextrose added to sugar-free urine. If much dextrose should be present in the sample, it must be suitably diluted, and the sugar-free urine likewise. L. DE K.

Estimation of Reducing Sugars by Lehmann's Method. LÉON GRIMBERT (*J. Pharm. chim.*, 1913, [vii], **7**, 105—109; *Bull. Soc. chim.*, 1913, [iv], **13**, 117—120. Compare A., 1898, ii, 264, 535; 1899, ii, 529).—Modifications of Lehmann's method proposed by Riegler and Maquenne (*loc. cit.*) are open to the objection that the solution has to be filtered before the titration, or that the titration has to be carried out in a relatively concentrated solution; further, the time of boiling the sugar solution with the reagent varies in each method. Garnier's modification of the method (A., 1899, ii, 701) lengthens and complicates the process. The author recommends that, after the sugar solution has been boiled for three minutes with a definite volume of Bertrand's reagent (A., 1907, ii, 136), the whole solution should be diluted to 200 c.c. with boiled water, filtered, and the excess of copper in an aliquot portion of the filtrate titrated with thiosulphate solution after the addition of sulphuric acid and potassium iodide. It is preferable to add an excess of thiosulphate solution, and to titrate this with $N/10$-

iodine solution. The copper sulphate solution used is standardised in the same way. W. P. S.

Quantitative Study of Some Aldehyde Reactions. B. G. FEINBERG (*Amer. Chem. J.*, 1913, **49**, 87—116).—This investigation was undertaken with the object of determining the best methods for estimating various aldehydes. The following methods have been studied: (1) the combination of aldehyde with alkali hydrogen sulphite; (2) the reaction with the normal sulphites; and (3) the precipitation of the aldehydes as hydrazones. These methods have been applied to formaldehyde, benzaldehyde, salicylaldehyde, *p*-hydroxybenzaldehyde, and vanillaldehyde, and in all cases attempts have been made to establish conditions for the accurate estimation of the compounds.

The compounds of the aldehydes with alkali hydrogen sulphite are resolved into their components by dilute acid or alkali hydroxide, and the readiness with which this decomposition takes place is increased by the presence of a hydroxyl group in proximity to the aldehyde group. Formaldehyde can be estimated accurately by means of alkali hydrogen sulphite, and vanillaldehyde and benzaldehyde can be approximately estimated, but the method does not give satisfactory results with salicylaldehyde, *p*-hydroxybenzaldehyde, or anisaldehyde.

It has been found that sodium sulphite does not combine with aldehydes with formation of sodium hydroxide, as is generally supposed, but that a reaction takes place on the addition of acid, indicating that sodium hydrogen sulphite is first produced and unites with the aldehyde. Formaldehyde and benzaldehyde can be estimated fairly accurately by means of sodium sulphite, and anisaldehyde can be estimated approximately, but the method is inapplicable to salicylaldehyde, *p*-hydroxybenzaldehyde, and vanillaldehyde.

Precipitation with *p*-bromophenylhydrazine gives good results with anisaldehyde, *p*-hydroxybenzaldehyde, and vanillaldehyde, but not with formaldehyde, benzaldehyde, or salicylaldehyde.

p-Nitrophenylhydrazine has been found generally applicable, and is very suitable for the estimation of vanillaldehyde and *p*-hydroxybenzaldehyde, whilst with benzaldehyde, salicylaldehyde, and anisaldehyde, it yields results from 2 to 4% too low.

A bibliography of the subject is appended. E. G.

Estimation of Formaldehyde. GAILLOT (*Ann. Chim. anal.*, 1913, **18**, 17—18).—A definite quantity of the formaldehyde solution under examination is neutralised, treated with an excess of neutralised ammonium sulphate solution, and the resulting acidity of the mixture is titrated (compare this vol., ii, 240); this acidity is equivalent to the amount of formaldehyde present. W. P. S.

Detection of Citric Acid in Wine. WILHELM FRESENIUS and LEO GRÜNHUT (*Zeitsch. anal. Chem.*, 1913, **52**, 31—35).—A criticism of some of the processes employed. The following conclusions are

arrived at: (1) The process given by Denigès (based on oxidation and treatment with a mercuric salt) cannot serve to prove the presence of added citric acid in wine. (2) The reaction of Möslinger, as modified by Kries (based on precipitation of potassium hydrogen tartrate by addition of alcohol and precipitating the filtrate, after evaporating off the alcohol and largely diluting with water, with acetic acid and lead acetate), is applicable, and is fairly delicate. (3) The reaction of Schindler (based on the different solubilities of the barium salts of citric and malic acids and subsequent use of lead acetate) is only serviceable when large quantities of citric acid are present. L. DE K.

Hardened (Hydrogenised) Oils and the Detection of Arachidic Acid. HANS KREIS and EMIL ROTH (*Zeitsch. Nahr. Genussm.*, 1913, **25**, 81—85).—Sesame, arachis, and cottonseed oils still yield a coloration with Bellier's resorcinol test after they have been "hardened" by treatment with hydrogen in the presence of a catalyst. Hydrogenised whale oil gives an orange colour with this test. The sesamol of sesame oil is not affected by the treatment, and the hydrogenised oil gives the reaction described by Kreis (A., 1904, ii, 75, 790). Arachis oil, either natural or hydrogenised, may be detected in admixtures with other oils by saponifying 20 grams of the oil under examination, separating the solid fatty acids, and dissolving them in 100 c.c. of alcohol; in the case of hydrogenised oils, 200 c.c. of alcohol are required. The boiling solution is then treated with 1·5 grams of lead acetate dissolved in 50 c.c. of alcohol; the precipitated lead soap is collected after about twelve hours, decomposed with hydrochloric acid, and the liberated fatty acids crystallised three times from alcohol, using successively quantities of 50 c.c., 25 c.c., and 12·5 c.c. of alcohol for these operations. Should the oil contain not less than 5% of arachis oil, the fatty acids obtained after the third crystallisation will have m. p. above 70°. This process may be shortened by acidifying the saponified oil with 50% acetic acid, and then adding the lead acetate solution without previously separating the fatty acids. W. P. S.

Estimation of Caoutchouc in Vulcanised Rubber Materials. PAUL GOLDBERG (*Chem. Zeit.*, 1913, **37**, 85—86).—For the indirect method of estimating caoutchouc, in which the mineral matter present in the material is estimated by ignition and the caoutchouc taken by difference, the following process for estimating the ash is recommended, as it prevents certain chemical changes taking place, during the ignition, between the constituents of the ash and the oxygen of the atmosphere. One gram of the sample, previously extracted with acetone, and dried at 50°, is placed in a weighed porcelain boat, which is inserted in a tube through which a current of nitrogen is passed. When all the air has been displaced from the tube, the boat is heated until the caoutchouc melts and distils, and at the end of the operation the mineral matter remaining in the boat is weighed. When the added mineral matter consists of

calcium oxide, magnesium oxide, calcium carbonate, litharge, red lead, lithopone, zinc sulphide, zinc oxide, barium sulphate, silicates, etc., this method of incineration yields trustworthy results, the error not exceeding 0·3%, but when magnesium carbonate is present, the carbon dioxide liberated must be absorbed and estimated. If the rubber material contains "sulphur auratum," the antimony trisulphide is estimated in the ash and calculated into pentasulphide; cinnabar, if present, is volatilised completely, and must be estimated separately by the method described by Frank and Birkner (A., 1910, ii, 244), and its quantity added to the amount of ash found. W. P. S.

The Prussian Blue Reaction. DANIEL VORLÄNDER (*Ber.*, 1913, **46**, 181—192).—The author finds that the reaction between ferric chloride and potassium ferrocyanide is a time-reaction, which is retarded by acid and salts; the extent of the retardation increases with the strength of the acid. In very dilute solutions, such as often occur in analytical practice, it is possible for no blue colour to be produced at all, and only an indefinite green colour after a few hours; after twenty-four hours a few coagulated flocks of Prussian blue may be found.

When a ferrous salt is used instead of ferric chloride the formation of ferrous ferrocyanide is an instantaneous reaction, which is followed by oxidation to Prussian blue by means of the dissolved oxygen. The presence of dilute hydrochloric or sulphuric acid accelerates the formation of a blue colour, as also does the use of excess of the ferrous salt. The test is so delicate that a millimol. of potassium ferrocyanide per litre can be detected.

In carrying out the test for cyanides (or nitrogen) it is best to filter the solution after boiling with ferrous sulphate and sodium hydroxide. The filtrate should then be acidified with dilute hydrochloric acid, and 3—10 drops of fresh ferrous chloride or sulphate added.

Ferrous salts react immediately with potassium ferricyanide, which points to the fact that the slow reaction between ferric salts and potassium ferrocyanide is not due to the formation of a colloidal reaction product, but depends on the condition of the ferric salt solutions.

Examination with the ultramicroscope of the solutions of the various iron salts used, leads the author to the conclusion that solutions of ferric salts may be considered as incomplete colloidal solutions in which the particles are scarcely visible in the ultramicroscope, although much greater than in disperse molecular solutions.

Further experiments with colloidal ferric hydroxide solutions indicate that the colourless solutions obtained by acidifying the colloidal solution prepared from alcoholic ferric chloride and sodium ethoxide are not identical with the colourless solutions obtained from ferric salts and nitric acid. The latter are practically optically clear in the ultramicroscope, whereas the former are seen to consist of colloidal solutions containing large submicrons. T. S. P.

Rapid Estimation of Tannin Matters and Acidity in Tanning Liquors. RUDOLF VANIČEK (*Zeitsch. angew. Chem.*, 1913, **26**, 68—70).—The process is briefly as follows: The acidity of 50 c.c. of the liquor is taken by means of $N/10$-sodium hydroxide, using phenolphthalein (or phenolphthalein test paper) as indicator, before and after treatment with 50 c.c. of gelatin solution (6 per 1000). The difference in acidity $(a-b)$ is due to the acid principle of the tannin matter.

If a gravimetric analysis of a particular "tannin" has been made, the titre of the soda solution may be found by dividing the number of grams found in 50 c.c. by $(a-b)$. Working with solutions of unknown strength, the result of the titration $(a-b)$ has only got to be multiplied by the titre in order to find the total content in tanning matter. L. DE K.

Comparative Examination of Methods for the Estimation of Dyes. H. SALVATERRA (*Monatsh.*, 1913, **34**, 255—281).—Knecht's reduction process with titanium chloride and the method elaborated by Pelet-Jolivet and Garuti (A., 1908, ii, 441) for the estimation of pure dyes, dyed silks, and dye vats (waste vat liquors), have been compared, the colouring matters examined being malachite-green, crystal-violet, magenta, naphthol-yellow-S, Martius-yellow, crystal-ponceau-6B, fast-ponceau-B, cotton-scarlet extra, fast-scarlet-PX, orange-G, and orange-GRX. Both methods give satisfactory results when pure materials are to be estimated, although Knecht's process gives values which are too high with malachite-green and too low with orange-G. The trouble experienced in preparing suitable type solutions is, however, a drawback to Pelet's method.

Only Knecht's method gives good results for the titration of dyed silk, and in the case of easily reduced dyes, it may be applied directly. For the examination of waste vat liquors, both methods are trustworthy, whereas colorimetric comparisons with standard solutions are quite impossible. Experiments have been conducted in order to ascertain whether dyes are taken up by silk in molecular proportions, but no such rule could be discovered. It can only be said that with an increase in the number of sulphonic groups, the affinity of silk for the dye diminishes. J. C. W.

Chemical Detection of Veronal Poisoning. W. MACADIE (*Pharm. J.*, 1913, **90**, 134).—The following methods were employed for the detection of veronal in a suspected case of poisoning by this substance. The stomach wash-out was acidified with hydrochloric acid, shaken out several times with ether, and the ethereal solutions were evaporated; the residue obtained was then extracted with alcohol, the solution evaporated to dryness, the residue dissolved in a small quantity of dilute sodium carbonate solution, filtered, and the filtrate extracted with ether after the addition of hydrochloric acid. On evaporating the ethereal solution, a residue was obtained which was dissolved in a small quantity of alcohol; a portion of this solution was treated with alcoholic sodium hydroxide

solution, heated to remove the alcohol, and the heating then continued until the mixture fused. The fused mass, when treated with sulphuric acid, yielded carbon dioxide and an odour resembling that of a mixture of acetic and butyric acids (compare A., 1911, ii, 670). Another portion of the alcoholic solution was evaporated to dryness, and the residue tested with Millon's reagent in the presence of nitric acid; a gelatinous precipitate, soluble in excess of nitric acid, but not in an excess of the reagent, was obtained. Veronal was also separated from the urine of the patient; for this purpose the urine was treated with calcium chloride to precipitate uric acid, and, after the precipitate had been removed by filtration, the filtrate was acidified and shaken out with ether, the residue of veronal obtained being identified by means of the tests mentioned.

W. P. S.

Rapid Estimation of Pyridine in the Presence of Ammonia in Gas Liquors. OTTO BAESSLER (*J. Gasbeleuchtung*, 1912, **55**, 905—906).—The total ammonia and pyridine are first titrated together with standard sulphuric acid; the mixed vapours are then distilled through a warm solution of sodium hypobromite, whereby the ammonia is oxidised to water and nitrogen; the pyridine is carried on into standard sulphuric acid, the excess of which is subsequently titrated. F. M. G. M.

Micro-chemical Tests for the Identification of Some of the Alkaloids. EARL B. PUTT (*J. Ind. Eng. Chem.*, 1912, **4**, 508—512).—An account of the preparation, with micro-photographs, of the characteristic crystals formed by alkaloids with certain reagents which affords a ready means for their identification. Alkaloids producing characteristic crystals with iodine are: (1) morphine, shining red plates; (2) codeine, clusters of yellow, blade-like needles; (3) dionine (ethyl-morphine), similar to codeine; (4) atropine, small red crystals, whilst heroine, *apo*morphine, and narcotine furnish amorphous precipitates.

Alkaloids producing characteristic crystals with palladous chloride are (1) morphine, light brown clusters of sheaf-like crystals; (2) codeine yields first a labile form, which rapidly changes to clusters of needles. (3) β-Eucaine, deep yellow characteristic crystals.

Alkaloids yielding characteristic crystals with platinic chloride are (1) cocaine; (2) β-eucaine, clusters of golden (flower) petal-like-crystals; (3) nicotine resembles those obtained with cocaine, but are only formed in neutral or faintly acid solution, whereas the cocaine precipitate is insoluble in acids; (4) antipyrine, yellow, branching, feathery crystals; (5) strychnine, peculiar chisel-shaped clusters which rapidly separate into individual needles; (6) heroine, golden-yellow clusters of needle-like crystals which when fully formed disintegrate. F. M. G.M.

Factors Affecting the Measurements of Absorption Bands. H. HARTRIDGE (*Proc. Roy. Soc.*, 1913, *B*, **86**, 128—140).—In estimating

the absolute value of the carbon monoxide saturation of hæmoglobin, the spectroscopic method is complicated by the fact that each observer must obtain a calibration curve for himself, because individual differences to the threshold values at different wave-lengths occur. These detract from the value also of accurate measurements of absorption bands. Other factors to be considered are the initial intensity of the light and contrast. Provided work is carried out under standard conditions, accurate carbon monoxide estimations are obtainable. W. D. H.

Behaviour of Copper Salts towards Ganassini's Reagent for Blood. DOMENICO GANASSINI (*Boll. chim. farm.*, 1912, **51**, 815—818).—Possible confusion between traces of copper salts and traces of blood (compare Pazienti, this vol., ii, 154) can be avoided by adding to the blue liquid a small quantity of potassium cyanide; if copper is present, the solution at once becomes yellow. Blood does not give this reaction. If copper is absent, the usual blood test is then performed by adding a drop of hydrogen peroxide to the same solution. If copper is present, a trace of potassium cyanide is added to another portion of solution, then the blue reagent, and finally a drop of peroxide; the presence of blood will be indicated by a change of colour from blue to yellow. R. V. S.

Schardinger's Reaction for Cow's Milk. W. RULLMANN (*Biochem. Zeitsch.*, 1913, **48**, 155—156. Compare A., 1911, ii, 667).—A reply to Römer (A., 1912, ii, 610). S. B. S.

Nephelometry in the Study of Proteases and Nucleases. I. PHILIP ADOLF KOBER (*J. Biol. Chem.*, 1913, **13**, 485—498).—A microchemical method for following the digestion of a soluble protein, edestin, based on the use of a nephelometer, is given. This instrument can be easily made from a Duboscq colorimeter. Its readings follow a curve which can be expressed by a mathematical equation. W. D. H.

The Nature of Peroxydase. WALTHER GRIMMER (*Zeitsch. Nahr. Genussm.*, 1913, **25**, 85—88).—The author controverts the statement made by Hesse and Kooper (A., 1912, ii, 1107), that the peroxydase reaction of milk is brought about by the catalytic action of iron salts, such as ferrous lactate. He argues that milk does not contain iron compounds of this type, and that the albumin solutions used in Hesse and Kooper's experiments contained upwards of thirty times more iron than is found in milk. Further, when these iron solutions are heated and then cooled, they regain their power of giving the peroxydase reaction, but such is not the case with milk when it is heated; protein solutions, when mixed with ferrous lactate solution, inhibit the activity of the latter, owing to the formation of insoluble iron-protein compounds. The presence of chloroform, or of mercuric chloride, interferes with and may inhibit the peroxydase reaction of milk. W. P. S.

General and Physical Chemistry.

Change in Refractive Index with Temperature. III. K. GEORGE FALK (*Zeitsch. physikal. Chem.*, 1913, **82**, 504—505).—In the two previous papers (A., 1909, ii, 197, 629) an account was given of measurements of the refractive indices of a number of organic liquids. The present paper deals with a theoretical consideration of these results on the basis of new determinations of the atomic refractions by Eisenlohr (A., 1910, ii, 365; 1911, ii, 81). The author compares the observed molecular refractions of the substances di*iso*amyl, *n*-heptyl alcohol, *n*-butyric acid, methyl hexyl ketone, *iso*butyl acetate, ethyl *n*-butyrate, and *iso*amyl acetate with those calculated from Eisenlohr's atomic refractions. It is shown that for the values at 20° there is a small but generally unimportant difference between the two values. The Lorentz-Lorenz formula is considered. It is written $(n^2-1)/(n^2+a)d$, and the value of a is calculated from the experimental values of the specific refraction of the substances mentioned above. It is shown that a varies between 3·6 and 6·9, but the value for the two isomeric substances, *iso*butyl acetate and ethyl *n*-butyrate, is practically the same for the α-, β-, and γ-hydrogen lines and for the *D*-sodium line, and is equal to 4·5 as a mean. J. F. S.

The Spectrochemistry of Compounds with a *gem*-Dialkyl Group. KARL VON AUWERS (*Ber.*, 1913, **46**, 494—514).—It is found that the presence of a *gem*-dialkyl group in a molecule generally causes a depression of the molecular refraction and dispersion, the effect being most marked when the group is substituted into a conjugation of double linkings; thus ethyl *d-cis*-camphorate, ethyl *l-trans*-camphorate, and dimethyl *iso*dehydrocamphorate (Bredt, A., 1909, i, 498; this vol., i, 338) show such a depression, whilst methyl *d*-dehydrocamphorate and ethyl *dl*-dehydrocamphorate, although containing conjugated double linkings, show no sign of exaltation; ethyl bornylenecarboxylate, in which the dimethyl group is outside the conjugation, exhibits an exaltation. The influence of the *gem*-dimethyl group is less marked when present in a substance of normal spectrochemical behaviour, but becomes more appreciable as the size of the alkyl radicles increases; for example, although ethyl dimethylacetoacetate is normal, a slight depression is observable with ethyl methylethylacetoacetate, and this becomes still more marked with ethyl diethylacetoacetate. Especial care was taken to ensure the purity of the last three substances, and hence probably arises some divergence in the figures quoted below from those already published by Brühl (A., 1894, ii, 433). With ethyl malonate, also, the introduction of two ethyl groups or of a methyl and ethyl group has a marked depressing effect, whilst two methyl radicles have no apparent action on the refraction.

The refraction of the following substances was measured for the

α-, β-, γ-, and D-lines, but only the value for the last is quoted below.

Methyl *d*-dehydrocamphorate, $\begin{array}{l}CH{:}C(CO_2Me){-\!\!-\!\!-}\\ |\\ CH_2{\cdot}CMe(CO_2Me)\end{array}\!\!>CMe_2$, b. p. 132—132·5°/9 mm., $D_4^{15\cdot4}$ 1·0915, $n_D^{15\cdot4}$ 1·47509; ethyl *dl*-dehydrocamphorate, b. p. 145—146°/10 mm., $D_4^{16\cdot3}$ 1·0400, $n_D^{16\cdot4}$ 1·46588; methyl *iso*dehydrocamphorate, $\begin{array}{l}CH{\cdot}CH(CO_2Me)\\ \|\\ CH{\cdot}CMe(CO_2Me)\end{array}\!\!>CMe_2$, b. p. 128—129°/8·5 mm., $D_4^{17\cdot4}$ 1·0852, $n_D^{17\cdot5}$ 1·46782; ethyl bornylenecarboxylate,

$$\begin{array}{l}CH_2{-}CH{-}C{\cdot}CO_2Et\\ |\qquad\; CMe_2 \;\;\|\\ CH_2{-}CMe{-}CH\end{array},$$

b. p. 122°/16 mm., $D_4^{20\cdot1}$ 0·9826, $n_D^{19\cdot8}$ 1·47604.

Ethyl methylacetoacetate, b. p. 75·5—76·5°/12 mm., $D_4^{18\cdot0}$ 1·0008, $n_D^{17\cdot8}$ 1·42066; ethyl ethylacetoacetate, b. p. 80°/10 mm., $D_4^{16\cdot6}$ 0·9831, $n_D^{16\cdot1}$ 1·42366; ethyl dimethylacetoacetate, b. p. 78°/14 mm., $D_4^{18\cdot1}$ 0·9777, $n_D^{18\cdot8}$ 1·41828; ethyl methylethylacetoacetate, b. p. 85°/12 mm., $D_4^{17\cdot8}$ 0·9734, $n_D^{17\cdot7}$ 1·42586; ethyl diethylacetoacetate, b. p. 92—92·5°/10 mm., $D_4^{16\cdot7}$ 0·9710, $n_D^{16\cdot1}$ 1·43266; methyl acetoacetate, b. p. 72—72·5°/12 mm., $D_4^{20\cdot6}$ 1·0755, $n_D^{20\cdot5}$ 1·41837; methyl methylacetoacetate, b. p. 80°/20 mm., $D_4^{23\cdot3}$ 1·0308, $n_D^{23\cdot8}$ 1·41629; methyl dimethylacetoacetate, b. p. 74°/15 mm., $D_4^{23\cdot4}$ 1·0002, $n_D^{24\cdot1}$ 1·41789.

Ethyl malonate, b. p. 198—198·6°, $D_4^{17\cdot6}$ 1·0566, $n_D^{17\cdot2}$ 1·41508; ethyl methylmalonate, b. p. 201·2—201·4°, $D_4^{18\cdot7}$ 1·0192, $n_D^{18\cdot7}$ 1·41369; ethyl dimethylmalonate, b. p. 88·7°/21 mm., $D_4^{25\cdot0}$ 0·9910, $n_D^{24\cdot1}$ 1·41049; ethyl methylethylmalonate, b. p. 102°/17 mm., $D_4^{18\cdot2}$ 0·9970, $n_D^{18\cdot2}$ 1·41896; ethyl diethylmalonate, b. p. 109—110°/21 mm., $D_4^{16\cdot6}$ 0·9880, $n_D^{16\cdot6}$ 1·42516; methyl dimethylmalonate, b. p. 71°/22 mm., $D_4^{23\cdot9}$ 1·0591, $n_D^{24\cdot2}$ 1·41312; methyl diethylmalonate, b. p. 97—98°/22 mm., $D_4^{24\cdot1}$ 1·0315, $n_D^{24\cdot5}$ 1·42528.

D. F. T.

Arc and Spark Spectrum of Lead. FRITZ KLEIN (*Zeitsch. wiss. Photochem.*, 1913, **12**, 16—30).—These spectra have been re-examined in order to obtain data expressed in terms of the International normal lines. The measurements were made with a Rowland concave grating, the spectrum of the second order being used for the great majority of the lines which covered the region between $\lambda = 7228$ and $\lambda = 2088$. The recorded data are compared with the results obtained by previous observers. The existence of three groups of ten lines in the arc spectrum, the corresponding members of which show the same difference in frequency on passing from one group to another, is clearly shown by the author's data, which thus confirm the relationship first indicated by Kayser and Runge.

H. M. D.

Selective Dispersion of Mercury Vapour at the $\lambda = 2536$ Absorption Line. ROBERT W. WOOD (*Physikal. Zeitsch.*, 1913, **14**, 191—195).—Quantitative measurements have been made of the dispersion produced by mercury vapour in the immediate neighbourhood of the mercury line $\lambda = 2536·5$. The observations were carried

out with mercury vapour, saturated at temperatures between 34° and 58°, the iron lines of wave-lengths $\lambda = 2535{\cdot}6$, $\lambda = 2536{\cdot}9$, and $\lambda = 2539{\cdot}0$ being submitted to examination. For these three lines, the displacement increases as the wave-length becomes more nearly equal to that of the absorption line, being greatest for the second and least for the third line. The displacement is not proportional to the pressure of the mercury vapour, but increases much less rapidly than this. In the case of the iron line $\lambda = 2535{\cdot}6$ the displacement was found to increase in the ratio 1 : 3 when the pressure was raised from 0·0031 to 0·0215 mm., that is, in the ratio 1 : 7. From this it would appear that the molecules, which are directly responsible for the dispersion in the neighbourhood of the absorption line, are not the normal molecules of mercury. Whether the active molecules are complex aggregates or ionised molecules cannot be determined. H. M. D.

Relationship between the Absorption Spectrum and the Constitution of Complex Cobaltammine Salts. ROBERT LUTHER and ANDREAS NIKOLOPULOS (*Zeitsch. physikal. Chem.*, 1913, **82**, 361—378).—In determining the absorption spectrum of twenty complex cobaltammine salts, the visible portion of the spectrum was measured by a spectro-photometer using a mercury vapour lamp as the source of light, and the ultraviolet portion was measured by Hartley's method using a quartz spectrograph and an iron spark as source of light. The various errors of the method are discussed, and an approximate estimate of their dimensions is made. It is shown that the light absorption is only dependent on the composition of the complex. The replacement of NH_3 by NO_3, H_2O, Cl, and Br in the complex causes a displacement of the absorption toward the red end of the spectrum. Replacement of NH_3 by NO_2 causes a displacement toward the violet end. In accord with the electron theory, the stability of analogous compounds is greater the further the absorption bands extend toward the violet, and the photochemical sensitiveness is greater the steeper the absorption curve. J. F. S.

Quantitative Investigation of the Absorption of Ultraviolet Rays by the Fatty Acids and their Esters in Aqueous and Alcoholic Solutions. JEAN BIELECKI and VICTOR HENRI (*Compt. rend.*, 1913, **156**, 550—552).—In continuation of this investigation (compare this vol., ii, 86) the authors have studied the absorption by the fatty acids and their esters in alcoholic solutions and by sodium formate and acetate in aqueous solutions, and from the results have calculated the molecular coefficients of absorption. The figures are tabulated, and show that the absorption of the ultraviolet rays is almost the same for the esters as for their acids, the absorption of a compound of the type $C_nH_{2n+1}{\cdot}CO_2R$ being determined by the acid group, the alcohol radicle having only a feeble influence. Alcoholic solutions have a stronger absorptive power than aqueous solutions, due probably to the displacement of the absorption bands, in alcoholic solution, towards the red end

of the spectrum. The acids, arranged in ascending absorptive power, are acetic, propionic, formic, butyric, and valeric, or, leaving out formic acid, the absorption increases with addition of CH_2 to the molecule. No change occurs in the form of the absorption curve, but a displacement of the bands towards the red is produced.

The sodium salts of the acids studied are less absorbent than the acids themselves, probably owing to the greater ionisation of the salts in aqueous solution. W. G.

Spectrographic Studies in the Anthraquinone Group. RICHARD MEYER (*Ber.*, 1913, **46**, 617. Compare this vol., ii, 168).—The author acknowledges that Formánek has dealt with the anthraquinone dyes in a work entitled "Investigation and Identification of Organic Dye-stuffs by means of the Spectroscope," and points out the difference between the aims of this investigation and of his own. H. W.

Absorption Spectra of Fluorescein, Eosin, Erythrosin, and Rose-Bengal in the Visible and Invisible Regions. GUSTAVE MASSOL and A. FAUCON (*Bull. Soc. chim.*, 1913, [iv] **13**, 217—221).—The authors have examined the absorption spectra of fluorescein, eosin, erythrosin, and rose-bengal (dichlorotetraiodofluorescein). In the visible portion the spectra obtained closely resemble one another, giving a band extending over the blue and green portion, the limits of which have been defined with regard to the yellow sodium, green thallium, blue strontium, and violet potassium lines. In the ultraviolet, fluorescein gives three bands between $\lambda = 260$ and $\lambda = 335$, depending on the thickness of the layer; eosin gives only one band between $\lambda = 325$ and $\lambda = 345$, only visible in thickness above 50 mm.; erythrosin and rose-benzal only show a progressive absorption without bands, the latter being much the more powerfully absorptive. All the substances were examined in aqueous solution (concentration, 1 in 10,000). H. W.

Optical Investigations of Diazo compounds. ARTHUR HANTZSCH and ISRAEL LIFSCHITZ (*Ber.*, 1913, **46**, 414—416. Compare A., 1912, ii, 1116).—Polemical; a reply to Cain (this vol., i, 169). The authors dissent from Cain's views, and reaffirm the correctness of their own interpretation of the phenomena. D. F. T.

The Theory of Fluorescence. HUGO KAUFFMANN (*Zeitsch. Elektrochem.*, 1913, **19**, 192—196).—Polemical. An answer to Stark (this vol., ii, 2), and a further criticism of Stark's theory of fluorescence (A., 1911, ii, 786). J. F. S.

The Theory of Fluorescence. JOHANNES STARK (*Zeitsch. Elektrochem.*, 1913, **19**, 196—197).—Polemical. An answer to Kauffmann (see preceding abstract). J. F. S.

The Theory of Fluorescence. HUGO KAUFFMANN (*Zeitsch. Elektrochem.*, 1913, **19**, 197).—Polemical. An answer to Stark (see preceding abstract). J. F. S.

[Rotation Dispersion.] JOH. PLOTNIKOV (*J. pr. Chem.*, 1913, [ii], **87**, 236—237).—A note on the author's light filter, the efficiency of which was called into question by Deussen (this vol., ii, 88).

F. B.

Energy Absorbed and Mass Formed in a Photochemical Reaction. MARCEL BOLL (*Compt. rend.*, 1913, **156**, 691—694).—A mathematical paper, in which the author deduces the following laws: (1) When an absorbent substance is the seat of a chemical reaction the emergent energy decreases according to the exponential function of the thickness of the layer and the concentration at each instant. (2) The mass formed, $m=(kst)/\chi \cdot cWa$, where s = surface, t = time, χ = coefficient of absorption, Wa = incident energy, c = concentration. (3) In the case of a bimolecular reaction, Grotthus's law of photochemical absorption does not hold good, there being no ratio between the mass formed and the energy absorbed. W. G.

Photochemical Behaviour of Colloidal Tungstic Acid. ALEXANDRA WASSILJEWA (*Zeitsch. wiss. Photochem.*, 1913, **12**, 1—15).—If dilute hydrochloric acid is added to a solution of sodium tungstate until the liquid becomes slightly acid, a colloidal solution of tungstic acid is obtained, which in presence of various organic substances, such as formaldehyde, sucrose, dextrose, dextrin, etc., undergoes reduction on exposure to light, with the formation of an intense blue solution. If the undialysed solution is kept for some time, it is found that the above reduction process does not occur when the solution is exposed to light; on raising the temperature, however, the blue reduction products are obtained, as in the case of the freshly prepared colloidal solution.

It is suggested that this is due to the existence of two forms of colloidal tungstic acid, one of which is photochemically sensitive and the other not. The former changes spontaneously into the latter, but the reverse transformation is brought about by a rise of temperature.

The absorption spectra of the two modifications are found to differ appreciably, the region of ultraviolet absorption extending further towards the visible spectrum in the case of the photochemically sensitive modification.

Kinetic experiments have also been made in order to ascertain the nature of the change in which the photochemically active form is converted into the inactive modification. These show that the change proceeds in accordance with the equation for a unimolecular reaction. The rate of transformation was ascertained by measurements of the photochemical activity of the colloidal solution after measured intervals of time. This was effected by exposing the colloidal solution, containing dextrose as reducing agent, to the light from an arc lamp for five minutes, and estimating the amount of the reduction which occurred during this period by titration with a permanganate solution. From the photochemical sensitiveness obtained in this way it was possible to ascertain the corresponding concentration of the active form by reference to a curve con-

necting the two quantities, this curve being plotted from data obtained in experiments which were carried out to determine the connexion between the two factors.

By similar measurements it has been found that a colloidal solution, which had become quite inactive at 7°, regained 31% of its original photochemical activity when heated to 43°, and 81% when heated to 96°. That this is not due simply to an acceleration of the photochemical change with rise of temperature is shown by measurements of the influence of temperature on the reactivity of the freshly prepared colloidal solution. In common with all photochemical reactions, the temperature-coefficient was found to be very small, the velocity increasing by only 1% when the temperature was raised from 8° to 96°.

As regards the chemical relationship between the active and inactive colloids, very little information has been obtained. The spectroscopic data would seem to show that both are colloidal and of similar composition, and it is suggested that the change from the active to the inactive form may consist in the addition of water or in the combination of the tungstic acid with sodium salts according to $3WO_3 + Na_2WO_4 = Na_2O,4WO_3$, which substance was obtained by Sabanéev (A., 1897, ii, 456) by subjecting the solution to dialysis.

H. M. D.

The Activation of Oxygen by Radiation. FRITZ WEIGERT (*Ber.*, 1913, **46**, 815—820).—In order to investigate the photochemical reaction of ozone it was necessary to use a part of the spectrum where ozonisation of oxygen does not occur. This was attained by using a quartz-mercury lamp, and allowing the rays to pass through a layer of air before entering the reaction vessel. The apparatus was similar to that previously used by the author (A., 1912, ii, 715) in the investigation of the decomposition of ozone by ultraviolet light, and the particular reaction used was that between ozone and hydrogen. No trace of hydrogen peroxide was formed (compare Coehn, A., 1910, ii, 608), and there was only an extremely slow reaction in the dark. In ultraviolet light, however, about one-third of the ozone originally present disappeared in two minutes, the disappearance being due to the two reactions: $2O_3 = 3O_2$ and $H_2 + O_3 = H_2O + O_2$. The total amount of ozone decomposed is proportional to the ozone concentration, whilst the amount of hydrogen oxidised approached asymptotically an upper limit, which was attained at an ozone concentration which was the lower the lower the concentration of the hydrogen. This limit is approximately proportional to the concentration of the hydrogen (compare Clausmann, A., 1910, ii, 608).

The above results indicate that in the activation of oxygen by ultraviolet rays two photochemical reactions occur. In the formation of water from hydrogen and oxygen the oxygen is first ozonised by the short rays, and then reacts with hydrogen under the influence of the long rays. In the photochemical dissociation of water vapour a further photochemical reaction plays a part, namely,

$$H_2O = H_2 + O,$$

which is affected by the short rays. The complicated relations observed by Coehn (*loc. cit.*) are thus explained.

It is possible that the deviation of the nitric oxide equilibrium from the position calculated thermochemically is due to the photochemical action between nitrogen and ozone, the latter being formed from oxygen by the ultraviolet rays, as, for example, in the experiments of Fischer and Hene (this vol., ii, 317). T. S. P.

Absorption of the Ultraviolet Rays by Acetylene. VICTOR HENRI and MARC LANDAU (*Compt. rend.*, 1913, **156**, 697—699).—A study of the ultraviolet absorption spectra of acetylene, first, in a gaseous state at the ordinary temperature, under a pressure of one-tenth to one atmosphere, using a thickness of 40 cm. of gas, and secondly in alcoholic solution. In the first case there are three distinct groups of bands. The first extends from λ 3157 to 2880; the second beginning to appear at λ 2960, and being most marked between λ 2800 and 2500; the third extends from λ 2327·5 to 2236·4, and is in turn capable of resolution into a series of very fine bands. Between λ 2500 and 2327·5 acetylene in the gaseous state under the given conditions shows no sensible absorption. In alcoholic solution acetylene presents only one very broad band, commencing at λ 2850 and attaining a maximum at λ 2631. The ultraviolet absorption by acetylene commences approximately at the region where the solar ultraviolet spectrum ends. W. G.

The Inversion of Sucrose by Ultraviolet Rays. DANIEL BERTHELOT and HENRY GAUDECHON (*Compt. rend.*, 1913, **156**, 468—470).—A résumé of work already published (compare A., 1910, ii, 813; 1912, i, 750, ii, 1120; this vol., i, 16, ii, 4), and a reply to Bierry, Henri, and Ranc (this vol., ii, 4). W. G.

A Lævulose Actinometer for Ultraviolet Rays. Influence of Concentration on the Rate of Photochemical Action. DANIEL BERTHELOT and HENRY GAUDECHON (*Compt. rend.*, 1913, **156**, 707—710).—A 10 per cent. aqueous solution of lævulose can be used to give a direct measure of the intensity of the radiation, the volume of the gas evolved being directly proportional to the time for any given radiation, and inversely proportional to the (distance)$^{3/2}$. Further, for dilute solutions (4·5 to 18 grams per litre) the velocity of the reaction is proportional to the concentration, whilst for strong solutions (720 to 1080 grams per litre) it is constant and independent of the concentration. These facts are best explained on the hypothesis that the velocity of reaction is proportional to the quantity of light absorbed per unit of time. W. G.

The Most Recent Value for the Atomic Weight of Radium. STEFAN MEYER (*Physikal. Zeitsch.*, 1913, **14**, 124—125).—Hönigschmid has verified his atomic-weight value, 225·97, found from the determinations for radium chloride by determinations for radium bromide, and, in common with Haschek, shown by spectro-

scopic tests that not more than 0·004% of barium can be present. Theoretical grounds can be adduced for the value 226. From magnetic deviation experiments and the value of the faraday, it can be deduced that the atomic mass of the α-particle is 3·8 or 5% smaller than that of helium. Subtracting five times 3·8 from 226 gives 207·0, agreeing with the atomic weight of lead. This suggests an error in the determination of the atomic weight of helium, but the possibility is referred to that helium and the α-particle may represent "non-separable" elements (Soddy). The value 3·8, however, makes the atomic weight of uranium 237·4 instead of 238·5, and until the complex (UI + UII + UX + UY) has been further studied, arguments from the atomic weight of uranium are indefinite. There is no ground for doubting the value 226·0 for the atomic weight of radium or the purity of the International Standard (Marckwald, A., 1912, ii, 323). F. S.

Revision of the Atomic Weight of Radium by Analysis of Radium Bromide. OTTO HÖNIGSCHMID (*Monatsh.*, 1913, **34**, 283—309).—The material which had given the value, Ra = 225·95, by analysis of the chloride (A., 1912, ii, 523) was converted into bromide and fractionally crystallised thirty times. No change of atomic weight occurred during the process. Very full details are given of the analytical operations. Six analyses, with nearly a gram of radium bromide, in which the ratio $RaBr_2/AgBr$ was determined gave the mean value Ra = 225·96, with a mean variation in the separate experiments of 0·01, and a mean error of 1 in 40,000 of the weight of the radium bromide. Two analyses in which the ratio $RaBr_2/Ag$ was found, gave in both cases Ra = 225·97. The purest preparations of bromide did not show the barium line 4554·2, and were absolutely free from barium so far as spectroscopic test revealed. It is calculated that not more than 0·004% of barium could have been present.

The results of Whytlaw-Gray and Ramsay (A., 1912, ii, 413) are criticised in detail, and corrected for a constant error in the reduction of the weights to a vacuum. Their mean value recalculated should be 226·26, with a mean error of $\pm$0·21.

Two determinations by their method, converting the bromide into the chloride by heating in hydrogen chloride, the second with nearly a gram of radium bromide, gave the value Ra = 225·94.

It is estimated that the heat generated by the radium compounds may raise the atomic weight by 0·01. Seventeen analyses of radium chloride and bromide by two independent methods, in which the extreme values are included between 225·99 and 225·93, give the final value 225·97 (Ag = 107·88; Cl = 35·457; Br = 79·916). The mean departure from the mean is $\pm$0·012. F. S.

The Purity of the International Radium Standard. EDUARD HASCHEK and OTTO HÖNIGSCHMID (*Monatsh.*, 1913, **34**, 351—357).—By means of a large Rowland grating, radius of curvature 15 feet, with 72,000 lines at 20,000 to the inch, the spectrum in the neighbourhood of 4500 Å. units was examined of the purest radium bromide used in the atomic-weight determinations (preceding

abstract), and of the mother liquors, in which all the impurities in the material, which was that employed in the atomic-weight determinations on the chloride (A., 1912, ii, 523), had been accumulated after twenty-five crystallisations of the bromide. A rod of electrolytic copper which was completely free from barium was used for the electrode. The rod was 7 mm. thick and provided with grooves, and one drop of the purest bromide solution containing 0·15 mg. of radium (metal) was tested with a powerful spark discharge. No trace of the barium line, 4554·24, was seen in the photograph. On a new electrode, a drop of a barium solution of strength 0·1% of the radium solution previously tested, showed this line faintly but clearly.

The mother liquors containing 75 mg. of radium bromide were tested as in the first case, a drop containing 0·25 mg. of radium (metal) being employed. The barium line was plainly visible. Addition of 0·1% barium increased the intensity of the line four times. If the original barium content of the mother liquors is taken as 0·03%, it follows that the original chloride, out of which the Austrian standards have been prepared, does not contain more than 0·004%, and the radium bromide used in the final atomic-weight estimations, not more than 0·002% of barium. This can make no appreciable difference in the values found. A similar degree of purity can be assumed for the International radium standard as for the Austrian standards, and for the barium to cause any error in the radioactive determinations, methods a hundred times more sensitive than the present must be employed. F. S.

Heating Effect of Radium and its Emanation. ERNEST RUTHERFORD and H. ROBINSON (*Phil. Mag.*, 1913, [vi], **25**, 312—330). —The heating effect of any α-ray would not be a measure of the energy of the expelled α-particle if the α-particle lost energy before escaping from the atom. Experiments on the distribution of the heating effect among the emanation and its first three products were made to see if the observed emission of heat agreed with that calculated from the energy of the radiations expelled, and also to determine the heating effect of the β- and γ-rays. The relative calculated heating effects of the emanation, radium-*A* and -*C*, 28·8, 30·9, and 40·3%, agree with the observed values, 29, 31, and 40%, but as the β-rays of radium-*B* are included in the results for radium-*C*, it follows that the percentage for this number should have been about 42·6 instead of 40·3. The difference is small, but it may prove to be significant. The heating effect of one curie of emanation and its products, in terms of the Vienna standard, is 103·5 gram-calories per hour, when more than 90% of the energy of the β-rays is included. Under these conditions 99·2 calories are estimated to be due to α-rays, 4·2 to β-rays, and 0·1 to γ-rays. The total heating effect of 1 gram of radium is estimated to be 134·7 calories per hour, made up as follows: 25·1 due to α-rays of radium-*A*, 28·6 to the α-rays of the emanation, 30·5 to the α-rays of radium-*A*, 39·4 to the α-rays, 4·7 to the β-rays, and 6·4 to the γ-rays of radium-*B* and -*C*. F. S.

Decomposition of Water by α-Rays. WILLIAM DUANE and OTTO SCHEUER (*Compt. rend.*, 1913, **156**, 466—467*).—A study of the decomposition of water in the solid, liquid, and gaseous state by α-rays, care being taken to avoid excess of water, to have it in as thin a layer as possible, and to remove the gaseous products from the radiation as soon as formed. With ice at $-183°$, hydrogen and oxygen are obtained in the proportion of 2 : 1 by volume. With water, the hydrogen is at first in excess, due to the formation of hydrogen peroxide, this in its turn being decomposed, and giving oxygen in excess. With water vapour, the hydrogen is largely in excess, and may amount to 50% of the total volume of gas liberated.

A radiation, capable of producing an ionisation current of one ampere in air, decomposes water, giving 0·1594 c.c. hydrogen and 0·0797 c.c. oxygen per second, these amounts being of the same order as those obtained by the electrolysis of water at 15°. W. G.

The β-Rays of Radium-*B*, -*C*, -*D*, -*E*. JEAN DANYSZ (*Le Radium*, 1913, **10**, 4—6).—The experiments before carried out with thin-walled glass tubes of radium emanation (A., 1912, ii, 219, 220) have been repeated with thin wires of silver and platinum made active in the emanation. There was no difference in the results, but the photographs with the glass tubes are much superior in sharpness. Tables are given of the character, value of $H\rho$, velocity, and energy of twenty-seven groups of β-rays from radium-*B* and -*C*, and of five groups from radium-*D* and -*E*. These results are corrected for slight retardation of the β-rays in passage through the walls of the tube. Some of the original photographs are reproduced. F. S.

The Penetrating Power of the γ-Rays of Radium-*C*. ALEXANDER S. RUSSELL (*Proc. Roy. Soc.*, 1913, *A*, **88**, 75—82).—Experiments were carried out with 300 millicuries of radium emanation in the attempt to detect the presence of a radiation more penetrating than the γ-rays of radium-*C* after passage through great thicknesses of mercury. With from 1 to 22·5 cm. of mercury the γ-rays are absorbed strictly according to an exponential law, and over this range are reduced in intensity from $3·6 \times 10^5$ to 1. The value of μ/d is $4·38 \times 10^{-2}(\text{cm.})^{-1}$. This value is practically the same as that previously found for lead over the range from 2 to 22 cm., namely, $4·37 \times 10^{-2}$ (A., 1909, ii, 851). It is calculated that after passage through 28·5 cm. of mercury the γ-rays unabsorbed from 10 grams of radium would produce an effect less than 5 per cent. of the natural leak. If any ionising radiation exists more penetrating than the γ-rays, its intensity must be less than 2×10^{-6} of the initial γ-rays. F. S.

The Chemical Action of Penetrating Radium Rays. V. Influence of Penetrating Rays on Sterilised Aqueous Sucrose Solutions. ANTON KAILAN (*Monatsh.*, 1913, **34**, 359—364. Compare this vol., ii, 8).—Normal sucrose solutions were sterilised by long heating at 100°, and subjected to the action of the penetrating

* and *Le Radium*, 1913, **10**, 33—46.

rays of radium, in closed flasks in the absence of light, for several months, blank experiments without the radium being also performed. Formation of acid and a decrease in the rotation still took place in the solutions after sterilisation, although it is much smaller than in unsterilised solutions, rather less effect being produced after 2800 hours' exposure to the rays than formerly after 500 to 700 hours. The acid so produced must be relatively feebly dissociated, but its quantity is completely sufficient to account for the loss of rotatory power of the sucrose, through the inversion brought about by the hydrogen ion. The solutions, after exposure to the rays, reduce Fehling's solution, and the amount of invert sugar present, as so determined, agrees approximately with that calculated from the decrease of rotatory power. F. S.

Theory of the Concentration Variations in Radioactive Solutions. EGON VON SCHWEIDLER (*Physikal. Zeitsch.*, 1913, **14**, 198—200).—The mathematical theory of the von Schweidler variation in the emission of rays from a radioactive solution is considered in which the instantaneous concentration also undergoes a probability variation. Experimental complications, for example, when only a small part of the total radiation is for various causes observed by the observer, do not affect the general character of the results to be expected, as regards the relative magnitude of the variations and the law of distribution of the rays in time.

F. S.

The Solubility of Radium Emanation in Water as Regards its Dependence on the Temperature. MARTIN KOFLER (*Monatsh.*, 1913, **34**, 389—400. Compare A., 1908, ii, 80).—The following results have been obtained, showing the variation of the solubility of radium emanation in water with temperature:

Temperature	0·5°	17·5°	35°	41°	51°	60°	74°	79°	82°	91°
Solubility	0·526	0·283	0·185	0·161	0·138	0·127	0·112	0·111	0·111	0·108

Both the solubility and the change of solubility with temperature decrease with increase of temperature. It is shown that the percentage change of solubility between 0° and 18° for a large number of gases increases with the molecular weight of the gas. It is 7% for helium, 33% for argon, and 49% for the radium emanation. Above 70° the solubility changes so little that it may be considered practically constant, but no evidence of a minimum solubility, as in the case of hydrogen and helium, was obtained. The solubility of gases generally is discussed. F. S.

A Relation between Ionisation by Cathode Rays and Certain Chemical Effects. E. JACOT (*Phil. Mag.*, 1913, [vi], **25**, 215—234).—The investigation is concerned with the proportion of the chemical action of the cathode rays due (1) to direct action, as supposed by Schmidt (A., 1902, ii, 237), of the negative charge neutralising the positively charged ion and causing chemical dissociation, (2) to thermal effects, (3) to the secondary action of the

gases in the tube. In the case of yellow phosphorus, the rapid transformation into the red variety is attended by rapid exhaustion of the nitrogen in the tube. The mass of phosphorus so transformed exceeds the amount that could be formed as a direct thermal effect, assuming the energy of the cathode rays to be quantitatively converted into heat, and when the phosphorus is screened from direct impact of the rays the transformation attended by absorption of gas still goes on. The absorption is proportional to the equilibrium ionisation of the nitrogen. The ionisation is inversely proportional to the kinetic energy of the cathode rays for a range of velocities from 2·92 to 4·76 ($\times 10^9$ cm./sec.), and varies linearly with the pressure from 0·083 to 0·025 mm. But the total number of active atoms or molecules in the gas is of a much higher order than the number of ions. Most probably the absorption is not due to the ions, but to an atomising effect of the rays, the active agent being monatomic nitrogen, and the number of such molecules being proportional to the ionisation of the gas. F. S.

Positive Ionisation Produced by Platinum and by Certain Salts when Heated. FRANK HORTON (*Proc. Roy. Soc.*, 1913, *A*, **88**, 117—146. Compare A., 1910, ii, 176).—The thermionic currents, resulting from the emission of positive ions by heated platinum, aluminium phosphate, sodium phosphate, and sodium pyrophosphate, have been investigated at 1080° and 1190°.

In the case of platinum and pure aluminium phosphate, the initial thermionic emission decreases very rapidly with time, and after a few hours becomes extremely small. With sodium phosphate the emission increases at first, this stage being followed by one in which the effect slowly decreases, but even after many hours' heating a very considerable thermionic current is obtained with this substance.

The view is put forward that the positive ionisation exhibited by platinum (and by metals generally) is largely due to the emission of absorbed gases, but that in the case of sodium phosphate a considerable part of the effect is due to the emission of positively charged sodium atoms. This view is discussed in reference to the observations of other workers on the ionic emissive power of heated substances. H. M. D.

Ionisation Produced by Heated Salts. CHARLES SHEARD (*Phil. Mag.*, 1913, [vi], **25**, 370—389).—An examination has been made of the ions which are emitted by cadmium iodide when this substance is heated out of contact with metal. The observations show that both positive and negative ions are emitted by the salts under these circumstances. The initial emission consists almost exclusively of negative ions, but when the temperature is maintained for some time at 350° to 500° the positive ionisation increases, reaches a maximum, and then gradually diminishes; the negative ionisation, on the other hand, falls away continuously. In addition to the emission of ions from the heated salt, it is found that the observed ionisation must be partly due to ionisation of

the vapour. This may arise from the action of the vapour on the electrodes, or it may be a volume ionisation, or possibly is a combination of the two effects. The distilled salt is less active than the undistilled, and successive distillations are found to exhibit alternations in their power of emitting positive and negative ions. These distillations, which give rise to a comparatively large negative thermionic current, exhibit a small positive emission and vice versa. The fact that continued distillation leads to a diminution in the percentage of iodine in the substance, and that iodine itself exhibits ionisation effects of a similar kind seems to show that the negative ionisation observed with cadmium iodide is largely due to the negative constituent. H. M. D.

Separation of Corpuscles in Chemical Reactions. SEBASTIAN M. TANATAR and E. BURKSER (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1—6).—Immersion of a charged conductor connected with an electroscope into the gas evolved during the catalytic decomposition of hydrogen peroxide by platinum-black shows the gas to be strongly ionised. A thin aluminium plate placed under the base of the glass vessel retards the loss of charge. Similar experiments were also made on the oxidation of sodium sulphite or arsenic trioxide by hydrogen peroxide solution.

The results do not allow of any definite statement concerning the cause of the ionisation observed. T. H. P.

A New Method for Concentrating Polonium. FRITZ PANETH (*Monatsh.*, 1913, **34**, 401—402).—Pure polonium, formed from radio-lead, may be obtained as well by the electrolysis of lead nitrate as lead acetate solution, when the voltage and acid concentration are such that lead is no longer deposited on the cathode. Polonium diffuses either not at all or only in extremely minute amount through animal bladders or parchment paper, and may be separated from lead and radio-lead by this method. By dialysing a solution of radio-lead through thin parchment paper it may be obtained practically free from polonium, which remains behind in the cell. F. S.

Solubility of the Active Deposit of Thorium in Various Solvents. CHARLES FREDERICK HOGLEY (*Phil. Mag.*, 1913, [vi] **25**, 330—332).—Water, solutions of salts, hydroxides, and acids always dissolve thorium-*B* in relatively larger amount than thorium-*C*, especially in the case of short treatments. Boiling water for fifteen minutes dissolves about 35%, and for an hour 70%; potassium iodide solution dissolves the deposit about twice as fast as water; dilute acids dissolve it much more rapidly. Organic solvents dissolve it at the same rate as water, but thorium-*C* is dissolved more easily than thorium-*B*, the latter being insoluble in carbon disulphide and methylene iodide, which dissolved some 20% of the thorium-*C* in ten minutes. Benzene, bromoform, etc., behaved very similarly, but the thorium-*B* was slightly soluble. F. S.

The Chemical Properties and Relative Activities of the Radio-products of Thorium. HERBERT N. MCCOY and CHARLES H. VIOL (*Phil. Mag.*, 1913, [vi], **25**, 333—359).—The results of experiments on the chemical nature of the various thorium products agree with the known behaviour of these substances. Mesothorium-II is separated from thorium by hydrogen peroxide at 60° or 70°, and is left in the solution. It is carried down by a precipitate of barium sulphate in slightly acid solution. In absence of thorium, radiothorium is partly precipitated with barium sulphate in acid solution, up to 50%, and to about 5% by mercuric or lead sulphide. Very numerous other reactions are given confirming previous knowledge.

A comparison of the α-activities of thorium-*B*, -*C*, and -*D* with that of thorium-*X*, emanation and -*A*, gave the ratio of the first to the second as 0·427. The products of radiothorium are 5·23 times as active as radiothorium itself. A redetermination of the range of the α-particles of thorium-*X* gave the value 4·1 cm. (of air at 0° and 76 cm.), instead of 5·7 cm. as previously found. The new value agrees with what is to be expected from the period of the substance. The values found for the activities of the various groups of products are in excellent agreement with the theoretical law that the total ionisation produced by an α-particle is proportional to the two-thirds power of its range. The following is the distribution of the α-activity among the separate products: Th, 11·4%; Ra–Th, 14·4%; Th-*X*, 15·5%; Th Em., 17·6%; Th-*A*, 18·6%; Th-*C*, 22·5%, as calculated from this relation, and in agreement with the determined values. F. S.

Tables of Radioactive Constants. LÉON KOLOWRAT (*Le Radium*, 1913, **10**, 1—4).—These tables are similar to those published in former years, and give the present knowledge with regard to the radio-elements, their periods, and radiations, together with particulars of the physical constants of the latter, and some other data relative to radioactivity. F. S.

Periodic System and Radio-elements. ALEXANDER S. RUSSELL (*Chem. News*, 1913, **107**, 49—52).—The known rule as regards the change of family in the Periodic Table of an element undergoing an α-ray change is modified and supplemented by a similar rule with regard to the β-ray changes. (1) The α-ray change results in a product belonging to a family the number of which is either two units greater or two units less than that of the parent. (2) The β-ray change or rayless change results in a product the number of which is either one unit greater or one unit less than that of the parent. Tables are given showing how well these rules are obeyed in the three series. Branch products are not considered. Uranium-*X* is put intermediate between uranium-*I* and -*II*, and a new member, uranium-X_2, in group V*A* of the table is predicted. The recent results for radioactinium (Russell and Chadwick, *Nature*, Dec. 26th, 1912) are discussed. Radioactinium-*II*, a new member giving α- and β-rays, is placed in group V*A*, and its product, actinium-*X*, in group II*A*. The rules were obtained independently

of, and are supported by, Fleck's results on the chemical nature of the *B*-members, the *C*-members, radium-*E*, and mesothorium-*II* (see T., 1913, **103**, 381). F. S.

Radio-elements and the Periodic Law. FREDERICK SODDY (*Chem. News*, 1913, **107**, 97—99*).—The known disintegration series, many of the members of which have recently been shown by Fleck to be non-separable from other elements (T., 1913, **103**, 381), agree with the author's α-ray change rule and the corollary with regard to the β-ray change (Russell, preceding abstract). The expulsion of the α-ray lowers the number of the group in the Periodic Table to which the radio-element belongs by two, and the expulsion of the β-ray increases the number of the group by one. This holds throughout the disintegrations, including the branch series which commence at the *C*-members. The emanations in the zero group, which expel α-rays, furnish short-lived *A*-members, which it is predicted are in the VI*B* group in the place already occupied by polonium. Fleck's results (*loc. cit.*) are in accord with the rules, and for the members the chemical nature of which cannot be directly determined, owing to too short period of existence, it is predicted that the *A*-members and the *C′*-members are in group VI*B*, and will be non-separable from polonium, whilst thorium-*D*, actinium-*D*, and the corresponding member in the radium series, radium-C_2, are in the III*B* group, and should be non-separable from thallium. Whenever a radio-element falls in a place in a Periodic table occupied by another, it is chemically identical with, and non-separable from, that element, independently of the atomic weight of the radio-element and of the series in which it originates; thus, occupying the place in the IV*A* group already occupied by thorium, are ionium, radiothorium, radioactinium, and uranium-*X*, a group the members of which vary in atomic weight by about 6 units. The unknown product of uranium-*X* (group IV*A*) by a β-ray change is called "eka-tantalum," and occupies a vacant place in the table in the group V*A*, the heaviest member of the family known being tantalum. It should prove to be separable from tantalum. Actinium should also be separable from lanthanum. All the members expelling α-rays occupy even-numbered groups, except the *C*-members in group V*B*, non-separable from bismuth. These disintegrate dually, in one mode a β-ray change preceding, and in the other mode following an α-ray change. It is suggested that eka-tantalum may disintegrate similarly, in one mode a rayless change producing uranium-*II* (group VI*A*), and in the other an α-ray change producing actinium (group III*A*). Evidence is given of an excessively minute growth of actinium over a term of years from the old preparations of uranium-*X* separated in 1909 from 50 kilograms of uranyl nitrate.

The six end-products all occupy the place in group IV*B* occupied by lead, and the atomic weight of lead, 207·1, is intermediate between the calculated atomic weights 206·0 and 208·5 of the main end-products of the uranium–radium and the thorium disintegra-

* and *Jahrb. Radioaktiv. Elektronik.*, 1913, **10**, 188—197.

tion series. These end-products should be non-separable from lead, and lead may be a mixture of these end-products.

In the case of thorium and ionium the two elements possess, so far as can be seen, identical spectra. A chart is given showing graphically the passage of the radio-elements from place to place through the Periodic Table.

The prediction with regard to the non-separability of thorium-*D* and thallium has since been confirmed by Fleck, who finds that thorium-*D* can be quantitatively separated from the *B*- and *C*-members by precipitating in the solution potassium by means of platinum chloride. F. S.

The Position of the Radio-elements in the Periodic System. KASIMIR FAJANS (*Physikal. Zeitsch.*, 1913, **14**, 136—142*).—Soddy's α-ray change rule, that the position of the radio-element changes into the next group but one from right to left in the horizontal row of the periodic system, is shown to be general. In the same way the β-ray change in general causes a change of one from left to right in the system. By the aid of these rules all the radio-elements can be placed without uncertainty in the Periodic Table. In all properties the disposition of the elements so obtained corresponds with what is to be expected for the members of the last two horizontal rows of the periodic table, which shows that these two rows are the expression of the law of change of the elements.

The only difficulty in the application of the α-ray rule is in the change of the alkaline-earth elements, as radium, into the emanations, which occurs with expulsion of both α- and β-rays. From the rules, mesothorium-*II* is placed in the third group, and radium-*E* in the fifth. The short-lived C'-members come into the sixth group. The change from radium-*A* to lead is written VI, IV, V, VI, IV, V, VI, IV, which is analogous to the change of uranium-*I* into ionium, VI, IV, V(?), VI, IV. The unknown fifth group member is regarded as a short-lived element intermediate between uranium-*X* and uranium-*II*, which is supported by the fact that uranium-*X* gives two types of β-rays, one very hard, such as would be given by a short-lived element. The members Ra-C_2, Th-*D*, and Ac-*D* are placed in the third group with thallium.

The remarkable fact shown by the table so constructed is that places which elsewhere in the Periodic Table contain only one element here contain several, in some cases six. All the elements of one group, with atomic weights differing from one another by two units, are so completely similar that it has not been possible to separate them by chemical or crystallisation methods, and a mixture of such elements, separated from a mineral, behaves chemically as one element. The atomic weight found for such a complex element would be nearest to that member with the longest period of life, and therefore present in the greatest quantity. It is suggested that thallium is formed in an α-ray change from bismuth, itself regarded as the product of "thorium-D_2" in a β-ray change.

The discrepancy between the atomic weight of lead, 207·1, and that of the end-product of the uranium series, 206·5, would be

* and *Le Radium*, 1913, **10**, 61—65.

explained if common lead were a mixture of the latter and "thorium-D_2," which is the product of thorium-C', and must be very similar to lead.

The question of the origin of actinium is discussed, and two possible alternatives are considered. The results throw much new light on many questions arising out of the Periodic Law. F. S.

Radioactive Changes and the Periodic System of the Elements. KASIMIR FAJANS (*Ber.*, 1913, **46**, 422).—The paper contains a fuller account of the author's views (preceding abstract). It is probable that what holds good among the radio-elements applies also in other parts of the Periodic Table, and that elements there may also be mixtures of unseparable groups of elements. The position of the rare-earth elements in the Periodic Table is discussed at length. It is supposed that these elements may be in process of continuous change with loss of hydrogen, nebulium, or protofluorine atoms rather than of helium. Tantalum appears as the parent of the rare-earth group and columbium of yttrium. The anomalies in the Periodic Table, such as tellurium and iodine, are also referred to. F. S.

Some Relations between the Radio-elements giving α-Rays. RICHARD SWINNE (*Physikal. Zeitsch.*, 1913, **14**, 142—145).—The experimental values for the velocity of the α-particles found by Geiger and Nuttall are compared with the values calculated from the periods of the elements producing them according to the three relations proposed by Geiger and Nuttall, Swinne and Wilson, and it is shown that all three formulæ show nearly equally good agreement with the observed values. From the author's formula it can be deduced that the difference between the initial velocity of the α-ray member of one series and that of the analogous member in another series is approximately constant for the two series. Expressing this difference as Δv_a for the radium and thorium, and $\Delta v'_a$ for the radium and actinium series respectively, the values of these two constants are 0·13 and −0·20 ($\times 10^9$ cm./sec.). The calculated value for the velocity of the α-ray of the unknown C'-member of actinium is 2·27.

The disintegration constants of analogous α-ray-giving members of different series stand in constant ratio to one another. The logarithm of this ratio between the radium and actinium series is $1{\cdot}3 \times 10^{-5}$ and between the radium and the thorium series $4{\cdot}8 \times 10^{-5}$. F. S.

A Relation between the Kind of Radioactive Change and the Electrochemical Behaviour of the Resulting Radio-element. KASIMIR FAJANS (*Physikal. Zeitsch.*, 1913, **14**, 131—136*).—Two rules are proposed, and shown to be followed in all cases where they can be tested:

(1) An α-ray change gives a product more electropositive than the parent substance.

* and *Le Radium*, 1913, **10**, 57—60.

(2) A β-ray change gives a product more electronegative than the parent substance.

The rule with regard to the β-ray change is considered to apply also to rayless changes, and β-rays of very low velocity, not yet detected, may be supposed to be emitted in these cases also. The three disintegration series are discussed in detail in so far as there is evidence of the electrochemical character of the members.

It is assumed that uranium-*X* is intermediate between uranium-*I* and -*II*, which then conform to the rules. The change of radium and of thorium-*X*, in which both α- and β-rays are emitted, is supposed to be complex, an alkali-metal first resulting as the product of the α-ray change, which then in a subsequent β-change suffers transformation into the much more "noble" emanations. It is predicted that radium-*C′* should be nobler than radium-*C* or -*D*. Such simple relations, the change in the character of the atom being analogous to electrochemical changes, are very unexpected, for it has always been considered that these atomic changes are concerned with regions of the atomic structure quite different to those conditioning chemical changes. F. S.

The Radioactivity of the Mineral Springs of Tyrol. IV. MAX BAMBERGER and KARL KRÜSE (*Monatsh.*, 1913, **34**, 403—423. Compare A., 1911, ii, 1049).—Tables are given of the amount of radium emanation of numerous Tyrolese springs in Mache units, together with particulars of the locality, the kind of rock in which the spring occurs, and its temperature.

R. GRENGG contributes the results of a petrographic study of the rocks. The decay curves of the active deposit from the iron spring of Bad Ratzes and the strongly active potable water of Schreiberhof in Tscherms are shown, and are in agreement with that due to radium. F. S.

Electrical and Chemical Effects of the Explosion of Azoimide. PAUL J. KIRKBY and JAMES E. MARSH (*Proc. Roy. Soc.*, 1913, *A*, **88**, 90—99).—Measurements have been made of the quantity of electricity which is set free when azoimide is exploded by the passage of an electric spark through the vapour contained in a vessel provided with electrodes which were connected in series with a ballistic galvanometer and a potential difference of about 100 volts. The galvanometer readings show that the number of ions set free is exceedingly small in comparison with the number of molecules decomposed in the explosion. The ratio was always less than 1 to 100,000, and this seems to indicate that dissociated atoms do not in general carry electrostatic charges. It is supposed that the formation of the ions is due to those impacts between the dissociated atoms which occur under specially favourable conditions, amongst which a relatively high velocity is probably the most important. Except under these circumstances, the combination of the dissociated atoms takes place without the production of ions.

From experiments at different pressures it was found that the azoimide could not be exploded when the pressure was less than

about 10 mm. In the case of pure azoimide this limiting pressure would probably be smaller. The value of the limiting pressure is much smaller than that obtained in previous experiments with electrolytic gas, for which 80 mm. was observed as the lower limit.

In drying the gas it was observed that azoimide is very readily absorbed by phosphoric acid, although no change in volume occurs when fresh phosphoric oxide is employed as drying agent. After the explosion experiments, copper azoimide was found to be present in the gold-plated brass explosion vessel, and it is shown that this is probably formed in the actual explosion, the dissociated N_3-group being driven through the layer of gold into the brass as a consequence of the forces developed in the molecular disruption.

H. M. D.

Duration of Luminosity of Electric Discharge in Gases and Vapours. (Hon.) ROBERT J. STRUTT (*Proc. Roy. Soc.*, 1913, *A*, **88**, 110—117).—Some experiments are described, which show that the luminosity accompanying the electrical discharge persists for an appreciable period after the cessation of the discharge. This is not only the case for discharge through vapours of metals and non-metals, but can be observed when the discharge takes place through gases such as hydrogen, oxygen, carbon dioxide, and air between non-volatile electrodes. The luminosity gradually fades away when the discharge ceases, but there is no immediate alteration in the spectrum, although a change may sometimes be observed in the later stages in consequence of a difference in the rate of decay of the lines. The effects in question, the duration of which is less than one-thousandth of a second, are quite distinct from the after-glow effects in nitrogen and in gaseous mixtures containing oxygen or hydrogen.

H. M. D.

Electrical Discharge in Helium and Neon. HERBERT E. WATSON (*Proc. Camb. Phil. Soc.*, 1913, **17**, 90—107).—Measurements have been made of the sparking potentials in pure helium and neon at different pressures, the discharge taking place between plane aluminium electrodes, 15 mm. apart. The minimum spark potential was found to be 184 volts for helium and 200 volts for neon, the pressures corresponding with these minima being 2·4 and 2·8 mm. respectively. For pressures greater than 10 mm. the relation between the spark potential and the pressure is represented graphically by a straight line, the increase in the potential being 30 volts per cm. pressure in the case of helium and 22 volts per cm. for neon.

With a cathode of sodium–potassium alloy the minimum spark potential in neon is near to and not greater than 145 volts, and the cathode fall amounts to 85 volts. With aluminium electrodes which have been run for a sufficiently long time, the cathode fall is at most 164 volts for helium and 170 volts for neon. The cathode fall in neon with cathodes of copper, carbon, magnesium, and calcium is approximately 221, 217, 150, and 150 volts respectively.

The electrodes have been found to exhibit marked fatigue effects,

and these appear to be of two kinds, one representing a true fatigue and the other a reluctance to allow the current to start for a second time when one discharge has already taken place.

In view of the brilliancy of the discharge through pure neon, some measurements were made of the efficiency of the negative glow, but the data showed that the actual intensity of the light was much smaller than the estimated intensity. At pressures between 10 and 16 mm. the efficiency was raised to about 4 watts per candle by making use of a sodium-potassium electrode.

The light emitted by both helium and neon under the influence of the discharge produces very marked physiological effects. When, for instance, the light from a tube of about 0·1 candle power was allowed to fall on the unprotected eyes for about fifteen seconds, it gave rise to a violent headache, followed by temporary blindness. On this account it was necessary to wear dark brown glasses during the whole of the experiments. Similar effects have been noticed with argon, krypton, and xenon, and it is suggested that the phenomenon may be connected with the fact that the spectra of these elements contain a comparatively small number of intensely bright lines. H. M. D.

The Hall Effect. JOHANNES KOENIGSBERGER and G. GOTTSTEIN (*Physikal. Zeitsch.*, 1913, **14**, 232—237).—Evidence is brought forward to show that the Hall effect can be accounted for on the basis of the electron theory. By reference to the data for graphite, molybdenite, and a silicon-iron alloy (containing 5·2% of iron), it is shown that the Hall effect changes with temperature to about the same extent as the number of electrons. It is further found that the ratio of the Hall effect to the specific resistance is of the same order of magnitude for metalloids, metals, and alloys, although the two quantities vary to the extent of 1 to $1 \cdot 10^7$ when the extreme members of the composite group are compared. The behaviour of alloys, such as German silver and constantan, suggests that the low conductivity which they exhibit is not due to the smallness of the free path or the energy of the electrons, but to the presence of a very small number of electrons. H. M. D.

The Changes in the Electrical Resistance of Wires which have been Drawn and Subjected to Torsion, and also of Drawn and Twisted Wires on Warming: Gold, Silver, Copper, Nickel, and Iron. FRITZ CREDNER (*Zeitsch. physikal. Chem.*, 1913, **82**, 457—503).—The paper commences with a critical résumé of the work which has been done on this subject. The experimental part of the paper consists in an account of the changes in the resistance of wires which have been warmed to definite temperatures for measured periods of time. It is shown: (1) That the resistance of drawn wires of gold, silver, and copper falls at a constant temperature, and the rate of decrease is more rapid the higher the temperature. After a time the resistance reaches a constant minimum; on further increasing the temperature after the minimum has been reached, an increase in the resistance takes

place; for gold the increase commences at 300°, and for silver and copper at 400°. (2) On successively warming drawn wires for periods of three minutes and measuring the cold wires, it is shown that a minimum specific resistance is obtained at a definite temperature, and that this minimum specific resistance is independent of the cross-section of the wire. For gold the minimum is found at 480°; silver, 480°; and copper, 450°. The temperature at which the minimum occurs is the same as that at which the coarse recrystallisation of the crystallite begins, and so is the same as the temperature at which small crevices begin to be formed in the wires, which naturally cause an increase in the resistance. In the case of nickel the minimum value of the specific resistance is obtained at 550°, and remains constant whilst the temperature is raised 300°. The minimum for iron wires is found at 600°, and this increases on increasing the temperature due to chemical changes in the substance of the wire. (3) Laminæ are produced on drawing a wire due to a movement of parallel crystallite surfaces, and at the same time an increase in the resistance is brought about. On warming such drawn wires to the temperature of the minimum resistance, the laminæ are destroyed and replaced by an irregular, crystallite mass, and the resistance falls to its original value before drawing. (4) On bending or subjecting a wire to a strong torsion the resistance of a wire is increased, due to the formation of small crevices; this increased resistance is not changed by warming. (5) On lowering the temperature, the resistance, in the direction of the axis of a wire made up of laminæ, decreases more quickly than the resistance in the direction at 90° to the axis. (6) The greater specific resistance of drawn wires is due to the orienting laminæ lying in the direction of their poorest conductivity, and is apparently uninfluenced by the loosening of the crystals. (7) Permanent changes in the resistance only occur when there is a definite change in the crystal structure. The hypothesis that on working metals a new phase appears is shown to be incorrect. J. F. S.

The Theory of Electrolytic Ions. VI. The Conductivity of Pure Water. RICHARD LORENZ (*Zeitsch. physikal. Chem.*, 1913, **82**, 612—620. See A., 1912, ii, 323 and also *Festschrift W. Nernst*, 1912, 276).—The author calculates the mobilities of the hydrogen and hydroxyl ions at various temperatures from molecular kinetic considerations; the values obtained are compared with those obtained from the Kohlrausch measurements. It is shown that in every case the Kohlrausch value is much larger than the calculated value, in many cases the Kohlrausch value being more than four times as large as the calculated. A theory of the migration of ions, resembling the Grotthus theory, is then considered. In this case the passage of an ion is supposed to be partly due to its own actual motion and partly due to colliding with an undissociated molecule with which it combines and sets free the corresponding ion of the undissociated molecule. In this way part of the distance, proportional to the number and diameter of the undissociated molecules lying in the path, is covered at an extremely high velocity, thus making

the apparent velocity much larger than that calculated on the molecular kinetic hypothesis. On comparing the values obtained in this way with the experimental results, the former are found to be somewhat larger than the latter. Hypotheses are considered which would slightly reduce the calculated values. J. F. S.

Conductivity, Dissociation, and Temperature-coefficients of Conductivity of Certain Inorganic Salts in Aqueous Solution, as Conditioned by Temperature, Dilution, Hydration, and Hydrolysis. E. J. SHAEFFER and HARRY C. JONES (*Amer. Chem. J.*, 1913, **49**, 207—253. Compare Hosford and Jones, A., 1911, ii, 960; Winston and Jones, A., 1911, ii, 961; Howard and Jones, this vol., ii, 11).—In continuation of earlier work, conductivity measurements have been made at temperatures between 0° and 65° of ammonium hydrogen sulphate, tetraethylammonium iodide, ammonium sodium hydrogen phosphate, sodium chloride, chlorate, and perchlorate, disodium hydrogen phosphate, potassium chlorate, perchlorate, and phosphate, calcium chloride, strontium chloride, barium bromide and formate, magnesium chloride and sulphate, manganous chloride and nitrate, aluminium chloride, nitrate, and sulphate, the violet forms of chromic chloride, nitrate, and sulphate, lead nitrate, nickel nitrate, copper ammonium sulphate, and uranyl sulphate.

The results confirm the more important relations established by the earlier work. The dissociation was found to decrease with rise of temperature in all cases except that of potassium phosphate.

It has been found that the hydrolysis of chromium salts increases rapidly with rise of temperature, and that the hydrolytic products only slowly recombine as the solution cools. It follows, therefore, that in purifying a chromic salt for conductivity experiments, it must not be heated to a higher temperature than that at which the conductivity is to be determined, since the dehydrolysis time factor persists for months. This precaution does not appear to be necessary in the case of other salts.

It is shown that considerable error may be introduced into conductivity measurements unless the proper water corrections are applied. The purity of the air in the room must be the same when the water-cell is filled as when the solutions are prepared. Care should also be taken to ensure that the air is as free from impurities as possible.

The influence of hydration, hydrolysis, and polymerisation in conductivity determinations is discussed, and it is pointed out that the Kohlrausch method is not suitable for measuring the dissociation of highly polymerised sulphates or for determining the dissociation of any electrolyte which is both hydrated and hydrolysed.

E. G.

Citrophosphate Solutions. II. Electrical Conductivity of Aqueous Solutions of Citric Acid and Phosphoric Acid. UGO PRATOLONGO (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 86—89. Compare A., 1911, ii, 865).—The paper records the results of con-

ductivity measurements of binary mixtures of citric acid with phosphoric acid, arsenic acid, and hydrochloric acid in aqueous solution. The curves present no abnormality, and therefore show no evidence of the existence of complex ions. R. V. S.

Electrical Conductance of Non-aqueous Solutions. Leon Irwin Shaw (*J. Physical Chem.*, 1913, **17**, 162—176).—The conductivities of mercuric chloride, iodine, and lithium chloride in acetone, and of mercuric chloride and iodine in epichlorohydrin were compared with the dielectric constants of the purified solvents. The molecular conductivity of lithium chloride in acetone first increases, then decreases, and finally increases again on dilution. None of the solutions examined approached a constant molecular conductivity at infinite dilution, so that the "degree of dissociation" could not be calculated.

The dielectric constants of acetone and epichlorohydrin, according to Walden, are 21·0 and 26·0 respectively. Neglecting the question of ionic mobility, mercuric chloride is in accord with Nernst's hypothesis in having a higher conductivity in epichlorohydrin than in acetone, but iodine, on the contrary, has a much higher conductivity in acetone. The author did not make any measurements of dielectric capacity, but it is to be noted that his solvents by the conductivity test were somewhat purer than Walden's.

Solutions of a number of metallic chlorides, iodides, etc., in ten organic solvents of various types were examined qualitatively. No relationship appears to exist between the dissociating power of a solvent and its dielectric constant, degree of association, or residual affinity. R. J. C.

Abnormal Electrical Conductivity Changes. IV. Alexander Nicolaevitsch Sachanov (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 102—136. Compare A., 1912, ii, 422, 730).—Theoretical considerations, together with the results obtained on investigating the conductivity and viscosity changes of solutions in aniline, acetic acid, etc., with dilution, lead to the following conclusions.

The molecular conductivity increases with dilution in the more concentrated solutions, and later diminishes continuously with dilution; the maximum value is reached at a dilution corresponding with $x=(m-2)/(2m-2)$, m being the number of molecules of dissolved salt in the complex, mC,pB (see A., 1911, ii, 689), and x the number of polymerised molecules. The rate of diminution occurring on dilution increases with m, that is, with the complexity of the group conducting the current.

This appearance of a maximum conductivity in concentrated solutions is regularly met with in cases of abnormal conductivity changes. The formation of a minimum molecular conductivity with increasing dilution is also a regular phenomenon, increase of dilution beyond the point of minimum conductivity being accompanied by normal increase of the latter.

It is shown that cases of masked abnormality in the change of

molecular conductivity on dilution may occur when either the concentration of the polymerised molecules is not high, at any rate for low dilutions, or the degree of electrolytic dissociation of these molecules is not considerably higher than that of the simple molecules. Those cases must also be termed abnormal in which $d\mu/dv$ has a positive value (the molecular conductivity increasing with the dilution) and $d^2\mu/dv^2$ changes its negative sign at a certain dilution. Masked anomalies may also give rise to a fold in the molecular conductivity-dilution curve, $d\mu/dv$ assuming the value zero, although positive for all neighbouring dilutions.

T. H. P.

The Addition of Alkyl Halogens to Thiocarbamides. HEINRICH GOLDSCHMIDT and HANS KRF. GRINI (*Zeitsch. Elektrochem.*, 1913, **19**, 226—234).—The electroconductivity of allylthiocarbamide ethiodide, C_3H_5·NH·CS·NH_2EtI, is determined in aqueous solution at 25°. It is shown that this substance is not hydrolysed in aqueous solution, and has a value $\lambda_\infty = 102 \cdot 2$. From this value the migration velocity of the cation, C_3H_5·NH·CS·NH_2Et, is calculated as 25·9. The electroconductivity is also determined in absolute alcohol, and in alcohol containing water; the water concentrations measured are 0·02*N*, 1·0*N*, 2·0*N*, and 10·0*N*. It is shown that small additions of water do not effect the conductivity; the 2·0*N*-water-alcohol solution shows an increase, which is comparatively small, whilst in the case of the 10·0*N*-solution there is a great increase. In the very dilute solutions of the salt it is shown that in all cases the conductivity is approximately the same. The change in the conductivity is shown to be due to an increased ionisation, and not to a change in the migration velocities of the ions. The equivalent conductivity of a number of thiocarbamide derivatives was determined in absolute alcohol and in alcohol containing 0·02*N*-water. The following values for λ_∞ in absolute alcohol were obtained. Allylthiocarbamide ethiodide, $\lambda_\infty = 43 \cdot 8$; ethobromide, $\lambda_\infty = 41 \cdot 5$; methiodide, $\lambda_{1024} = 38 \cdot 63$. Phenylthiocarbamide ethiodide, $\lambda_{1024} = 39 \cdot 26$ in 0·02*N*-water-alcohol; ethobromide, $\lambda_{1280} = 37 \cdot 19$ in 0·02*N*-water–alcohol; methiodide, $\lambda_{1280} = 37 \cdot 83$ in 0·02*N*-water–alcohol. Thiocarbanilide methiodide, $\lambda_\infty = 48$ in absolute alcohol. The velocity of combination of the various thiocarbamides with alkyl haloids was determined by measuring the conductivity in water–alcohol solutions at measured intervals of time, and so determining the amount formed from curves obtained in the abovementioned conductivity determinations. Allylthiocarbamide reacts with ethyl and methyl iodides at approximately the same rate; diphenylthiocarbamide reacts with methyl iodide much more slowly. The addition of water to the alcohol solutions makes only a small difference in the velocity constant; up to 2·0*N*-water there is no appreciable change in the velocity constant, but with a 10*N*-water–alcohol solution in the formation of allylthiocarbamide ethiodide the constant increased from 0·253 to 0·296. The slight influence of water on the velocity of reaction is remarkable in view of its great influence on hydrolysis in non-aqueous solutions. J. F. S.

The Reduction to Hydrogen Peroxide of Oxygen Dissolved under Pressure. FRANZ FISCHER and OTTO PRIESS (*Ber.*, 1913, **46**, 698—709).—The authors have confirmed the experiments of Moritz Traube with respect to the formation of hydrogen peroxide at the cathode when air is led through the catholyte. When the air is replaced by oxygen at atmospheric pressure, a 0·32% solution of hydrogen peroxide is obtained, as against a 0·26% with air, the current density being 0·02 ampere per square dcm. The effect of various conditions on the yield was studied in detail. The current yield is diminished by rise in temperature, and increased by vigorous stirring. The best electrolytes are sulphuric acid (0·1%) and phosphoric acid; boric acid may also be used. Solutions of neutral salts are not suitable, owing to the formation of alkali at the cathode, unless an insoluble derivative of hydrogen peroxide is formed, as, for example, calcium hydroperoxide from an ammoniacal solution of calcium chloride. The best electrode material is mercury; when, however, the catholyte is stirred, mercury goes into solution, so that all the experiments were made with amalgamated gold electrodes. The current yield diminishes with time, and the concentration of the hydrogen peroxide increases to a maximum and then falls, owing to the reduction of the hydrogen peroxide formed. The current-yield increases with diminution in current density.

A special steel apparatus was constructed, which permitted electrolyses in a divided cell being carried out under pressures up to 100 atmos., the catholyte being stirred by means of an electromagnetic attachment.

Under high oxygen pressures the current yield and concentration of hydrogen peroxide increase with the pressure, the voltage necessary diminishing at the same time. At 100 atmos. pressure and a current density of 2 amperes per sq. dcm., using 2 volts, 2·7% solutions of hydrogen peroxide can be obtained, that is, 300—400 grams of hydrogen peroxide per kilowatt-hour and a current-yield of 83%. A 5% solution is obtainable when the best current-yield is not insisted on. Experiments with various electrolytes and electrodes gave the same results as at atmospheric pressure.

The investigation of the effect of 1% sulphuric acid under an oxygen pressure of 25 atmos. on the various materials used for electrodes, showed that all metals, with the exception of tin and iron, which go into solution without current being necessary, produce hydrogen peroxide at the same time. Zinc amalgam gives the most hydrogen peroxide, nickel gives a third as much, and then follow the other metals. T. S. P.

The Form of Electrolytically Deposited Metals. I. Silver-black. VOLKMAR KOHLSCHÜTTER and THEODOR TOROPOFF (*Zeitsch. Elektrochem.*, 1913, **19**, 161—168. Compare A., 1912, ii, 253, 845).—An account is given of the formation of silver-black by electrolytical methods, of its properties, and the transformation of it into grey, crystalline silver. It is shown that silver-black can be obtained by the action of organic reducing agents on silver solutions, and

also by the action of zinc, copper, and cadmium on dilute solutions of silver salts. Electrolytically, silver-black is best obtained from dilute solutions by the use of comparatively high current density. Silver-black cannot be preserved; no matter how prepared, it speedily changes into grey or white, crystalline silver. The rate of passage into the crystalline variety is about ten times as rapid in the presence of dilute acid as in the presence of dilute alkali, whilst in the latter case the change is quicker than in pure water. Black silver is regarded as in a condition between the colloidal and the crystalline states. This substance when examined microscopically during the electrolytic preparation is seen to be crystalline, but it behaves as a colloid towards electrolytes. At the moment at which the current is stopped, in the preparation of silver-black, it begins to pass over into the grey, crystalline variety, as evidenced by the change in colour and by the shrinking together of the mass. Experiment shows that there is no real volume change in the passage from coherent massive silver to silver-black and to grey, crystalline silver.

To obtain evidence which should indicate the reason for the formation of silver-black, a number of measurements were made on the potential difference of the electrodes during deposition, and from these results it was deduced that the formation in dilute solution is due to the relative lack of crystal centres, so that each discharged ion finds itself more or less isolated, and consequently deposits as such, and does not attach itself to a crystal centre with the formation of the grey, crystalline silver. The sudden change to grey silver on breaking the current is explained as an electro-surface tension phenomenon. The silver-black with very large surface takes up the form of smallest surface on stopping the current, but while the current is flowing and it is negatively polarised the electrostatic repulsions of the charged particles overcome the tendency to a surface diminution. J. F. S.

The Form of Electrolytically Deposited Metals. II. Silver Deposited by Metals. VOLKMAR KOHLSCHÜTTER, THEODOR TOROPOFF, and W. PFANDER (*Zeitsch. Elektrochem.*, 1913, **19**, 169—172. Compare preceding abstract).—It is shown that different metals precipitate silver in different, but perfectly definite, conditions, which depend to some extent on the concentration of the silver solution. The experiments were carried out with copper, zinc, cadmium, iron, tin, aluminium, and magnesium. It is shown that the observed differences are due to the velocity with which the precipitation takes place. The addition of neutral salts causes an increase in the velocity of precipitation. This is explained in the following way: In neutral salt solution when copper is the metal, a colloidal copper hydroxide is formed by hydrolysis; this is adsorbed by the copper, and so prevents its further rapid solution, but by the addition of an electrolyte this colloidal substance is removed, either by chemical solution or by coagulation. The addition of such substances as sugar, starch, gum, and gelatin cause the reaction to take place more slowly, but at the same time they cause a very dark powder

to be formed, which is more stable than that usually obtained. The course of the reaction is followed in all cases by means of potential difference measurements between the depositing metal and the solution. J. F. S.

The Form of Electrolytically Deposited Metals. III. The Influence of Foreign Substances on the Deposition of Silver. VOLKMAR KOHLSCHÜTTER and HERMANN SCHACHT (*Zeitsch. Elektrochem.*, 1913, **19**, 172—181. Compare preceding abstracts).—Silver was deposited electrolytically from a 0·05*N*-solution of silver nitrate, to which had been added just sufficient ammonia to redissolve the precipitated silver oxide; 100 c.c. of this solution were electrolysed after the addition of one or two drops of sodium hydroxide solution, and a small amount of the solution of the metallic nitrate. The nitrates used in the various experiments were those of copper, zinc, cadmium, lead, glucinum, chromium, aluminium, and thallium. The solutions were electrolysed by a current of 3 milliamperes, which corresponded with a cathode current density of 0·001—0·005 ampere per sq. cm. The silver was deposited in different forms in each case, which were easily reproducible; micro-photographs of the various forms are given in the paper. It is shown that if the solutions are kept more than fifteen to twenty hours quite different forms are obtained, so that in all the experiments described freshly prepared solutions were employed. It is also shown that the amount of silver deposited under these conditions is more than that demanded by Faraday's Law, and that it does not contain more than the merest trace of the added metal. The action of the added substances in producing the different deposits is held to be due to the formation of colloidal metal hydroxides which are deposited on the cathode, and form a type of filter which conditions the distribution of the centres of crystallisation. The excess of silver deposited above that required by Faraday's Law is supposed to be due to causes other than electrolysis, since it does not increase with the concentration of the silver solution. J. F. S.

The Form of Electrolytically Deposited Metals. IV. The Deposition of Silver from Solutions of Complex Salts. VOLKMAR KOHLSCHÜTTER (*Zeitsch. Elektrochem.*, 1913, **19**, 181—184. Compare preceding abstracts).—The reasons for the compact adhesive deposition of silver in the electrolysis of complex solutions of silver are discussed in the present paper. It is shown that in the first stages of the deposition colloidal silver in the complex silver compound is deposited; this is demonstrated by the reddish-violet coloration on the cathode, which is the characteristic of the so-called "subhaloids." It is also shown that if a platinum cathode on which this deposit has been formed is removed from the electrolyte and washed, the blue colour vanishes, but that if such an electrode is now placed in a solution of a non-complex silver salt, such as silver nitrate, the further deposition is of the same compact form characteristic of silver deposited from complex solutions, such as $KAg(CN)_2$.

It is thought that this first deposit determines the number and position of the crystal centres on which the further deposition takes place. It is shown from theoretical grounds and from analogy to the results of the addition of foreign metals (see last abstract) that the silver salts are also present in the colloidal form in the complexes, and that these colloids are determinative of the peculiar form of the silver deposition.

Experiments in confirmation of the author's views were made with complex cyanide, thiosulphate, and ammoniacal solutions. The author's views all confirm the work of Danneel (*Zeitsch. Elektrochem.*, 1903, **9**, 762), Haber (A., 1904, ii, 607, 808), and Bodländer and Abegg (A., 1904, ii, 713), which point to the fact that silver deposition is not a secondary reaction due to the primary deposition of potassium, which then reacts chemically to produce silver.

J. F. S.

Variation of Magnetic Susceptibility with Temperature. II. Aqueous Solutions. A. E. OXLEY (*Proc. Camb. Phil. Soc.*, 1913, **17**, 65—89. Compare A., 1912, ii, 325).—The influence of temperature on the magnetic susceptibility of aqueous solutions of ferric chloride, ferrous sulphate, and ferric nitrate has been examined.

On the assumption that the susceptibility is independent of the intensity of the magnetic field, and that complex molecular aggregates containing water of hydration are formed, the composition of which varies with the temperature in accordance with van Laar's theory, a formula is deduced for the susceptibility χ, which may be written in the form $\chi = A/\theta + B + C\theta$, where θ denotes the absolute temperature. In the case of dilute solutions, this reduces to the simpler form $\chi = A/\theta + B$. The experimental observations are shown to be satisfactorily represented by means of these formulæ, and this would seem to indicate that if the Curie-Langevin theory is strictly applicable to aggregates, the composition of which is independent of the temperature, the complexity of the aggregates present in the aqueous solutions which have been examined varies with the temperature in accordance with a linear formula.

H. M. D.

Magnetic Double Refraction and Chemical Constitution. A. COTTON and HENRI MOUTON (*Ann. Chim. Phys.*, 1913, [viii], **28**, 209—243).—A résumé of work published in A., 1906, ii, 146; 1907, ii, 727; 1908, ii, 745; 1909, ii, 773; 1910, ii, 368; 1911, ii, 4; 1912, ii, 426.

H. W.

The Critical Points of Iron. WITOLD BRONIEWSKI (*Compt. rend.*, 1913, **156**, 699—702).—Using electrolytic iron, the author has studied the variation of its thermoelectric force with respect to copper and platinum, its electrical resistance, and its dilatation with variation in temperature, and curves are given showing these variations. He finds three critical points on the curves, one corre-

sponding with α-iron, stable below 730°, another with β-iron, stable at 950°, and the third with γ-iron, stable above 1020°. W. G.

The Thermoelectric Properties of Some Irreversible Nickel and Manganese Steels. SIEGFRIED HILPERT and FRITZ HERRMANN (*Zeitsch. Elektrochem.*, 1913, **19**, 215—219).—Steels containing 12·6% and 27·5% of nickel, and 4·58%, 11·7%, and 20·8% of manganese were examined as to their thermoelectric properties after they had been subjected to definite temperatures. The steels after treatment were made into thermo-couples with either constantan or copper, and the two ends subjected to different, but not widely separated, temperatures, and the *E.M.F.*, produced by the temperature difference, measured. With the steel containing 27·5% nickel it is shown that after subjecting the steel to $-75°$ a difference of 1° between the ends of the couple produces an *E.M.F.* of 21·1 microvolts, whereas after cooling to $-185°$ 1° difference gives 7·7 microvolts. From this temperature up to 400° the same thermo-electromotive force is produced for 1° difference between the ends; after treatment at 500° the value rises to 16 microvolts, and at 600° it reaches 36·4 microvolts. This case is analogous to the behaviour of the magnetic properties of this steel when it has been subjected to various temperatures (A., 1911, ii, 1057; 1912, ii, 229). Steel with 12·6% nickel showed similar properties to a very slight extent. Steels containing 4·58% and 11·7% manganese, which are strongly magnetic, do not show these properties. It is suggested that the observed differences in the *E.M.F.* have their cause in a considerable volume change, which is accompanied by an internal tension, and that there is a marked hysteresis of the specific volume.

J. F. S.

The Gas Thermometer as the Basis for High-temperature Measurements. FRITZ HENNING (*Zeitsch. Elektrochem.*, 1913, **19**, 185—192).—A theoretical paper in which the following points, relating to the gas thermometer for use at high temperatures, that is, up to 1500°, are discussed: (1) Material of which the thermometer is to be made. (2) Gas with which it is to be filled. (3) Precautions to be taken in use. (4) The dead space. (5) Fixed points to be used in the calibration of such a thermometer. (6) Subsidiary thermometers for controlling temperatures, and for determining the temperatures required for the calculation of the necessary corrections. It is shown that a platinum iridium vessel is the best for this purpose, and that the dead space can conveniently be brought down to about 1 cubic centimetre. A platinum-platinum rhodium (10% rhodium) thermocouple is recommended as subsidiary thermometer for temperatures up to 1100°, for which the formula for calculation of the temperature is:

$$\epsilon = -310 + 8{\cdot}048t + 0{\cdot}00172t^2 \text{ microvolt.}$$

Above 1100° to 1600° it can still be used, but the temperature is obtained from the formula: $\epsilon = 30600\log(1{\cdot}3 + t^2 \times 10^{-6}) - 1590$. As fixed points for controlling the temperatures, the following melting and boiling points are recommended: Naphthalene, b. p. 218·0°;

tin, m. p. 231·8°; benzophenone. b. p. 305·9°; cadmium, m. p. 320·9°; zinc, m. p. 419·4°; sulphur, b. p. 444·5°; antimony, m. p. 630°; aluminium, m. p. 658°; silver, m. p. 961°; gold, m. p. 1064°; copper, m. p. 1084°; nickel, m. p. 1452°; cobalt, m. p. 1490°; and palladium, m. p. 1587°±12°. J. F. S.

A Simple Method for Maintaining Constant Temperatures in the Region of the Room Temperature. FRITZ BAHR (*Zeitsch. angew. Chem.*, 1913, **26**, 135).—The action of the gas regulator in a thermostat working at the ordinary temperature may be assisted by regulating the flow of water by means of a sensitive syphon. For this purpose a hole is blown in a piece of glass tubing, which is then drawn out at this point, and cut off across the narrow slit. The tube is then bent near the end through 360°, so as to form a syphon, which is then hung in the full thermostat. J. C. W.

The Specific Heat of Bismuth Oxide. OTTO HAUSER and W. STEGER (*Zeitsch. anorg. Chem.*, 1913, **80**, 1—6).—The specific heat of bismuth oxide, Bi_2O_3, has been determined by heating the oxide, enclosed in a silver case, to a temperature of 100—507° in an electric furnace, and then rapidly dropping into a copper calorimeter enclosed in a vacuum vessel. The values obtained are: 20—100°, 0·0568; 20—312°, 0·0604; 20—503°, 0·0623.

It has not been found possible to dehydrate bismuth peroxide without loss of oxygen. C. H. D.

Effect of High Pressures on the Physical and Chemical Behaviour of Solids. JOHN JOHNSTON and LEASON H. ADAMS (*Amer. J. Sci.*, 1913, [iv], **35**, 205—253*).—In any discussion of the influence of pressure on solid systems, it is necessary to distinguish between the effects of uniform pressure and of non-uniform pressure. The effects produced by non-uniform compression are in general such that the original state of the system is not re-established when the pressure is released. Most of the work on the influence of high pressures on solids has been carried out under these conditions, and it seems probable that many of the apparently contradictory statements recorded in the literature are due to the disregard of the distinction between the two types of compression.

In general, uniform pressure raises the melting point by an amount which seldom exceeds 10° per 1000 atmospheres; its effect on solubility is also very slight. Non-uniform pressure, on the other hand, always lowers the melting point and raises the solubility, and by amounts which are many times greater than the corresponding variations produced by the application of uniform pressure. The actual cause of the phenomena recorded as occurring when solid systems are subjected to high pressure is supposed to be the local melting produced by non-uniform compression, and on the assumption that permanent deformation of a crystalline aggregate is always conditioned by liquefaction, it is found that the pressure required to produce this change at the ordinary temperature is well within the bounds of probability.

* and *Zeitsch. anorg. Chem.*, 1913, **80**, 281—334.

From an examination of the available data, and in particular of the results obtained by Spring, the authors draw several conclusions with respect to the physical and chemical behaviour of solids under high pressures.

The pressure necessary to produce local melting of crystalline aggregates depends mainly on the melting point, the heat of fusion, the density of the substance, and the temperature at which the compression is applied. Generally speaking, those substances which, at a given temperature, require the largest pressures to weld them, are those which have the highest melting points.

Compression alone will not in general produce crystallisation or bring about the transformation of one modification of a substance into another. If the conditions are such that the velocity of transformation is appreciable, it may give rise to such changes in certain cases; and if, further, the conditions are such that partial melting may occur, then the compression will be followed by a partial transformation.

In regard to chemical reactions between solids, non-uniform pressure will also have a much greater effect than uniform pressure. In the latter case, the reaction can only occur at the surfaces of contact between the solids, whereas the conditions obtaining with non-uniform compression will assist the reaction by a renewal of the contact surfaces in consequence of local melting and the flowing away of the fusion. With reference to the alleged reaction between barium sulphate and sodium carbonate and between potassium nitrate and sodium acetate, it is pointed out that the methods adopted in the examination of the product after compression afford no certain information as to the actual condition of the dry mixture.

Apart from the question of the direct influence of pressure on reactions between solids, it is probable that the more intimate contact which is attained under pressure will result in an increased rate of interdiffusion of the substances, and to this extent pressure will have an influence on the reaction. The formation of alloys may be referred to as a special case of such interaction. Where the formation of solid solutions is possible, pressure will have an effect by promoting indirectly the rate of diffusion, but there is no evidence in the available data to show that compression itself has any specific influence on the formation of alloys. H. M. D.

Fusibility of Natural Fats. HENRI LE CHATELIER and (Mlle.) CAVAIGNAC (*Compt. rend.*, 1913, **156**, 589—594).—The authors have made a careful study of the temperatures of fusion and solidification of two natural fats, vegetalin and stearin, under varying conditions, and find that they obey the general laws of change of state in that their fusion and solidification is a reversible phenomenon the temperature of which can be determined to one-tenth of a degree by sufficient experiments. The melting point as rapidly determined does not, as a rule, differ by more than a degree from the true value; the solidification temperature, however, shows greater variation. Foreign substances have a marked effect on the

melting point, and these fats exhibit the phenomenon of superfusion. W. G.

Influence of Chemical Constitution on the Thermal Properties of Binary Mixtures. II. Mixtures containing Unsymmetrical Constituents. PAUL PASCAL and LÉON NORMAND (*Bull. Soc. chim.*, 1913, [iv], **13**, 207—216).—The authors have examined the melting-point curves of a series of mixtures composed of the following pairs of constituents: (1) dibenzyl and benzylaniline, (2) azobenzene and benzylideneaniline, (3) stilbene and benzylideneaniline, (4) benzylideneaniline and benzylaniline, (5) phenyl benzyl ether and benzylaniline, (6) phenyl benzyl ether and dibenzyl, (7) benzylaniline and hydrazobenzene, (8) dibenzyl and benzylideneaniline, (9) hydrazobenzene and benzylideneaniline, (10) tolane and benzylideneaniline, (11) benzylaniline and azobenzene, (12) benzylaniline and stilbene, and (13) tolane and benzylaniline. In every case a eutectic mixture was obtained. In the first seven cases, in which the constituents of the mixtures have either different central atoms or different central linkings, the extent of the region of syncrystallisation (defined by the difference in percentage of either of the constituents of the mixed crystals which form the eutectic mixture) lies between 20% and 40%, whilst in the last six cases, in which the constituents of the mixtures possess different central linkings and central atoms, it lies between 40% and 60%, attaining a maximum of 65% in the case of mixtures of tolane and benzylaniline. H. W.

The Fusion Curves of Several Substances. ERNST AUGUST BLOCK (*Zeitsch. physikal. Chem.*, 1913, **82**, 403—438).—A method due to Tammann is used for the determination of the equilibrium pressure in the melting of the substances: veratrole, *p*-chlorotoluene, *p*-iodotoluene, *p*-bromotoluene, anethole, diphenylmethane, dichlorobenzene, benzylaniline, thymol, and menthol. It is shown that the equilibrium pressure is independent of the proportions of crystalline and liquid substance, and a method is given for ascertaining whether the substance under examination is pure. If the substance is pure, the equilibrium pressure is constant for all proportions of melted and crystalline substance, but if impure the equilibrium pressure increases very rapidly when only a small proportion of the substance is melted. The fusion curves of the ten substances mentioned above are determined for pressures 1—3000 kilog. by Tammann's method, and the temperature readings compared with those calculated by the Tammann formula:

$$t = t_{p=1kg} + ap - bp^2.$$

The agreement is very good, the differences being in every case smaller than the mean probable error. The substances examined are, according to the Eötvös formula, non-associated when molten, and, according to the Tammann theory (this vol., ii, 193), should only form one kind of crystals. This statement is confirmed by the melting curves obtained. It is, however, remarkable that two of these substances, menthol and veratrole, are known to exist in a

second unstable form. The fusion curve for benzene is determined by means of a series of determinations of pT curves at constant volume. The method is due to Tammann (A., 1912, ii, 630). The curve is determined for pressures up to 3050 kilog., and the temperature values are found to agree with those calculated by the Tammann formula: $t = 5{\cdot}40 + 0{\cdot}0283p - 0{\cdot}00000196p^2$, within limits of $+0{\cdot}25°$ and $-0{\cdot}26°$, the mean divergence being $0{\cdot}03°$. It is shown that the coefficient dp/dt is smaller for the molten substance than for the crystalline substance, and that the value increases for both with increasing pressure. These two facts are both in accord with the Tammann theory (*loc. cit.*). The value dp_T is not constant for the different pT curves, but increases with increasing temperature. It is shown that the quantity of material employed is without influence on the p and T values of the equilibrium point between liquid and crystals, but that the dp_T values are smaller at low temperatures for smaller amounts of material than for larger amounts. This is explained by a change in the apparent compressibility of the material. The volume change Δv_{pT}, at constant temperature and constant pressure, in melting is redetermined for benzene. The values obtained confirm the Tammann formula (*loc. cit.*), and are also in good agreement with those of Tammann and Cowper (A., 1910, ii, 20). The fusion curve of Glauber's salt is determined by means of pT curves, and agrees well with that calculated from Tammann's formula: $t = 32{\cdot}6 + 0{\cdot}000507p - 0{\cdot}00000055p^2$. A method is described by which impurities may be removed from the substances examined. Finally, the relationship between the fusion curves of different substances is discussed. It is shown that the ratio between the absolute melting points of two substances at the same pressure is a constant. This formula is of the same nature as that given by Ramsay and Young for the vapour pressures. The relationship is examined for twenty pairs of substances up to pressures of about 3000 kilog., and for a given pair shown to hold very well. The constant varies for different pairs between $0{\cdot}9733$ for aniline and water, and $1{\cdot}2240$ for diphenylamine and aniline. It is further shown that $T_2/T_1 - T'_2/T'_1 = c$, where T_1 and T_2 are the melting points at a given pressure for a pair of substances, and T'_1 and T'_2 are the melting points of the same substances at a second pressure, and c is a constant. The value of c varies from zero for the pair benzylaniline, aniline to $+0{\cdot}0060$ for aniline, water, whilst sodium potassium gives $-0{\cdot}00139$, the divergence being in all cases well within the experimental error. J. F. S.

Molecular Attraction. K. K. JÄRVINEN (*Zeitsch. physikal. Chem.*, 1913, **82**, 541—574).—A mathematical paper, in which an attempt is made to deduce a formula which shall give the molecular attraction. The general form of the Newton Law of Gravitation, $F = m^2k/r^n$, is made the basis of the calculations. It is found that if $n = 5$, 6, or 7, the formula represents in some cases the observed conditions, obtained from the heat of vaporisation. In general, the value $n = 6$ is better than the other values. A formula is also deduced for calculation of the heat of vaporisation, which has the

form $(C-2{\cdot}52-C_2)/L\beta=K=1{\cdot}63$, in which β is the coefficient of cubical expansion, L the heat of vaporisation, C the molecular heat, 2·52 cal., the quantity of heat used up in increasing the velocity of the molecules, and C_2 the quantity of heat used in intramolecular work. The formulæ which are deduced from considerations of the potential of the molecules are used for calculating the heat of vaporisation of several substances, and shown to hold within 2—3%. J. F. S.

The Latent Heat of Vaporisation of Metals. EDMOND VAN AUBEL (*Compt. rend.*, 1913, **156**, 456—457).—The author has calculated the constant in Trouton's Law for the metals mercury, cadmium, zinc, and bismuth, using the values obtained by Wehnelt and Musceleanu (this vol., ii, 23) for their latent heats of vaporisation, and finds that they obey the above law. Taking the value for this constant as 20, he calculates the boiling point of magnesium as 1792°. W. G.

Mechanism of Evaporation. RENÉ MARCELIN (*J. Chim. phys.*, 1912, **10**, 680—690).—The rate at which the meniscus is lowered by evaporation in capillary tubes containing "superheated" ether or carbon disulphide at a constant pressure is measurable by cathetometer and stop-watch. The surface layer is cooled by evaporation to the temperature at which it is in equilibrium with the vapour at the given pressure. The rate at which evaporation takes place is therefore governed by the rate at which heat is conducted through the glass tube from the thermostat under the temperature gradient which establishes itself near the meniscus; thus the rate of evaporation, $v_p=M(T_b-T_p)/rdL$, where M is a constant depending on the thickness and heat conductivity of the glass, T_b is the temperature of the thermostat, T_p is the temperature of the surface layer corresponding with vapour pressure p for the given liquid, r is the radius of the tube, d the density of the liquid, and L its latent heat.

This formula was verified experimentally, and the same constant M was obtained with ether as with carbon disulphide at a variety of temperatures and pressures, and also with tubes of different bore, but the same thickness of wall. The real rate of evaporation is apparently at least ten times as great as the apparent rate in these experiments.

It is deduced from the kinetic hypothesis that in a liquid of molecular weight W and vapour pressure P at temperature T evaporating into a vapour phase at pressure p, the rate of evaporation $V=\alpha(P-p)/4d\times\sqrt{(3W/RT)}$, where α is a fraction representing the proportion of the gaseous molecules which are re-absorbed on collision with the liquid surface.

The highest values of v observed lead to $\alpha=1/100$ as a minimum, but in view of the lowering of the surface temperature in the experiments α is probably greater than 1/10.

The author's method lends itself to the evaluation of the boiling points or vapour pressures of pure liquids. The variation of v

with T at any constant pressure p being a linear function, the curve can be exterpolated to $v=0$, when T becomes the boiling point at pressure p. R. J. C.

Chemical Affinity. VIII. Crystalline Change of the Alkali Salts. JOHANNES N. BRONSTED (*Zeitsch. physikal. Chem.*, 1913, **82**, 621—640. Compare A., 1911, ii, 381, 856; 1912, ii, 736).—A continuation of the work contained in the previous papers. The double decomposition of various pairs of alkali salts is investigated in the present paper. The solution affinity and the affinity of the double decomposition are determined. To arrive at these quantities the values of the dilution affinity, solubility, and vapour pressure of the solutions at the temperature of the experiments must be known. These values have been determined in the present work. The dilution affinity is calculated from freezing-point measurements for sodium chloride, sodium nitrate, sodium chlorate, sodium bromide, sodium sulphate, sodium fluoride, potassium iodide, potassium fluoride, potassium chlorate, potassium sulphate, potassium nitrate, and potassium chloride. From these measurements it is seen that work of dilution is generally less for a potassium salt than for the corresponding sodium salt. The solubilities of the above-mentioned salts at 100° are determined, and the following values obtained in grams per 100 grams water: $KBr=105{\cdot}3$; $NaCl=39{\cdot}22$; $NaI=303{\cdot}4$; $NaBr=121{\cdot}9$; $NaClO_3=204{\cdot}9$; $NaNO_3=176{\cdot}3$; $KCl=56{\cdot}05$; $KI=207{\cdot}7$; $KClO_3=57{\cdot}7$; $KNO_3=244{\cdot}8$; $Na_2SO_4=42{\cdot}19$; $K_2SO_4=24{\cdot}1$. The vapour pressures of the saturated solutions of the above salts at 100° were also determined, and the following values obtained: $NaCl=561{\cdot}5$ mm.; $NaBr=382{\cdot}9$; $NaI=174{\cdot}4$; $NaF=734{\cdot}0$; $NaClO_3=410{\cdot}0$; $NaNO_3=418{\cdot}9$; $Na_2SO_4=684{\cdot}7$; $KCl=567{\cdot}8$; $KBr=526{\cdot}3$; $KI=427{\cdot}0$; $KF=174{\cdot}3$; $KClO_3=668{\cdot}3$; $KNO_3=496{\cdot}0$; $K_2SO_4=723{\cdot}9$. From these data the energy change in the double decomposition of pairs of the salts mentioned is calculated, and the following results obtained: $NaF+KCl \longrightarrow NaCl+KF-6830$ cal.; $NaF+KBr \longrightarrow NaBr+KF-8520$ cal.; $NaF+KI \longrightarrow KF+NaI-10150$ cal.; $NaCl+KBr \longrightarrow KCl+NaBr-1690$ cal.; $NaCl+KI \longrightarrow KCl+NaI-3320$ cal.; $NaBr+KI \longrightarrow NaI+KBr-1630$ cal.; $NaCl+KNO_3 \longrightarrow NaNO_3+KCl-840$ cal.; $NaCl+KClO_3 \longrightarrow NaClO_3+KCl-2270$ cal.; $NaCl+\frac{1}{2}K_2SO_4 \longrightarrow \frac{1}{2}Na_2SO_4+KCl-340$ cal.; $NaNO_3+KClO_3 \longrightarrow NaClO_3+KNO_3-1430$ cal. The values obtained above by the new method are compared with those obtained by the older electrochemical method (*loc. cit.*), and a very good agreement is found between them. In the double decomposition between haloids of sodium and potassium, the tendency is, that the two elements of lowest atomic weights and those of highest atomic weights will combine. J. F. S.

Fractional Distillation with Steam. L. GURWITSCH (*Zeitsch. angew. Chem.*, 1913, **26**, 102—103).—From a consideration of the formula put forward by Vresvski (A., 1910, ii, 1038) for the composition of the vapour given off from a mixture of volatile liquids, the author deduces that when the temperature of

vaporisation of such a mixture is lowered, the proportion of the constituent with the lesser molecular latent heat of vaporisation should increase in the vapour phase. The temperature of vaporisation is lowered by steam distillation, and, therefore, in the case of a mixture of homologues, the proportion of the more volatile constituents should increase in the distillate.

The above deduction has been verified by experiments with a purified Russian illuminating oil (Meteor oil), consisting of a mixture of saturated hydrocarbons and naphthenes. In order to avoid dephlegmation, the whole of the distilling flask, together with the greater part of the side-tube, was immersed in the oil-bath. Instead of passing steam through the flask, water was added to the contents, together with numerous pieces of pumice stone, so that the surface of contact between the water and the oil should be as great as possible. T. S. P.

Triferrocarbide (Cementite), Fe_3C. OTTO RUFF and EWALD GERSTEN (*Ber.*, 1913, **46**, 394—400).—Jermilov (*J. Russ. Metall. Soc.*, 1911, 357—366) has found that the molecular heat of formation of triferrocarbide is $+2{\cdot}27$ Cal., whereas the authors have previously found it to be $-15{\cdot}1$ Cal. (A., 1912, ii, 260). In the authors' calculations the only thermochemical datum which had not been determined by themselves was the heat of oxidation of ferrous oxide to ferroso-ferric oxide (Fe_3O_4), the value used being that due to Le Chatelier. They have consequently redetermined this value, and find $28{\cdot}6 \pm 1{\cdot}8$ Cal. as the heat of oxidation of FeO to $\frac{1}{3}Fe_3O_4$, which is in fairly good agreement with Le Chatelier's value, $25{\cdot}7$ Cal. Using this value, the molecular heats of formation given in the previous paper (*loc. cit.*) are corrected to the following values: Fe_3O_4, $267{\cdot}1 \pm 0{\cdot}2$ Cal.; FeO, $60{\cdot}4 \pm 1{\cdot}8$ Cal.; Fe_3C (from α-iron and graphite), $-15{\cdot}3 \pm 0{\cdot}2$ Cal. The value for triferrocarbide is thus practically unaltered. Jermilov's value is due to the fact that he has taken too high values for the molecular heats of formation of Fe_3O_4 and FeO. T. S. P.

Heat of Formation of Additive Organic Compounds. I. Picrates. BARTOLO L. VANZETTI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 103—109).—The following heats of formation have been determined: naphthalene picrate (in two experiments), 1450 cal., 954 cal. (compare Brönsted, A., 1912, ii, 21); *iso*safrole picrate, 4430 cal. (mean of five experiments); eugenol picrate, 5940 cal.; 2-methylindole picrate, 2082 cal. R. V. S.

Physico-chemical Investigations with Aromatic Stereoisomeric Acids. I. WALTER A. ROTH and RICHARD STOERMER (*Ber.*, 1913, **46**, 260—280).—The mol. heats of combustion, dissociation constants, and solubilities of a number of carefully purified isomeric acids have been determined. The general rule indicated by Stohmann (A., 1892, ii, 153) that the stable acids have the lower heats of combustion and smaller dissociation constants, is confirmed. Some liquid esters have also been calorifically and optically

examined. The results are given in the following table, where *V* min. is the reciprocal of the solubility, that is, the number of litres of water required to dissolve 1 Mol. at 25°.

Substance.	M. p.	Heat of combustion.	Dissociation constant $\times 10^{-5}$.	*V* min.
Cinnamic acid	132—133°	1041·4 Cal.	3·81	270
*allo*Cinnamic acid	58°	1048·1	14·10	17·5
Methylcoumaric acid	182—183	1162·4	2·07	2120
Methylcoumarinic acid	91—92	1168·6	5·40	<250
Ethylcoumaric acid	133—134	1317·9	2·12	2110
Ethylcoumarinic acid	101—102	1324·4	4·54	333
Propylcoumaric acid	105—106	1472·0	—	—
Propylcoumarinic acid	83—84	1477·9	—	—
*Butylcoumaric acid	89—90	1632·4	—	—
*Butylcoumarinic acid	53—54	1638·8	—	—
i-Amylcoumaric acid	79—79·5	1791·5	1·4	11900
i-Amylcoumarinic acid	80—80·5	1793·1	4·24	2070
Acetylcoumaric acid	154—155	1209·0	5·0	1430
Acetylcoumarinic acid	85	1213·1	11 (approx.)	180
Piperonylacrylic acid	238	1068·8	2·5	7000 (approx.)
*allo*Piperonylacrylic acid	99—100	1077·8	10·91	<400
p-Hydroxycinnamic acid	206	992·4	2·34	126
allo-*p*-Hydroxycinnamic acid	126—127	997·5	8·44	41·6
p-Methoxycinnamic acid	170	1164·2	2·1	2500
allo-*p*-Methoxycinnamic acid	66	1173·6	9·29	90·6

Ethyl methylcoumarinate: b. p. 291—292·5°. Heat of combustion, 1495·7 Cal.; $D_4^{16·7}$ 1·1016; n_C 1·54697; n_D 1·55399; n_F 1·57303.

Methyl ethylcoumarate: b. p. 306—307°. Heat of combustion, 1491·8 Cal.; $D_4^{18·75}$ 1·0998; n_C 1·56318; n_D 1·57188; n_F 1·59680; n_G 1·6233.

Methyl ethylcoumarinate: b. p. 288·5—289·5°. Heat of combustion, 1496·5 Cal.; $D_4^{16·45}$ 1·0981; n_C 1·54724; n_D 1·55431; n_F 1·57381.

The compounds marked with an asterisk are new, and will be described in a future paper, whilst the majority of the others are the fruit of Stoermer's researches (A., 1910, i, 114; 1911, i, 295).

The "heat values" for particular substituents agree with Stohmann's; for example, the heats of combustion of the methyl esters are about 173 Cal. higher than those of the free acids. The proximity of the substituent to the carboxyl group has a great influence on the dissociation constant. Whereas *o*-methoxybenzoic acid has the constant $8·15 \times 10^{-5}$, methyl coumaric acid has the value $2·07 \times 10^{-5}$, and methyl coumarinic acid, $5·4 \times 10^{-5}$. A relation is established between the amount of transformation which takes place when the stable acid is exposed to ultraviolet light, and the ratio of the dissociation constants. When this ratio is smallest the transformation is most complete.

The optical properties of the three esters agree with those of the esters of non-substituted cinnamic acids described by Brühl (A., 1897, ii, 129). The stable forms have the higher densities and refractive indices, whilst an ether group in the ortho-position raises the specific exaltation slightly and the dispersion considerably.

J. C. W.

Densities at the Critical Point. MAURICE PRUD'HOMME (*J. Chim. phys.*, 1912, **10**, 636—639).—According to van der Waals' equation, the critical volume should be three times the volume at absolute zero, but as is well known, for many substances it assumes a value in the neighbourhood of four times. When van der Waals' equation is solved for density it is found that the three roots:

$$d_1 + d_2 + d_3 = m/b = \text{a constant} = m/n_1b + m/n_2b + m/n_3b,$$

where m is the molecular weight. At the critical point where the densities of vapour and liquid become equal, $d_1 = d_2$. Hence $2/n_1 + 1/n_3 = 1$. This equation has only two solutions in integers, namely, $n_1 = n_3 = 3$ and $n_1 = 4$, $n_3 = 2$.

The first solution is the ordinary one, where $V = 3b$. The second solution corresponds with the exceptional cases (formates, methyl acetate, fluorobenzene, etc.), where $V = 4b$, but it remains to give an explanation of the third root, namely, $V = 2b$, the density d_3 being twice the critical density, that is, $d_3 = d_1 + d_2$. According to Cailletet and Mathias $(d_1 + d_2)$ is a linear function of the temperature, whether n is normal or not. Hence, d_3 is also a linear function of the temperature, and in the exceptional cases an infinitesimal variation in the temperature corresponds with a variation in d_3, which is the sum of the variations in d_1 and d_2.

The author interprets d_3 as representing the density of the surface film separating the liquid from the vapour. At the critical point the density in the surface film must be twice the critical density for the substances mentioned. R. J. C.

Pressure, Density, and Expansion of Saturated Water Vapour. KONRAD W. JURISCH (*Zeitsch. physikal. Chem.*, 1913, **82**, 385—402).—A theoretical mathematical paper, in which the relationships of the pressure, density, and expansion are discussed.

J. F. S.

The Influence of Dissociation on the Density of Saturated Water Vapour. KONRAD W. JURISCH (*Zeitsch. physikal. Chem.*, 1913, **82**, 575—580; see also preceding abstract).—A mathematical paper, in which it is shown that the maximum density of water vapour lies at $T = 985°$. The diminution of density at higher temperatures is shown to be due entirely to a dissociation of the water vapour; a minimum density lies approximately at $T = 2260°$, at which point 55·66% is dissociated. J. F. S.

The Influence of Dissociation on the Expansion of Saturated Water Vapour. KONRAD W. JURISCH (*Zeitsch. physikal. Chem.*, 1913, **82**, 581—586; see also preceding abstracts).—A mathematical paper, in which it is shown that there is a maximum of the expansion at $T = 1000°$ and a minimum at $T = 1170°$. It is shown that this is due entirely to the dissociation, since this is the only volume changing function which is operative in the region mentioned (see last abstract). J. F. S.

The Temperature-coefficient of the Molecular Surface Energy and the Molecular Cohesion. PAUL WALDEN and RICHARD SWINNE (*Zeitsch. physikal. Chem.*, 1913, **82**, 271—313. Compare A., 1911, ii, 97; 1912, ii, 628).—New determinations of the density and surface tension of a number of substances are given for temperatures between 20° and 100°. The substances investigated are: octinene, undecinene, hexa-ethylbenzene, myricyl alcohol, the triethyl ester of aconitic acid, diethyl ester of sebacic acid, di*iso*amyl ester of sebacic acid, *l*-amyl ester of bromo-*n*-butyric acid, tetrachloroethane, tetrabromoethane, and dichlorobromomethane. The specific cohesion, free surface tension, free molecular surface energy, and the temperature-coefficients of the free molecular surface energy (dMa^2/dt) and molecular cohesion, dE_0/dt, were calculated. The results obtained in these experiments are compared with similar values calculated by other investigators, and it is shown: (1) That the coefficients dMa^2/dt and dE_0/dt increase as an homologous series is ascended. (2) That the substitution of hydrogen by the ethyl group causes an increase in the coefficients for members of the benzene series. (3) For alcohols the coefficient dMa^2/dt increases very much as the series is ascended. (4) The replacement of hydrogen by chlorine, iodine, or bromine causes an increase in the coefficients, which is greatest in the case of the iodine substitution and least in that of chlorine.

It is also shown that replacement of oxygen by sulphur causes the value dMa^2/dt to increase. The replacement of an atom of lower atomic weight by one of higher atomic weight causes the coefficient dMa^2/dt to increase. This is demonstrated in the case $CCl_4 \dashrightarrow SiCl_4 \longrightarrow SnCl_4$. For eight of the substances investigated the value dE_0/dt exceeds the normal value given by Ramsay and Shields, and in consequence these substances ought to be regarded as dissociated. On the other hand, the Dutoit-Mojoïu vapour pressure expression (A., 1909, ii, 470) and the Walden expression for the value dE_0/dt (A., 1908, ii, 1014) point to these liquids being normal. The Ramsay-Shields formula for the normal value of dE_0/dt is discussed, as also is the Guye theory of the dissociation in the surface layer. It is shown that the values dMa^2/dt and dE_0/dt are of an additive nature, and from an examination of 316 substances formulæ are deduced which give a means of calculating these coefficients. The formulæ for normal liquids are:

$$dMa^2/dt = -[0{\cdot}00027(\Sigma\sqrt{A}) + 0{\cdot}0103],$$
$$dE_0/dt = -[0{\cdot}011(\Sigma\sqrt{A}) + 1{\cdot}90],$$

where $\Sigma\sqrt{A}$ is the sum of the square roots of the atomic weights of the component atoms.

The agreement between the values of the coefficients calculated by the above formulæ and those obtained from experimental results is, on the whole, good. For elements and halogen derivatives the agreement is best; for hydrocarbons a variation of about 12% is found in some cases; esters, 6% is about the maximum divergence; oxides, 9% divergence, but the agreement is generally good; amines,

a mean divergence of about 10%, but some amines differ far more than this figure. Nitro-compounds, acid amides, nitriles, and hydroxy-derivatives are less in accord with the formulæ. J. F. S.

Dimensions of the Surface Energy of Solid Substances. WILLIAM J. JONES (*Zeitsch. physikal. Chem.*, 1913, **82**, 448—456).—The formulæ used by Ostwald (A., 1900, ii, 730), Hulett (A., 1901, ii, 493), and Freundlich for calculating the surface energy of solid substances are critically discussed. The author deduces a formula from considerations of a thermodynamical reversible process, which he applies to the experimental data of Hulett (*loc. cit.*). The formula is given by:

$$2\sigma/\rho(1/r_2 - 1/r_1) = RT/M[(n-1)(\gamma_1 - \gamma_2) - n/m - 1 \log_e(1-\gamma_1)/(1-\gamma_2) + m/(m-1) \cdot \log_e \gamma_1/\gamma_2],$$

in which r_1 and r_2 are the radii of the solid particles which are dissolving and being formed in the saturated solution, σ the surface energy per unit area, ρ the density of the solid, γ_1 and γ_2 the degrees of dissociation of the solid substance of radii r_1 and r_2 in the saturated solutions, m is a constant having a value between 1·36 and 1·55, M is the molecular weight, n is the number of ions furnished by the salt, and R and T have their usual meanings. The surface energy for gypsum calculates to 1050 ergs. per sq. cm., and for barium sulphate the value 1300 ergs. per sq. cm. is obtained. J. F. S.

Method of Determining "*a*" of van der Waals' Equation from the Surface Tension. ALBERT P. MATHEWS (*J. Physical Chem.*, 1913, **17**, 154—161).—The various known methods of computing a involve the assumption that b, the real molecular volume, is unaffected by changes of temperature and pressure. The author's method, which is based on the surface-tension formulæ of Young and Eötvös, is independent of any assumption as to the value of b.

Young's formula, $S = rK/3$, equates the surface tension to the radius of action r of cohesive attraction and the total cohesive pressure K. The rival formula, $S = 3rK/20$, due to Rayleigh, is rejected by the author because it leads to improbable values of a according to his method of treatment.

van der Waals' constant a, which expresses the cohesive power, may be equated to NM^2K, where N is the number of molecules in volume V. Hence, $a/V^2 = M^2K/v^2$, where v is the space occupied by a single molecule. At absolute zero, when the molecules are in contact, $r = v_0^{\frac{1}{3}}$. Hence, $Sv_0^{\frac{2}{3}} = M^2K/3v_0$.

Now, according to Eötvös' formula, $Sv_0^{\frac{2}{3}} = 2·19(T_c - 6)/N^{\frac{2}{3}}$. By equating the two values of $Sv_0^{\frac{2}{3}}$ and assuming N to have the value $6·21 \times 10^{23}$, the author deduces that $M^2K = 9·045 \times 10^{-16}(T_c - 6)v_0$. From M^2K, a and b can readily be calculated.

The values of b_c thus calculated for ether, pentane, and *iso*pentane are shown to be a constant fraction of the critical volumes, $V_c/b_c = 2·074$. This figure is very close to the various estimates by

van der Waals, and departs considerably from the theoretical value, namely, 3.

The values of M^2K calculated by the author for twenty-seven substances with the aid of Young's surface-tension data are very similar to the values obtained by the ordinary formula, but in some instances differ markedly from these. The new formula is considered to give the more accurate values because these exhibit more clearly the relationship of cohesion to molecular weight and valency deduced by the author. R. J. C.

Properties of a Liquid Connected with its Surface Tension. RICHARD D. KLEEMAN (*Proc. Camb. Phil. Soc.*, 1913, **17**. 149—159. Compare this vol., ii, 26).—In the previous paper a formula was deduced for the surface tension of a liquid on the assumption that there is no transition layer at the surface. By substitution of the experimentally determined surface tension, the formula may be inversely applied to calculate the absolute weight of a molecule. From the data for ethyl ether, carbon tetrachloride, methyl formate, and benzene, the mean weight of the hydrogen atom, which is obtained from the formula, is $1·56 \times 10^{-24}$ gram. This is in good agreement with the value $1·61 \times 10^{-24}$ gram obtained by Rutherford from experiments on the α-particle.

A number of relations have also been obtained connecting the surface tension of a liquid with its internal heat of vaporisation, compressibility, coefficient of expansion, and other quantities. Some of these may be utilised for the detection of association and estimation of the extent to which association occurs. H. M. D.

Determination of the Viscosity of Caoutchouc Solutions. J. G. FOL (*Chem. Weekblad*, 1913, **10**, 154—174*).—From the results of a number of determinations of the viscosity of a specimen of caoutchouc from Java, the author makes the following inferences: (1) In the determination of relative viscosity the type of viscometer employed has an important influence on the results. (2) The diameter of the capillary in Ostwald's viscometer should not be too small. (3) Violent shaking during the making of the solution considerably affects the viscosity. (4) There is a remarkable relation between the relative viscosity of caoutchouc solutions of similar concentration. (5) The viscosity is affected by the length of time which has elapsed between the preparation of the solution and the determination, especially for solutions of high concentration. (6) The relative viscosity of the solutions of the samples examined was affected by the temperature, but not the absolute viscosity. (7) With concentrated solutions the time of efflux diminishes between successive determinations, the greatest difference being observed between the first and second reading.

Details of a method of determining the viscosity of caoutchouc solutions are given. A. J. W.

Relationship between Molecular Weight and Turbulence Viscosity Constant. WALTHER SORKAU (*Physikal. Zeitsch.*, 1913, **14**, 147—152. Compare A., 1911, ii, 793; 1912, ii, 900).—From

* and *Zeitsch. Chem. Ind. Koll.*, 1913, **12**, 131—147.

experiments on the hydraulic flow of methyl propionate, propyl acetate, and butyl acetate at temperatures between 15° and 40°, it is found that the connexion between the time of flow (t), the pressure (p), and the temperature (θ) in the primary stage of turbulence is expressed by $t=C/p^{0\cdot658}\,.\,e^{\theta/273}$. The value of C for ethyl acetate is 114·3, methyl propionate 115·2, propyl acetate 125·8, and for butyl acetate 130·2. The constant C appears to be related to the molecular weight (M) by means of the equation $C=12\cdot25\sqrt{M}$.

In the third stage of turbulence, in which under very high pressures the liquid appears to be projected through the capillary like a frictionless, solid, cylindrical column, the time of flow is given by $t=C'/\sqrt{p}$, in which C' is equal to 33·4 for butyl acetate, 34·0 for propyl acetate, 34·6 for ethyl acetate, and 34·8 for methyl propionate.

The sequence, which is obtained when the esters are arranged according to the viscosity constants, is thus seen to be reversed when the numbers relating to the primary stage are replaced by those characteristic of the third stage. H. M. D.

The Adsorptive Power of the Hydroxides of Silicon, Aluminium, and Iron. VI. PAUL ROHLAND (*Zeitsch. anorg. Chem.*, 1913, **80**, 174—175. Compare A., 1912, ii, 1145).—The colloids of clay have very little adsorptive power for azo-dyes, and the colouring matter of unknown constitution which is present in the waste water from sulphite cellulose is not adsorbed. C. H. D.

Adsorption. VIII. Adsorption by Starch in Mixed Solutions. ADAM V. RAKOVSKI (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 7—12. Compare this vol., ii, 114).—The author has investigated the adsorption by starch of alkali in presence of salts and of two alkalis simultaneously.

Potassium and sodium salts of organic and inorganic acids cause considerable increase in the amount of sodium hydroxide adsorbed by starch, the carbonates being appreciably less effective than the other salts; the extent of the adsorption increases continuously with the concentration of the salt. The adsorption of the large proportions of alkali thus occurring is not accompanied by appreciable gelatinisation of the starch.

Barium salts exert a similar influence on the adsorption of barium hydroxide by starch, but the small amount of ammonium hydroxide adsorbed by starch is scarcely affected by the presence of ammonium salts. A more complicated course is followed by the adsorption when the hydroxide and salt possess dissimilar cations. The systems $NaOH+\frac{1}{2}BaCl_2$ and $\frac{1}{2}Ba(OH)_2+NaCl$ give identical results.

With the system $Ba(OH)_2+NaOH$ both alkalis are adsorbed, the former to a higher and the latter to a lower extent than when present alone, so that the adsorption of barium ions is raised and that of sodium ions diminished by excess of hydroxyl ions.

Ammonium hydroxide is practically without influence on the adsorption of sodium or barium hydroxide. T. H. P.

Adsorption. IX. Adsorption and Hydrolysis. ADAM V. RAKOVSKI (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 13—21).—The assumption is made that the action of alkali on starch yields "starchates" or chemical compounds analogous to alkoxides and sucrates. Since starch adsorbs both alkali and water simultaneously, in the solid phase hydrolytic decomposition of the starchate would occur, these changes being represented by the equation:

$$AmH + MOH \rightleftarrows AmM + H_2O,$$

where AmH indicates starch and AmM the starchate.

If the initial concentration of the alkali is a milli-equivalents in volume v, and the weight of starch m grams or $1000m/162{\cdot}08n$ or N milli-equivalents, and if, further, after the establishment of equilibrium, there are present x milli-equivalents of starchate, $N-x$ of free starch and $a-x$ of free alkali, then $x/(N-x)(a-x)=k_n$ should give constant values. The index n of the constant represents the number of $C_6H_{10}O_5$ groups present in the given starchate per equivalent of metal.

With potato and St. Vincent and Bermuda arrowroot starches constant values are obtained with lithium, sodium, and potassium hydroxides for k_n if $n=3$. In the case of starches with small granules, such as rice starch, the constancy is less satisfactory, and with wheat starch constant values are obtained for k_4. The starchates formed by the two latter starches hence differ in type from those given by potato and arrowroot starches.

With barium, strontium, and calcium hydroxides, less concordant numbers are obtained, but these are in fairly good agreement with the value $n=1$.

The constancy of the values of k, the negligible influence of change of temperature on the adsorption of alkali hydroxides by starch, and the intensification of the adsorption in presence of salts (compare preceding abstract), render highly probable the existence of starchates. T. H. P.

Influence of the Geometric Form of Solids on the Chemical Reactions which they Undergo. G. REBOUL (*Compt. rend.*, 1913, **156**, 548—550. Compare *ibid.*, 1912, **155**, 1227).—The author has measured any change of rate of attack of a gas on a solid, by varying the curvature of the solid, in such cases as the action of iodine vapour on silver, and finds that, either at the ordinary pressure or under reduced pressure, the action of the gas on the solid is most rapid at those points where the mean curvature is the greatest, and explains the phenomenon on the grounds of capillarity, the gaseous concentration being greatest at the points where the radius of curvature is least. W. G.

Capillary Phenomena in Gases. Extension of Laplace's Formula to the Contact Solid-gas. G. REBOUL (*Compt. rend.*, 1913, **156**, 688—691).—Working with copper cylinders of different diameter, subjected to the gas from vulcanised caoutchouc, the author shows that the amount of copper compound formed is given by $a^q = b/2R + c$, where q is the thickness of the layer of copper

compound formed, R the radius of the cylinder, and a, b, c three constants varying slightly with the pressure of the vapour. Assuming that there is an increase in the concentration of the gas at the surface of the metal, he obtains $a^q = k'\Gamma + c$, where Γ is the concentration of the reacting gas, which is thus a linear function of $1/R$; thus there is at each point of the surface of separation of solid-gas an excess of pressure proportional to the mean curvature, and so Laplace's formula holds good for such cases. W. G.

The Differential Tonometry of Solutions and the Theory of Arrhenius. EUGÈNE FOUARD (*Compt. rend.*, 1913, **156**, 622—625. Compare A., 1911, ii, 267, 1071; 1912, ii, 436).—A photograph and description is given of a tonometer, in which the author has made determinations on equimolecular solutions of potassium chloride and sucrose, and has obtained results which are in agreement with his measurements of osmotic pressure (*loc. cit.*), and thus opposed to the ionic theory of solution. W. G.

[Stratified Systems.] RAPHAEL E. LIESEGANG (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 74—77).—It is shown that the experiments described by Hatschek (A., 1912, ii, 439) cannot be accepted as disproving Ostwald's view that the formation of stratified layers of insoluble substances as a result of slow diffusion in jellies is due to the intervention of supersaturation phenomena.

The slow interaction of copper nitrate and sodium carbonate, which occurs when silicic acid jellies containing the two substances are brought into contact, has been found to give rise to irregularly stratified precipitation layers of basic copper carbonate, the structure of which resembles closely that shown by certain malachites.
H. M. D.

New Apparatus for Quantitative Dialysis. A. GOLODETZ (*Chem. Zeit.*, 1913, **37**, 259—260).—In order to dialyse a substance exhaustively, using a small volume of water, the material is enclosed in a suitable membrane, which is so placed in a modified Soxhlet apparatus that it presents as large a surface as possible to the water. Should it not be advisable to heat the product above 50° a capillary tube may be attached and ebullition maintained under reduced pressure. J. C. W.

Influence of Chemical Constitution on the Thermal Properties of Binary Mixtures. I. PAUL PASCAL and LÉON NORMAND (*Bull. Soc. chim.*, 1913, [iv], **13**, 151—161).—This is the first of a series of papers in which the authors propose to deal with binary mixtures of compounds of the type R–α–β–R′, where R and R′ are aromatic nuclei and α and β may be $\cdot CH_2\cdot$, $\cdot CH\colon$, $\cdot C\vdots$, $\cdot NH\cdot$, $\cdot N\colon$, or $\cdot O\cdot$. Such investigations have been made already by Beck (A., 1904, ii, 646) and by Bruni (A., 1912, ii, 1043). The authors propose to ascertain (1) whether "mixed crystals" are formed, and, if so, over what range of temperature, and (2) what relationship exists between the structures of the two components and the

property of simultaneous crystallisation. The mixtures now examined are: (1) stilbene with (*a*) dibenzyl, (*b*) tolane, (*c*) azobenzene, (*d*) hydrazobenzene; (2) tolane with (*a*) dibenzyl, (*b*) azobenzene, (*c*) hydrazobenzene; (3) dibenzyl with (*a*) hydrazobenzene, (*b*) azobenzene; and (4) azobenzene with hydrazobenzene. Tables and graphs showing the fusion curves of these mixtures are given. They show that compounds of the type R–*α*–*α*–R taken two at a time give a continuous series of mixed crystals, and are probably strictly isomorphous, although there are shades in this isomorphism, thus: in the case of a binary mixture of two compounds having the same multivalent central atoms, or the same central linkings, the fusion curve generally shows no minimal point, whilst a minimal point develops more and more clearly as differences in the two constitutional characters mentioned become more noticeable, and is most marked in a mixture of hydrazobenzene, NHPh·NHPh, and tolane, CPh⁝CPh. Further, hydrazobenzene shows an unforeseen tendency to produce minimal points on the curves, possibly owing to the ease with which its ·N⁚ atoms may become quinquevalent.

T. A. H.

Chemical and Crystal Molecules. EVGRAF S. FEDOROV (*Zeitsch. Kryst. Min.*, 1913, **52**, 22—43).—Several examples are quoted from the author's tables (A., 1912, ii, 772). In considering the symmetry relations of the chemical molecule the arrangement of the peripherically placed radicles must be taken into account in addition to the nucleus itself. As a rule, the symmetry relations shown by the crystal cannot be expressed by the chemical molecule alone, and two or more of these must be united to form the crystal molecule.

L. J. S.

Formation of Crystal Faces. A. BERTHOUD (*J. Chim. phys.*, 1912, **10**, 624—635).—According to Curie, crystals take the habit which gives them the minimum of superficial energy, so that the relative areas of the faces depend on their capillary constants. A crystal departing from the equilibrium shape when placed in a solution of suitable strength should dissolve from some faces and grow on others.

Actually the differences of solubility in crystals are so minute as to be without influence on their crystalline habit in comparison with the effect of different rates of crystallisation along different axes. Taking the surface energy of two faces of a crystal in its normal habit as of the order 100 and 800 ergs per sq. cm. respectively (Hulett), the author calculates that even in crystals departing very considerably from the normal habit an appreciable difference in solubility can only arise when the dimensions are microscopic. Surface energy might come into play in extreme cases, as, for example, in preventing a substance from crystallising in thin plates when normally it crystallises in slender needles.

The main factors which influence crystalline habit are the internal structure of the crystals and the degree of supersaturation and the nature of the concentration and other currents in the solution

during deposition. According to Noyes and Whitney (1897), the dissolution of a crystal is governed by the rate of diffusion of the dissolved molecules across the zone of falling concentration which, being replenished instantaneously from the crystal, remains saturated on one side. Le Blanc has applied this theory to the reverse process of crystallisation. The author agrees with Wagner that Le Blanc's theory fails to account for the varying rates of crystal growth on different faces. Wagner suggests that the thickness δ of the diffusion zone varies from one face to another, but δ being at least 0·03 mm. with the most violent agitation (Brunner), is not likely to be influenced by forces of molecular magnitude at the crystal surface.

The rate at which equilibrium tends to establish itself between a given area of crystal surface S and the solution is proportional to the difference in the concentration of the saturated solution c_0 and the solution in immediate contact with the crystal c'. Thus, $dx/dt = kS(c' - c_0) = SD(c - c_0)/(\delta + D/k)$, where k is the velocity constant of crystallisation of the given surface, D the diffusion constant, and c the mean concentration in the diffusion zone. This formula reduces to that of Noyes and Whitney when D/k is very small in comparison with δ, that is, when the solution is absolutely still. The more nearly this condition is attained in practice the more nearly the crystal faces approximate to equal rates of growth, and facets may then appear which are not seen when the solution has been agitated. R. J. C.

Chemical Analogies of Substances Showing a Crystallographic Relation to Potassium Sulphate. EVGRAF S. FEDOROV (*Zeitsch. Kryst. Min.*, 1913, **52**, 11—21).—A variety of substances of the hypohexagonal type having nearly the same symbols as potassium sulphate fall together in the author's tables (A., 1912, ii, 772), for example, SO_4K_2, $BeF_4(NH_4)_2$, $HgBr_4Cs_2$, $ZnCl_4K_2$, $CuCl_4(NMe_4)_2$, etc. These exhibit the same type of chemical formula (although the numbers of atoms and the valencies differ); and they are described as isotectonic substances, and their crystals as isogonal.

L. J. S.

Efflorescence of Crystals under Water. MORRIS FORT (*Chem. News*, 1913, **107**, 86).—If slightly effloresced crystals of sodium sulphite, $Na_2SO_3,7H_2O$, are placed in an excess of water in a test-tube, the opaque outer crust dissolves, and the crystals become clean and bright. On gently warming, the crystals rapidly become opaque and powdered in appearance, and analysis shows them to have effloresced to a considerable extent. The author considers that the best explanation is that dehydration of the crystals, due to rise in temperature, takes place faster than solution can be effected.

T. S. P.

Liquid Crystals of Ammonium Oleate. A. MLODZIEJOVSKI (*Zeitsch. Kryst. Min.*, 1913, **52**, 1—10).—The so-called liquid crystals of ammonium oleate may be obtained by the evaporation at the

ordinary temperature of a solution in water and alcohol. They are only formed in the presence of water or at a sufficiently high temperature, and by the addition of more water they exhibit myelin forms. The conclusion is drawn that the structure observed is of the nature of an emulsion rather than that of liquid crystals (compare A., 1912, ii, 109). L. J. S.

Nature of the Electrical Synthesis of Colloids. CARL BENEDICKS (*Koll. Chem. Beihefte*, 1913, **4**, 229—260. Compare Kutscherov, A., 1912, ii, 1148; Benedicks, this vol., ii, 99).—The micro-structural changes which are exhibited by the surfaces of the electrodes after electrical disintegration have been investigated with the object of throwing light on the nature of the disintegration process. The apparatus employed was practically identical with that described by Svedberg, ethyl ether being used as dispersive medium, and the current passed between electrodes of various metals and alloys.

The results obtained indicate that the process is essentially thermo-mechanical. When the conditions are such that arc discharge takes place for a very short time interval, as may easily be arranged if the current is furnished by an induction coil and a Leyden jar is placed in parallel with the discharge gap, it is found that the surfaces of the electrodes exhibit well-formed, eruptive craters, which are attributed to the melting of the metal under the influence of the discharge. When the discharge ceases, the surrounding liquid comes in contact with the hot metal, and this is supposed to be directly responsible for the disintegration of the electrodes. In support of this view it has been found that exactly similar crater-like structures can be obtained when a gentle current of hot air is allowed to impinge on the surface of a highly viscous substance, such as asphalt.

In accordance with the thermo-mechanical nature of the process, the most important factors in connexion with the electrical disintegration process are the latent heat of liquefaction and the thermal conductivity of the disintegrating metal.

Ultra-microscopic observations, made with the colloidal metal solutions obtained by Svedberg's method, have shown that the particles are spherical, the diameter varying over a wide range with an upper limit of about 5μ. H. M. D.

[Preparation of a Dispersoid Solution of any Substance.] P. P. VON WEIMARN (*Koll. Chem. Beihefte*, 1913, **4**, 175—194).—A theoretical paper in which the author discusses the conditions under which it is possible to obtain any substance in the form of a dispersoid solution. H. M. D.

Physical Properties of Colloidal Solutions. JOSEF FRANK (*Koll. Chem. Beihefte*, 1913, **4**, 195—228).—Measurements have been made of the volume changes which accompany the absorption of water by colloids, of the heat of liquefaction, and the coefficient expansion of various colloids, and also of the viscosity of certain colloidal solutions.

The absorption of water by gelatin or starch and of colophony

by oil of turpentine is attended by contraction, the magnitude of which, when referred to unit volume of the gelatin, starch, or oil of turpentine, is independent of the composition of the mixture. The transition from the solid to the liquid state shows no appreciable absorption of heat according to experiments with colophony, mixtures of colophony and oil of turpentine, and mixtures of gelatin and water. The coefficient of expansion of gelatin–water mixtures increases with rise of temperature to a maximum, afterwards falling to a minimum, and at still higher temperatures increasing again. The maxima and minima become more sharply defined as the proportion of gelatin in the mixture increases, and at the same time the temperatures at which they occur are found to rise. In the case of colophony and its mixtures with oil of turpentine, the coefficient of expansion rises with the temperature, at first quickly, then more slowly, and later again more rapidly. As the proportion of oil of turpentine in the mixture increases, the coefficient of expansion becomes greater, but the rate at which the coefficient increases with temperature becomes less.

From the examination of a large number of colloidal solutions of dyes, dissolved in water and alcohol, it has been found that the effect of the dye on the viscosity is in general greater for alcoholic than for aqueous solutions. The viscosity of solutions of malachite-green and safranine was found to vary with time. H. M. D.

Thermo-chemical Researches on Solution and their Bearing on Theoretical Considerations concerning the Relations between the Chemical Properties of Solutions. Nicolas A. Kolosovski (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 22—52.* Compare this vol., ii, 22).—On the assumption that the change of any property for mixtures or chemical compounds is an external manifestation of the action of chemical affinity, it may be asserted that, in the case of aqueous solutions of electrolytes, the divergence of any property from the mean of those of the solvent and solute is a consequence of the formation of hydrates. Assuming, further, the formation of hydrates of the ions, all such divergences must necessarily follow an additive law.

In order to ascertain the limits of applicability and a measure of the general character of this proposition, the author examines the relations between the values obtained, for various salts, of: (1) the lowering (V) of the coefficient of distribution of acetic acid between water and ether under the influence of 1 gram-equivalent of dissolved salt (compare A., 1911, ii, 591, 705); (2) the change (V') in the temperature of separation of an aqueous solution of *iso*butyric acid produced by a half gram-equivalent of dissolved salt (compare Smirnov, A., 1907, ii, 334); (3) the change (V'') in the absorbability of carbon dioxide by water caused by one gram-equivalent of dissolved salt (compare Sètschenov, A., 1875, 864, 1159; *J. Russ. Phys. Chem. Soc.*, 1886, **18**, and 1887, **19**). The constancy exhibited by the two ratios, $V'/V=K'$ and $V''/V=K''$, is regarded as evidence of the chemical nature of these properties.

* and *Bull. Acad. roy. Belg.*, 1913, 36—67.

With other properties, such as density, capillarity, etc., no such simple relations were obtained.

Measurements have been made of the heats of solution and specific heats of sodium and potassium chlorides and nitrates in water and in various mixtures of water and ethyl alcohol. In each of these solvents the differences between the heats of solution of (1) sodium and potassium nitrates, and (2) sodium and potassium chlorides are very nearly equal. Approximate equality is also exhibited between the differences for (1) potassium chloride and nitrate, and (2) sodium chloride and nitrate. T. H. P.

Influence of Temperature on the Velocity of Chemical Reactions. A. BERTHOUD (*J. Chim. phys.*, 1912, **10**, 573—597).—According to Arrhenius' theory, the "active part" in chemical change is formed reversibly in accordance with van't Hoff's equation for static equilibrium. The active part is supposed to be transformed chemically at a definite rate in accordance with the law of mass action. If k' is the rate of formation of the active part and k'' of the reverse action, and k the rate of chemical transformation of the active part, the concentration C of the latter is proportional to $k'/(k+k'')$. It is not permissible to assume with Arrhenius that k is independent of temperature.

The modification of Arrhenius' theory put forward by Trautz (A., 1911, ii, 381), in which the active part consists of molecules undergoing a preliminary dissociation, is open to a similar objection, as also is the additive compound hypothesis. According to Goldschmidt (A., 1909, ii, 390), only those molecules react the velocity of which exceeds a certain minimum. The author proposes a modification of this theory, in which velocity is replaced by "energy of internal atomic vibration." Those molecules the atoms of which are in an unstable configuration or are vibrating beyond a certain critical amplitude constitute the "active part." In gaseous actions other than intramolecular actions, it is necessary to assume that transient additive compounds are formed which are dissociated again into the original constituents or into new constituents according to their content of energy or their configuration.

The ordinary temperature-equation is modified by the addition of a new factor, $f(T)$, and thus becomes $\log k'/k'' = A/T + B/\log T + CT + D + f(T)$. The new term $f(T)$ is intended to take account of the effect on k of various factors, such as the increase in the proportion of active molecules exceeding the critical energy, the increase in the average energy of the molecules which exceed the critical energy, and, in the case of solutions, the viscosity. In practice, $f(T)$ is usually negligible in comparison with experimental errors.

R. J. C.

Action of Low Temperatures on Explosives. ANDRÉ KLING and DANIEL FLORENTIN (*Compt. rend.*, 1913, **156**, 694—696).—A study of the influence of cooling on the sensitiveness of different explosives, and the force and rate of their explosions, comparison being made between results obtained at the ordinary temperature and

at $-190°$ (liquid nitrogen). The sensitiveness to percussion is considerably diminished at low temperatures, the cooling effect being shown both by the detonator and the explosive itself. The force of the explosion does not appear to be diminished by cooling, providing that the percussion is sufficiently powerful to produce total deflagration of the explosive. When detonation occurs, the propagation of the explosion wave is not affected by cooling.

W. G.

The Oxidation of Complex Cobalto-organic Compounds H. COLIN and A. SÉNÉCHAL (*Compt. rend.*, 1913, **156**, 625—627).—A study of the rate of oxidation of solutions containing a cobalt salt and either glycerol or lactic acid, to which an excess of alkali hydroxide has been added, the amount of oxygen fixed by the cobalt in a given time being determined. The reaction is unimolecular, and the value of the constant K is independent of the concentration of the cobalt salt, but decreases rapidly with increase in concentration of the alkali. The author considers that the mechanism of the oxidation is similar to that in the case of the cobaltocyanides (compare Manchot and Herzog, A., 1901, ii, 549).

W. G.

Velocity of the Reaction between Sodium Thiosulphate and Sodium Bromoacetate. SERGIUS KRAPIVIN (*Zeitsch. physikal. Chem.*, 1913, **82**, 439—447).—The velocity of the reaction between sodium thiosulphate and sodium bromoacetate is determined by the same method as that employed for determining the velocity between sodium thiosulphate and chloroacetate (A., 1912, ii, 926). The reaction is bimolecular, the velocity constant depending on the concentration; for $0·25N$-solutions $k=1·605$; $0·05N$-solutions $k=0·697$, and for $0·01N$-solutions $k=0·456$. Doubling the concentration of either the bromoacetate or the thiosulphate brings about the same change in the velocity constant. The addition of $0·01N$-sodium bromide, sodium iodide, sodium nitrate, or sodium sulphate effects the velocity constant to the same extent as the addition of the same quantity of either sodium thiosulphate or sodium bromoacetate. The addition of alcohol to the reaction mixture causes an increase in the velocity constant. J. F. S.

Hydrolysis of Metallic Alkyl Sulphates. GEORGE A. LINHART (*Amer. J. Sci.*, 1913, [iv], **35**, 283—289. Compare A., 1912, ii, 927). —The rate of saponification of sodium ethyl sulphate by sodium hydroxide and of barium methyl sulphate and strontium methyl sulphate by barium hydroxide has been examined in aqueous solution at 60°. The data indicate that the reaction proceeds in all three cases in accordance with the equation for a bimolecular change. This result differs completely from that obtained in similar experiments by Kremann (A., 1910, ii, 596), and the author draws the conclusion that Kremann's data are untrustworthy, and that the interpretation of the results is consequently without foundation.

H. M. D.

Re-investigation of the Velocity of Sugar Hydrolysis. II The Rôle of Water. MARTIN A. ROSANOFF and H. M. POTTER (*J. Amer. Chem. Soc.*, 1913, **35**, 248—258).—In an earlier paper (A., 1912, ii, 34) it was shown that the hydrolysis of sucrose is a strictly unimolecular reaction.

Various explanations, including those of Cohen (A., 1897, ii, 484) and Arrhenius (A., 1899, ii, 359), have been offered for the fact that the velocity of hydrolysis of sucrose is a function of the initial concentration, but it is now shown that none of these is adequate. A new theory is therefore proposed, which states that water plays a double rôle in the reaction: (1) it takes part in the reaction, and contributes to its velocity in accordance with the law of mass-action, and (2) it acts as a negative catalyst by its dissociating power. In accordance with this view, the mechanism of sucrose hydrolysis appears to depend on the existence of a molecular complex, the concentration of which determines the velocity of the reaction. Water retards the reaction by dissociating this complex.

E. G.

Action of Neutral Salts on Bleaching Solution. SYDNEY H. HIGGINS (*J. Soc. Dyers*, 1913, **29**, 85—89).—See P., 1912, **28**, 130.

H. M. D.

Neutral Salt Reactions. II A Double Neutral Salt Reaction and the Action of Glauber's Salt on Wool. MORRIS FORT (*J. Soc. Dyers*, 1913, **29**, 80—85. Compare A., 1912, ii, 1047). —According to the views brought forward in the previous paper, salts which do not give an alkaline reaction with litmus or alizarin should exhibit alkalinity when more strongly acid indicators are added to the boiling solutions. In support of this it has been found that a hot solution of sodium chloride, which is inactive towards alizarin, gives a feeble alkaline reaction with nitroalizarin and a distinctly alkaline reaction with dinitroanthrachrysone sulphonic acid.

Although no alkalinity is indicated on the addition of alizarin to boiling solutions of either sodium chloride or calcium sulphate, yet when the solutions are mixed, an alkaline reaction is immediately developed. This is attributed to double decomposition, sodium sulphate being formed in sufficient quantity to give the alizarin reaction.

The action of aqueous solutions of sodium sulphate on wool has been investigated with reference to its tensile strength and dyeing properties, and the results are supposed to show that the basic properties of wool enable it to react with sodium sulphate in boiling solution in much the same way as other organic bases. Neutral salt reactions are considered to play a part in other technical processes and also in physiological changes. H. M. D.

Colour Changes Among Dyes of the Triphenylmethane Series as Influenced by the Hydrogen Ion Concentration of Acids of Different Dissociation Constants. HENRY C. BIDDLE (*J. Amer. Chem. Soc.*, 1913, **35**, 273—281. Compare A., 1912, i, 296; ii, 1048).—A study of the conversion of the benzenoid forms of

certain dyes of the triphenylmethane series into the quinonoid forms by acids of different dissociation constants has shown that there is a marked similarity between the action of the acids in this case and their catalysing influence in the case of the cinchona alkaloids.

The rate of development of colour in a solution of magenta in sulphurous acid to which a little formaldehyde has been added increases in equivalent solutions with acids of decreasing dissociation constant, and is retarded by acids of increasing dissociation constant. The reaction forms a useful lecture experiment for demonstrating the accelerating catalytic action of the slightly dissociated organic acids and the inhibiting action of the highly ionised mineral acids. The velocity of the reaction appears also to increase with the molecular concentration of an organic acid.

The action of excess of an acid on a rosaniline dye or its carbinol base leads to an equilibrium between the coloured and colourless forms which is largely dependent on the concentration of the hydrogen ions of the acid. The velocity of the reaction in the case of methyl-violet with acetic or chloroacetic acid seems to increase with the decreasing dissociation constant of the acid. E. G.

Xanthic Acid and the Kinetics of its Decomposition. HANS VON HALBAN and ALEXANDER KIRSCH (*Zeitsch. physikal. Chem.*, 1913, **82**, 325—360).—Xanthic acid usually decomposes violently in several minutes after preparation. It is shown that this is due to autocatalysis, in which the alcohol, formed as a product of the decomposition, is the catalyst. The authors show that if xanthic acid is intimately mixed with phosphoric oxide it becomes stable, and can be kept for weeks. The rate of decomposition of the acid is determined in solutions in benzene, chloroform, carbon disulphide, light petroleum (b. p. 65—80°), ether, nitrobenzene, acetone, and alcohol at temperatures 0°, 4·7°, 25°, 45°, 65°, and 80°. The course of the reaction is followed by titrating portions of the solution with a standard iodine solution when the undecomposed acid can be estimated according to the equation:

$$I_2 + 2OEt{\cdot}CS{\cdot}SH = 2HI + OEt{\cdot}CS{\cdot}S{\cdot}CS{\cdot}OEt.$$

The velocity of decomposition, in solutions where the decomposition is rapid, is in accordance with a reaction of the unimolecular type, but for those solutions in which the reaction is relatively slow the constant, calculated by the equation for unimolecular reactions, gradually increases, thus pointing to an autocatalysis. The velocity constant varies enormously in the different solvents; thus, if at 25° the constant for ethyl alcohol is 1,000,000, acetone gives 25,980, ether 485, nitrobenzene 315, benzene 5·15, chloroform 3·64, light petroleum 1·50, and carbon disulphide 1·0. It is shown that there is no connexion between the dielectric constants of the solvents and the velocity of the reactions. The effect of adding quantities of various substances to the various solutions is also investigated. The addition of alcohol to the benzene solutions causes an increase in the velocity of the reaction. The addition of many other substances causes a similar increase; thus the constant for a pure benzene

solution at 25° is 0·0000068 for a 0·01 normal solution of xanthic acid; if the following substances are added in quantities sufficient to form a 0·2 normal solution, the following values are obtained: methyl alcohol, 0·0028; ethyl alcohol, 0·0036; propyl alcohol, 0·0023; acetic acid, 0·00021; acetone, 0·000075; tribromophenol, 0·000015; triphenylcarbinol, 0·000031. In ethereal solution sulphuric acid causes a considerable increase in the velocity, whereas acetic acid and hydrochloric acid increase it to the same extent, which is, however, much less than with sulphuric acid. The temperature-coefficient of the reaction is much smaller than that usual for unimolecular reactions; it conforms well with the formula of Arrhenius. The molecular weight of xanthic acid was determined in solutions of benzene and carbon disulphide, and shown to be normal. J. F. S.

Structure of Some of the Elements. HAWKSWORTH COLLINS (*Chem. News*, 1913, **107**, 99—100).—Reference is made to the advertisement columns of *Nature* and *Chem. News*, 1906, for priority of the idea that "the acidity or non-metallic nature of an element is always due to a pair or pairs of electro-positive forces, each pair emanating from a portion of the element" of mass 4. Eleven pairs of elements are cited, differing in mass by four units and in valency by two units, such as phosphorus and aluminium, aluminium and sodium, etc. The combination of oxygen and helium to form neon is cited in support of these views of atomic structure. F. S.

Twentieth Annual Report of the Committee on Atomic Weights. Determinations published during 1912. FRANK W. CLARKE (*J. Amer. Chem. Soc.*, 1913, **35**, 227—235).—A summary of the atomic-weight investigations carried out during 1912 and the results obtained. E. G.

A New Source of Error in the Determination of Atomic Weights. ICILIO GUARESCHI (*Atti R. Accad. Sci. Torino*, 1913, **48**, 128—131).—Applying his reaction for the detection of bromine (A., 1912, ii, 989, and this vol., ii, 333), the author has been unable to find chlorides which do not contain bromides, or chlorates or iodates free from bromates. From preliminary colorimetric determinations it is probable that even the purest potassium chlorate contains bromate to the extent of one or two parts in ten thousand. This would be enough to cause perceptible error in atomic weights involving an analysis of these substances. R. V. S.

The Development of Avogadro's Theory. CARL GRAEBE (*J. pr. Chem.*, 1913, [ii], **87**, 145—208).—Historical. The author traces the position and development of the above theory from the time of its advancement in 1811 until its general acceptance more than fifty years afterwards. F. B.

What are Bases and Acids? RICHARD MEYER (*J. pr. Chem.*, 1913, [ii], **87**, 280—286).—A criticism of Vorländer's definitions (this vol., ii, 130). F. B.

Gas Generator. FRANK SOUTHERDEN (*Chem. News*, 1913, **107**, 86).—The apparatus has been designed more especially for the generation of hydrogen sulphide. The ferrous sulphide is contained in a tower, fitted at the top with a delivery tube and stop-cock; the constriction in the lower part of the tower contains a radially grooved plug, so that a drainage chamber is formed underneath. The side-tube from this drainage chamber is connected with a side-tube opening into the upper part of the acid reservoir, with the result that the dense stale liquor tends to sink in the reservoir as returned, relatively fresh acid being available on re-starting.

T. S. P.

A Reflux Condenser. S. W. WILEY (*J. Ind. Eng. Chem.*, 1913, **5**, 151).—The apparatus consists of tubes of block tin connected with bell-shaped condensers of spun copper. The bell is composed of two sections, which are separated by a perforated partition. The bell is surrounded by cold water, and condensation takes place on the upper surface of the bell. The condenser is very efficient, and can be used for ether extractions. T. S. P.

A New Form of Laboratory Extraction Apparatus. A. E. PERKINS (*J. Ind. Eng. Chem.*, 1913, **5**, 148—149).—The apparatus consists essentially of an extraction flask with a long neck, which is constricted at the base. The flask is flat-bottomed, and has a diameter of $2\frac{3}{4}$ inches, and a height of 2 inches to the base of the neck. The constriction is about half-an-inch in diameter as well as in height, and the neck above the constriction is 12 inches long by $1\frac{1}{8}$ inches in diameter. A tube through which cold water flows fits into the upper part of the neck, and acts as a condenser. The extraction thimble fits on to the constriction at the base of the neck. The apparatus is much simpler than the ordinary extraction apparatus, and rapid and complete extractions can be carried out. T. S. P.

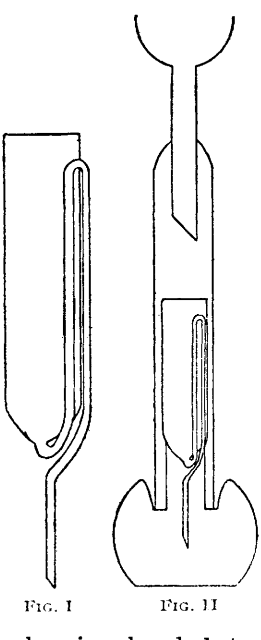


FIG. I FIG. II

A Modified Extraction Apparatus. G. M. MACNIDER (*J. Ind. Eng. Chem.*, 1913, **5**, 150—151).—The apparatus combines the best features of the Soxhlet and Knorr extractors, a small siphon extraction tube of the Soxhlet type fitting into a Knorr adapter. The principle is readily understood from the accompanying diagrams.

T. S. P.

A Useful Valve. NATHAN SMITH (*J. Ind. Eng. Chem.*, 1913, **5**, 235).—The valve is placed between the desiccator and the safety-bottle

when using a water-pump. A piece of glass tubing, drawn out evenly at one end (the delivery tube of a pipette answers very well), is fitted with a piece of rubber, which acts as a valve. A piece of wire is drawn through the centre of the rubber, and then coiled into a spiral outside the tube, so that the rubber is allowed some play, but cannot be sucked back right up the tube. Another piece of glass tubing is then fitted over the valve tube by means of a collar of rubber tubing, and connects with the desiccator.

T. S. P.

New Separating Funnel. C. E. Parker (*J. Amer. Chem. Soc.*, 1913, **35**, 295—297).—In order to overcome the difficulty due to the formation of persistent emulsions, which are often produced when animal or vegetable extracts are shaken with immiscible solvents, a special form of separating funnel has been devised. The separators are of flat shape, and are held in a horizontal position during the extraction and in a vertical position when the contents are to be withdrawn. The advantage of this form is that the liquids are distributed in thin layers over a large area, so that the contiguous surfaces are from eight to ten times as great as with the same amounts of liquid in separators of the ordinary kind. A gentle movement of the liquids in contact with one another can be effected by means of a nearly horizontal disk making 20 revolutions per minute. The separators lying on the rotating disk are tilted about gently in such a way that no actual mixing of the liquids takes place.

E. G.

Inorganic Chemistry.

Physico-chemical Studies on Tellurium. I. ERNST COHEN and J. F. KRÖNER (*Zeitsch. physikal. Chem.*, 1913, **82**, 587—611).—An account is given of the older investigations on tellurium. By means of density determinations it is shown that tellurium exists in two forms, Te_A and Te_B, which are present as dynamic allotropes in equilibrium $Te_A \rightleftarrows Te_B$. The equilibrium amounts are changed by change in temperature. It is shown that the treatment to which tellurium has been subjected influences the density in a marked degree. The density varies between 6·272 and 5·949, depending on the temperature. Some tellurium, prepared by the reduction of telluric acid by means of hydrazine sulphate, was found to have a density 3·242. The low value is shown to be due to the absorption of large volumes of nitrogen. The authors state that with the exception of the atomic weight, all physico-chemical constants of tellurium are to be doubted on account of the existence of the two forms of tellurium existing in unknown proportions in all specimens of tellurium. J. F. S.

After-Luminosity in Pure Nitrogen after the Passage of Electric Discharge. A. KOENIG and E. ELÖD (*Physikal. Zeitsch.*, 1913, **14**, 165—167).—From observations on the after-luminosity effect which is exhibited when a current of nitrogen is passed through a discharge tube (Strutt, A., 1912, ii, 153, 477, 935), the authors have obtained evidence in support of Strutt's view that the effect is due to the formation of an active modification of nitrogen. The opinion has been recently expressed by Comte (this vol., ii, 210) that the after-luminosity is dependent on the presence of small quantities of oxygen in the nitrogen, but this is not in agreement with the authors' results.

The nitrogen employed contained argon, 1·5% of carbon dioxide, and traces of oxygen. It was freed from carbon dioxide by means of potassium hydroxide, dried over calcium chloride, freed from oxygen by passing over heated copper, and then completely dried by passing through a spiral tube cooled to $-80°$.

The intensity and duration of the after-effect depend on the pressure of the gas. As the pressure falls, the duration of the after-effect increases. At very low pressures the luminosity can only be observed readily if the thickness of the layer of gas is sufficiently large. The addition of small quantities of oxygen appears to lessen the intensity and duration of the effect, and hydrocarbons have a similar influence. Traces of hydrocarbons, which can scarcely be recognised in the spectrum of the discharge tube, have an appreciable influence on the after-luminosity. The colour changes to red or violet-red, and the bands attributable to active nitrogen are almost completely extinguished by the cyanogen spectrum.

H. M. D.

The Chemically Active Modification of Nitrogen. (Hon.) ROBERT J. STRUTT (*Physikal. Zeitsch.*, 1913, **14**, 215).—In reply to Comte (this vol., ii, 210), who attributes the after-luminosity accompanying the jar discharge through nitrogen to the presence of small quantities of oxygen, the author points out that the effect in question is obtained with nitrogen, which shows no trace of cloud formation in contact with phosphorus. In regard to the sensitiveness of this test for oxygen, it has been found that the addition of the one hundred-thousandth part of oxygen to non-reactive nitrogen is sufficient to produce the cloud effect. If the nitrogen, purified by contact with a fresh surface of phosphorus, is passed over a long column of copper gauze at a red heat, the after-luminosity effect remains unchanged. If the nitrogen is passed through a tube containing copper gauze which is cooled to $-190°$, the after-luminosity becomes intensified, and this is attributed to the removal of traces of condensible impurities. H. M. D.

Extraction with Liquefied Gases and the Ammonolysis of Hydrazine Sulphate. FRITZ FRIEDRICHS (*J. Amer. Chem. Soc.*, 1913, **35**, 244—247 *).—Apparatus has been devised for carrying out extractions with liquefied gases as solvents. The extraction apparatus is a modification of the Landsiedl form (A., 1902, ii, 390), and

* and *Zeitsch. angew. Chem.*, 1913, **26**, 201—203.

the condenser is of the screw type; both are enclosed in vacuum jackets

The apparatus has been found of considerable service in a study of the ammonolysis of hydrazine sulphate. Browne and Welsh (A., 1911, ii, 1084) have shown that this salt is decomposed by liquid ammonia, thus:

$$N_2H_4,H_2SO_4 + 2NH_3 \rightleftarrows (NH_4)_2SO_4 + N_2H_4,$$

and have suggested that as ammonium sulphate is insoluble in liquid ammonia, whilst hydrazine is soluble, the reaction might be useful for the preparation of anhydrous hydrazine. It has now been found that the ammonolysis proceeds quantitatively, and that a yield of 90—95% of hydrazine can be obtained; it is considered that the base could be readily prepared in large quantities by this method if the apparatus were constructed of iron instead of glass.

E. G.

Chemistry of the Formation of Nitric Oxide in the High Tension Arc. II. FRANZ FISCHER and EMIL HENE (*Ber.*, 1913, **46**, 603—617).—Details are given of the apparatus and methods used to obtain the results described in a previous paper (this vol., ii, 132). The authors maintain that the criticisms of König (this vol., ii, 210) are invalidated by the publication of these details, and do not need further reply.

T. S. P.

Formation and Properties of Nitrosyl Chloride. EMIL BRINER and (Mlle.) Z. PYLKOV (*J. Chim. phys.*, 1912, **10**, 640—679. Compare Boubnov and Guye, A., 1911, ii, 599).—The known methods of preparing nitrosyl chloride are due to Gay Lussac, Tilden, and Muller respectively. Gay Lussac's method of synthesis by admixture of nitric oxide and chlorine leads to a product containing chlorine in solution. The animal charcoal sometimes employed as a catalytic agent is not really necessary, and does not affect the yield. Muller's method of preparation by passing gaseous hydrogen chloride into liquid nitrogen dioxide at -10° also leads to a product which is contaminated with chlorine and oxides of nitrogen. The authors find that when hydrogen chloride is passed into liquid nitrogen trioxide, nitrosyl chloride is produced according to the equation $N_2O_3 + 2HCl = 2NOCl + H_2O$, but the interaction of nitrosyl sulphate (chamber crystals) and potassium chloride (Tilden) gives the least contaminated product.

The nitrosyl chloride was purified by crystallisation and fractional distillations in presence of phosphoric oxide. The densities, viscosities, surface tensions, vapour tensions, and critical temperature were measured over a range of temperatures from -68° to $+40^\circ$, and from these the latent heat of vaporisation and the critical pressure were obtained by calculation.

Since the atomic volumes of nitrogen and chlorine are somewhat uncertain, the molecular weight of nitrosyl chloride cannot be estimated from the density measurements alone, but the values obtained for the other properties are available for this purpose. Ramsay and Shields' method and the ratio of the boiling point to

the density (Longinescu) lead to the conclusion that nitrosyl chloride is slightly polymerised. From the boiling point and surface tension values (Kistiakovski's formula), b. p., surface tension, and vapour tension (Dutoit and Mojoïu), b. p., surface tension, and critical temperature (Walden), surface tension and latent heat (Walden), and the viscosity-temperature curve (Batschinski), the conclusion is drawn that nitrosyl chloride is not polymerised. It is urged that Ramsay and Shields' method gives no certain information as to polymerisation in the bulk of the liquid away from the surface film.

The heat developed on passing nitrosyl chloride into excess of potassium hydroxide in a Dewar calorimeter was compared with the heat of neutralisation of sulphuric acid under like conditions, and the following thermal equation was deduced:

$$NOCl + 2KOH = KNO_2 + KCl + H_2O + 31{\cdot}5 \pm 0{\cdot}5 \text{ cal.}$$

The following equations are exothermic, and the thermal values give some idea of the relative facility with which nitrosyl chloride is prepared by different methods: $\frac{1}{2}N_2O_3 + HCl = NOCl + \frac{1}{2}H_2O + 8{\cdot}4$ cal.; $NO + \frac{1}{2}Cl_2 = NOCl + 14{\cdot}4$ cal.; $\frac{1}{2}N_2O_4 + 2HCl = NOCl + H_2O + \frac{1}{2}Cl_2 + 18{\cdot}5$ cal. The following equations being endothermic, the reactions do not occur at ordinary temperatures: $\frac{1}{2}N_2 + \frac{1}{2}O_2 + \frac{1}{2}Cl_2 = NOCl - 7{\cdot}2$ cal.; $\frac{1}{2}N_2O_4 + \frac{1}{2}Cl_2 = NOCl + \frac{1}{2}O_2 - 4{\cdot}6$ cal.

The heat of dissociation into nitric oxide and chlorine being negative ($-14{\cdot}4$ cal.), dissociation should increase with rising temperature. The heat of dissociation calculated from Sudborough and Millar's vapour-density measurements (T., 1891, **59**, 74, 271) by van't Hoff's formula varies somewhat, but in all cases considerably exceeds $-14{\cdot}4$ cal., a result which is attributed to a disturbance of the equilibrium by the partial dissociation of nitric oxide at the temperatures employed. R. J. C.

Borates. The System B_2O_3–$(NH_4)_2O$–H_2O at 30°. II. UMBERTO SBORGI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 90—95. Compare this vol., ii, 213).—The paper contains the numerical results of this investigation, of which the conclusions have already been described. R. V. S.

The System SiO_2. ANDREAS SMITS and KURD ENDELL (*Zeitsch. anorg. Chem.*, 1913, **80**, 176—184. Compare Endell and Rieke, this vol., ii, 134).—The relations of tridymite to cristobalite and quartz are still very uncertain. The attempt is now made to apply Smits' dynamic theory of allotropy to the case of silica.

It is sufficient to assume only two different kinds of molecules, which together form solid solutions. Three discontinuities in the solid solutions are assumed. β-Cristobalite is stable between 1685° and 800°, and is then converted by slow cooling in presence of mineralisers into β-quartz, which in turn always changes into α-quartz at 575°. Under ordinary conditions of cooling, however, β-cristobalite persists below 800°, and passes at 230° into α-cristobalite. In similar manner, the metastable tridymite has a transformation point at 130°, but in order to account fully for tridymite it may be necessary to assume a pseudo-ternary system.

A pressure-temperature diagram has also been constructed, which takes account of α- and β-quartz, α- and β-cristobalite, and silica glass. In all cases increase of pressure raises the melting and transformation points. C. H. D.

The Crystallising Power of Silicates. ERWIN KITTL (*Zeitsch. anorg. Chem.*, 1913, **80**, 79—92. Compare this vol., ii, 47; Schumov-Deleano and Dittler, A., 1912, ii, 170).—The possible forms of the relation between velocity of crystallisation and viscosity are discussed. Complete crystallisation usually occurs when the maximum velocity falls in the region of low viscosity, whilst in the opposite case the silicate forms a glass. The number of crystallisation centres per sq. cm. is given for a series of silicates, and varies, under the conditions of the author's experiments, between 1·3 for calcium magnesium metasilicate and 220,000 for magnesium orthosilicate or 430,000 for a mixture, $5Mg_2SiO_4 + Fe_2SiO_4$. Manganese orthosilicate has a much smaller number of centres than other orthosilicates, and, unlike them, forms radiating groups of crystals.
C. H. D.

Equilibria in Binary Systems of Fluorides. NIKOLAI A. PUSCHIN and A. V. BASKOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 82—101).—Investigation of the melting-point curves of mixtures of fluorides leads to the following results.

With the fluorides of all the alkali metals, aluminium fluoride forms definite compounds of the cryolite type, $AlF_3,3MF$. Further, in the cases of sodium, potassium, and rubidium fluorides, there probably exist other compounds with compositions analogous to that of chiolite, $2AlF_3,3MF$. Cryolite, $AlF_3,3NaF$, and the similar compounds, $AlF_3,3KF$ and $AlF_3,3RbF$, form polymorphous modifications, stable below 600°, below 300°, and below 350° respectively.

Some of the fused mixtures of aluminium fluoride with potassium and rubidium fluorides are red, and some of those with cæsium fluoride are red and others green.

The systems $NaF + PbF_2$, $NaF + CdF_2$, and $KF + BaF_2$ form eutectic mixtures containing 67·5 mol. % PbF_2, 47·5 mol. % CdF_2, and 56% BaF_2 respectively, the corresponding melting points being 540°, 660°, and 750°. Cadmium fluoride melts at 1110°.

With $KF + CeF_3$ the eutectic point lies at 660°, and corresponds with 24 mol. % CeF_3, whilst with $NaF + FeF_3$ the eutectic temperature is 892° and the content of ferric fluoride, 35 mol. %. Zinc and sodium fluorides form a eutectic mixture, melting at 682°.

The molecular lowering of the crystallising temperature of sodium fluoride (100 grams) by lead, cadmium, and aluminium fluorides amounts to 187, 189·5, and 221 respectively.

In none of the systems examined was the formation of solid solutions observed. T. H. P.

Double and Complex Salts. I. NILRATAN DHAR (*Zeitsch. anorg. Chem.*, 1913, **80**, 43—58).—The methods of distinguishing between double and complex salts are reviewed, and determina-

tions of conductivity of a number of salts are given, with the object of filling gaps in the investigations of Werner and others.

Potassium cobaltinitrite, $K_3Co(NO_2)_6$, and the sodium salt are complex salts with four ions. Potassium bismuth thiosulphate, $K_3Bi(S_2O_3)_3,1\frac{1}{2}H_2O$, is a complex salt yielding four ions, one of which, $Bi(S_2O_3)_3$, is tervalent. It does not give the reactions for bismuth. Barium chromioxalate and potassium ferrioxalate are complex, whilst potassium antimonyl oxalate is a double salt. Potassium cobalticyanide and cobaltous mercurithiocyanate contain stable complexes, whilst potassium cobaltothiocyanate is a typical double salt. Other complex salts are potassium chromithiocyanate, sodium nitroprusside, and a number of cobaltammine salts, the latter undergoing partial resolution in dilute solution. C. H. D.

The Transformation Undergone by Heated Calcium Carbide. EMIL BRINER and A. KUHNE (*Compt. rend.*, 1913, **156**, 620—622).—Contrary to the results of Erlwein, Warth, and Beutner (A., 1911, ii, 396), the authors find that, on heating calcium carbide to 900° in unglazed porcelain tubes it is partly decomposed into its elements, and does not form a lower carbide. The residue does not give off hydrogen on treatment with water, but the absence of calcium thus proved is probably due to volatilisation or combination with the substances of which the tube is made. W. G.

Supposed Occurrence of a Peroxide in Calcium Hydroxide, which has been Exposed to Air, and in Aragonite. HUGO DITZ (*J. pr. Chem.*, 1913, [ii], **87**, 208—227).—On exposure to air, calcium hydroxide gives, with hydrochloric acid and starch-potassium iodide solution, a blue coloration, the intensity of which increases with the time of exposure. This coloration is considered by Vaubel (A., 1912, ii, 1172) to be due to formation of a hydroperoxide.

The author finds, however, that even after long exposure no hydrogen peroxide could be detected either by the chromic acid or titanic acid reactions, on treating the hydroxide with hydrochloric acid, although the starch–iodide reaction was quite pronounced. The exposed calcium hydroxide gives a pink coloration with an acetic acid solution of sulphanilic acid and α-naphthylamine, indicating the presence of a nitrite, and it is therefore probable that the starch–iodide reaction is due to the formation of a nitrite by the absorption of nitrous oxides from the air. Vaubel has also shown (A., 1912, ii, 80) that aragonite rapidly develops a blue coloration on treatment with hydrochloric acid and starch–iodide, whilst in the case of calcite the coloration develops more slowly and is much less intense. This difference he referred to the presence of a small amount of peroxide in the aragonite.

The author shows, however, that the coloration is due to the presence of iron, the slower development in the case of calcite being due to its smaller iron content. F. B.

Preparation of a Complex Salt of the Apatite Type and its Bearing on the Formation of Bone. THEODOR GASSMANN (*Zeitsch. physiol. Chem.*, 1913, **83**, 403—408).—On heating phosphatocalcium

carbonate, $\left[Ca\left(\begin{matrix}OPO_3Ca\\>Ca\\OPO_3Ca\end{matrix}\right)3\right]CO_3$, derived from ashed teeth or bones, with somewhat more than the corresponding molecular quantity of calcium chloride for fifteen minutes at a red heat, and extracting the mass with acetic acid, a colourless amorphous residue of *phosphatocalcium chloride*, $\left[Ca\left(\begin{matrix}OPO_3Ca\\>Ca\\OPO_3Ca\end{matrix}\right)3\right]Cl_2$, is obtained.

The calcium chloride is not extracted from this by means of water; this disproves the composition, $9Ca_6PO_4,CaCl_2$. The conversion of the carbonate into the chloride is considered to establish the presence of the apatite complex in bones. E. F. A.

Dispersion of the Birefringence of Mixed Crystals of Strontium and Lead Dithionates. H. AMBRONN (*Zeitsch. Kryst. Min.*, 1913, **52**, 48—57).—The anomalous dispersion exhibited by these crystals is discussed. L. J. S.

The Hydrate and Ammoniate of Glucinum Chloride. K. MIELEITNER and H. STEINMETZ (*Zeitsch. anorg. Chem.*, 1913, **80**, 71—78).—When ether is added to an aqueous solution of glucinum chloride, and the mixture is cooled in ice and saturated with hydrogen chloride, a crystalline precipitate is formed, which, after drying in a vacuum over sulphuric acid, has the composition $GlCl_2,4H_2O$. It does not contain combined ether, as supposed by Parsons (*ibid.*, 1904, **40**, 408), and alcohol may be used in place of ether. The anhydrous chloride cannot be obtained by heating in dry hydrogen chloride or chlorine; the water is firmly held.

The anhydrous chloride is prepared by heating a mixture of pure glucinum chloride and carbon in dry chlorine. The carbon is sugar charcoal, purified by boiling with hydrochloric acid and heating to redness in chlorine. The sublimed chloride combines readily with dry ammonia, forming the *tetra-ammoniate*, $GlCl_2,4NH_3$ (compare Ephraim, A., 1912, ii, 546). If the mixture is allowed to become hot, the composition approaches more nearly to $GlCl_2,2NH_3$. C. H. D.

The Solubility of Sulphur Dioxide in Molten Copper Alloys. ADOLF SIEVERTS and E. BERGNER (*Zeitsch. physikal. Chem.*, 1913, **82**, 257—270. Compare A., 1910, ii, 410, 851).—The solubility of sulphur dioxide is determined in gold, silver, and platinum alloys of copper, and in copper containing known amounts of cuprous oxide or cuprous sulphide by the same method as previously described (*loc. cit.*). In the case of the metal alloys, particularly of those with gold, it is shown that solubility decreases with increasing gold concentration. This decrease in solubility is much more marked in the case of the oxide and sulphide mixtures, the oxide decreasing the solubility about three times as much as the sulphide. The amount of decrease in the solubility is approximately proportional to the concentration of these substances for dilute solutions, that is,

up to about 7%, but above this figure the proportionality ceases. The relationship between solubility, temperature, and pressure is the same as in the case of pure copper. The solubility increases with increasing temperature, and the quantity dissolved varies with the square root of the pressure, that is, $p^{\frac{1}{2}}/m$ is constant for concentrations up to about 7%. The experimental results can be partly explained by the assumption that the sulphur dioxide is decomposed in solution with the formation of cuprous sulphide and oxide,

$$SO_2 + 6Cu \rightleftharpoons Cu_2S + 2Cu_2O.$$

From this an equilibrium constant ought to be obtained from the expression:

$$(Cu_2O)^2 \cdot (Cu_2S)/(Cu)^6 \cdot (SO_2) = K_1,$$

and since in dilute solutions the concentration of the copper can be regarded as constant, and the pressure of the sulphur dioxide can be kept constant:

$$(Cu_2O)^2 \cdot (Cu_2S) = K_2.$$

This latter expression is only found to hold between the concentrations 0·85—1·7 molecules Cu_2S and 1·7—1·2 mols. Cu_2O. Consequently the expression can only be said to hold in a qualitative manner. The authors are of the opinion that a considerable loss of sulphur dioxide, and consequently of cuprous oxide, occurs through the formation of a slag due to interaction of cuprous oxide with the porcelain tube. J. F. S.

Volatilisation of Certain Binary Alloys in High Vacua ARTHUR J. BERRY (*Proc. Camb. Phil. Soc.*, 1913, **17**, 31—33. Compare A., 1912, ii, 161).—The behaviour of certain alloys when subjected to distillation in a high vacuum has been investigated. An alloy of copper and cadmium was found to have been completely separated into its constituents when distilled at about 600°. In the case of a cadmium-magnesium alloy containing excess of cadmium, both metals distilled over, and it seems probable that the composition of the distillate is dependent on the temperature of volatilisation. On distillation of alloys of lead and magnesium, containing the two metals in approximately equivalent proportions, at about 680°, it was found that the distillate consists almost entirely of magnesium, traces only of lead being present. Microscopic examination of the distillate showed the presence of small quantities of steel-blue crystals embedded in a matrix of magnesium. In the neighbourhood of these crystals, the distillate underwent rapid corrosion on exposure to the air, with the formation of a black powder. This seems to show that the crystals are those of the compound Mg_2Pb. H. M. D.

The Reduction of Solutions of Copper Sulphate by Sodium Hypophosphite and Sodium Hyposulphite. JAMES E. MYERS and JAMES B. FIRTH (*Zeitsch. anorg. Chem.*, 1913, **80**, 93—103. Compare P., 1912, **28**, 101).—An apparatus is described, in which the reacting liquids may be mixed and filtered in an atmosphere of carbon dioxide. Copper sulphate and sodium hypophosphite yield at 70° cuprous hydride, Cu_2H_2, which is reddish-brown and decom-

poses suddenly at 60° when dry. The longer the reaction lasts, the lower is the proportion of hydrogen in the product. At the ordinary temperature the product, after a few hours, contains cuprous oxide, hydride and phosphate, and is explosive. Cupric hydride is not an intermediate product.

Copper sulphate and sodium hyposulphite yield copper or copper sulphide. C. H. D.

The Purification and Atomic Weight of Yttrium. RICHARD J. MEYER and J. WUORINEN (*Zeitsch. anorg. Chem.*, 1913, **80**, 7—35). —The following methods are suitable for the fractionation of mixtures containing yttrium. The precipitation of dichromate solutions with potassium chromate separates yttrium well from terbium and gadolinium, but is most applicable to mixtures from which most of the terbium group has been removed by other methods, when it yields pure yttria.

Fractional crystallisation of the ethyl sulphates is tedious, but is suitable for large quantities. Precipitation with potassium ferrocyanide yields nearly pure yttria, but the yield is small, and the precipitates are not readily filtered. Crystallisation of the double ammonium tartrates is unsuccessful, as is also the fractional hydrolysis of these salts by water, ammonia, or magnesia.

A new method is described, depending on the hydrolysis of solutions of the phthalates by heat. This method rapidly removes the erbium group, and gives a large yield of a product consisting mainly of yttria, which is then conveniently purified by fractionally precipitating a slightly acid solution of the nitrates with potassium iodate.

The atomic weight of yttrium is found by the sulphate method to be 88·6, the international value, 89·0, being too high. The material used is purified by the iodate method, and allowance is made for the stability of traces of acid sulphate at 500°. Former determinations are critically reviewed.

The purified material gives only the strongest line or lines of erbium, ytterbium, gadolinium, terbium, dysprosium, and holmium in the arc spectrum. The phosphorescence in a cathode light vacuum is a bright yellow.

Yttria is diamagnetic, the values found [by EDGAR WEDEKIND], $x.10^6$, being for Sc_2O_3 $-0·05$; Y_2O_3 $-0·14$; La_2O_3 $-0·18$.

Pure yttria has D_{15} 4·84. C. H. D.

The Rare Earths of the Carolina Monazite Sands. CHARLES JAMES (*Chem. News*, 1913, **107**, 110—111; *J. Amer. Chem. Soc.*, 1913, **25**, 235—239).—The bromate method has been applied to the fractionation of the rare earths derived from the monazite sands of Carolina, and it is shown that these sands contain, in addition to lanthanum, cerium, praseodymium, and neodymium, considerable quantities of samarium, gadolinium, and yttrium; small amounts of dysprosium, holmium, and erbium; and minute amounts of europium, terbium, thulium, and ytterbium, etc. Erbium occurs in much smaller quantities than holmium and dysprosium, and this

fact probably accounts for the anomalous behaviour of certain fractions which has been observed by other workers.

The oxalates obtained from the more soluble double sulphates are recommended as a source of samarium, gadolinium, europium, terbium, dysprosium, and holmium. T. S. P.

The Electro-Metallurgy of Aluminium. P. P. FEDOTÉEV and VL ILJINSKY (*Zeitsch. anorg. Chem.*, 1913, **80**, 113—154).—The process of manufacture of aluminium by the electrolysis of solutions of alumina in fused cryolite has been investigated by physico-chemical methods. This has involved the study of the system AlF_3–NaF, and of the influence of other compounds on the equilibrium.

Pure aluminium fluoride cannot be obtained by heating the hydrated salt, as hydrolysis takes place, but the impure product may be sublimed at 1100°, yielding large crystals of the pure fluoride when the cooling is not too rapid. The anhydrous salt is not attacked, even by concentrated sulphuric acid.

The freezing-point curve shows that cryolite, $3NaF,AlF_3$, is a very stable compound, m. p. 1000°. A second compound is also formed, $5NaF,AlF_3$, identical with the mineral chiolite. This does not melt, but is transformed at 725° into cryolite and liquid. There are eutectic points at 880° and 685° and at 14 and 46·4 mol. % AlF_3 respectively. Solid solutions are only formed from 0 to 4 mol. % AlF_3. The transformation of monoclinic into regular cryolite takes place at 565°, and is accompanied by a change of volume. From 50 mol. AlF_3 onwards the mixtures volatilise.

Cryolite and alumina form solid solutions, the freezing-point curve up to 21% Al_2O_3 being continuous, with a minimum at 15% and 935°. The solubility of alumina in the eutectic $NaF-Na_3AlF_6$ is greater than in cryolite, and the curve also passes through a minimum. In this case cryolite and aluminate are probably formed: $6NaF + Al_2O_3 = Na_3AlF_6 + Na_3AlO_3$, the excess of cryolite acting as a solvent, as alumina is insoluble in fused sodium fluoride. The addition of aluminium fluoride to cryolite diminishes its solvent power for alumina.

A difference of potential of 2·1—2·2 volts is required for the continuous production of aluminium. The electrolysis observed with 1·3 volts is due to the formation of aluminium carbide, Al_4C_3. The anode effect sometimes observed is due in part to an accumulation of alumina in the neighbourhood of the anode.

The loss of aluminium by emulsification of the metal in the bath and by the formation of carbide has also been determined in certain cases. The yield does not exceed 70%, owing to emulsification of aluminium. It is necessary to stir the electrolyte, to add alumina, and to break up the crust from time to time. The use of a rotating anode may be of advantage.

A bath of low melting point is best obtained by using a chiolite mixture in place of cryolite, and keeping the concentration of the alumina near 7·5%. This mixture has a lower density than cryolite. Calcium fluoride lowers the melting point, but diminishes the

solubility of alumina and increases the density. Calcium and aluminium fluorides form a eutectic at 815—820°, containing 37·5 mol. % AlF_3. Some points in the ternary system have been determined. C. H. D.

Action of Distilled Water on Pure Aluminium. II. ALBERTO SCALA (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 95—102. Compare this vol., ii, 220).—The corrosion of impure aluminium by distilled water, previously described, is due to the traces of iron contained in the metal. The aluminium used, although much purer than ordinary commercial aluminium, had the following composition:

Al.	Fe.	Si.	Ca.	Na.	Total.
99·371	0·070	0·401	traces	0·039	99·881

If a piece of iron is immersed in water contained in an aluminium vessel, blackening and corrosion commences much sooner than in a similar vessel containing distilled water only. The presence of the actual metal is not necessary, for distilled water in which iron has previously been immersed is also very active in causing the corrosion. A solution of colloidal ferric oxide has no action on the aluminium. The solvent action of water is very rapid and pronounced when, instead of the impure aluminium, an alloy of iron and aluminium (about 15% of iron) is used. The author suggests a mechanism for the reaction, in which a colloidal ferrous oxide probably plays a part. R. V. S.

The Carbides of Manganese and Nickel. OTTO RUFF and EWALD GERSTEN (*Ber.*, 1913, **46**, 400—413).—Trimanganocarbide, Mn_3C (compare Stadeler, A., 1908, ii, 592), was prepared from manganese and carbon by heating a mixture of these two substances at 1600° for twenty minutes in a vacuum electric furnace under a pressure of 20 mm. The manganese was prepared by the thermit method, and had the following composition: Mn, 98·68%, Fe, 0·42%, Al, 0·55%, C, 0·02%, insoluble residue, 0·25%; melting-point determinations gave the values, 1242°, 1247°, and 1239°. The regulus obtained contained nests of crystals in the centre, which could be easily separated from the main mass; the crystals consisted of glistening fibres and needles, and after separating the admixed carbon by means of acetylene tetrabromide, were found to have a composition corresponding with the formula Mn_3C. The main mass of the regulus was then finely powdered, the graphite and carbon removed with acetylene tetrabromide, and the residue found also to consist of the pure carbide. The hardness of trimanganocarbide lies between that of talc and gypsum; the molecular volume is 25·70, as compared with the calculated value 29·80. The following thermochemical data were obtained, the products of combustion being analysed in each case, in order to make any necessary corrections. Molecular heat of formation of Mn_3O_4, 329·0 ± 0·74 Cal. (Le Chatelier's value is 327·23 Cal.); the manganese burns completely to Mn_3O_4. Molecular heat of combustion of trimanganocarbide, 410·9 ± 2·0 Cal., the product of combustion being Mn_3O_4.

The molecular heat of formation of trimanganocarbide from manganese and graphite is then calculated to be $12 \cdot 9 \pm 2 \cdot 14$ Cal. (Le Chatelier's value is 9·34 Cal.).

The solubility of carbon in nickel reaches a maximum at 2100°, and the composition of the fusion corresponds with the formula Ni_3C, that is, with trinickelocarbide (compare Ruff and Martin, A,, 1912, ii, 354). The carbide undergoes considerable decomposition on cooling, however, even when the fusion is quenched; also the resulting mass is so tough that it is impossible to powder finely the quenched mass, and then resort to levigation for obtaining the pure carbide. The following thermochemical data therefore hold for an impure material as far as the carbide is concerned, containing only 4·39% of carbide, but the substances used and the products formed were always analysed in order to make necessary corrections. Molecular heat of formation: of nickel oxide (NiO), $51 \cdot 5 \pm 0 \cdot 7$ Cal., of trinickelocarbide, $-394 \pm$ (ca.) 10 Cal.

Comparison of the molecular heats of formation of the carbides of iron (see this vol., ii, 296), manganese, and nickel accounts for the great instability of nickel carbide, corresponding with the fact that nickel is the noblest element. The molecular volumes of the carbides of iron and manganese indicate that the contraction occurring when formed from their elements is of the same order. Both the carbides of iron and manganese are soft, so that the hardness of alloys containing these substances cannot be due to them existing as such, but probably depends on the hardness of their solid solutions (compare Kurnakov and Shemtschushny, A., 1908, ii, 932). T. S. P.

Some Properties of an Industrial Electrolytic Iron. LÉON GUILLET and A. PORTEVIN (*Compt. rend.*, 1913, **156**, 702—705. Compare Broniewski, this vol., ii, 288).—A physical study of electrolytic iron prepared on an industrial scale. The metal, supersaturated with hydrogen, is very fragile, its hardness being considerably diminished by annealing, when its micrographic structure becomes normal. The presence of the hydrogen does not influence the transition temperatures. The electrical resistance of a centimetre cube, corrected for the presence of sulphur and arsenic, is 11·92 micro-ohms before annealing, and 9·98 micro-ohms after. W. G.

The Corrosion and Rusting of Iron which has been Treated by the Sherard Process. FRANZ HALLA (*Zeitsch. Elektrochem.*, 1913, **19**, 221—226).—The Sherard process consists in galvanising iron by surrounding it with zinc dust and then heating in a furnace for about two hours at a temperature somewhat below the melting point of zinc. Wrought iron nails were treated by this process and their corrosion studied by immersing them in 3·2% sulphuric acid for definite periods. The velocity of solution of the zinc coating was thus determined. It is shown that in all cases the velocity passes through a minimum, then reaches a constant stage, which is maintained until nearly the whole of the coating is dissolved, and then is slightly increased to the end of the process. Theoretical explanations are given for the changes in the velocity of solution.

Experiments on the rusting of specimens are also described. A quantity of treated nails are placed, some in water, and some above it. It is shown that even in one day rusting has taken place, as evidenced by the appearance of a white, flocculent precipitate of zinc hydroxide, which after a while is tinted brown. Iron treated by this process is shown to be more resistant to rusting and corrosion than that treated by the other processes, that is, galvanic deposition or immersion in molten zinc. J. F. S.

The Reactions between Ferrous Oxide and Carbon and between Carbon Monoxide and Iron. VICTOR FALCKE (*Ber.*, 1913, **46**, 743—750).—The object of the present investigation was to determine whether the equilibrium in the system with the solid phases FeO, Fe, and C, and the gas phase CO, CO_2, varies with the kind of amorphous carbon used (compare Baur and Glässner, A., 1903, ii, 423; Schenck and others, A., 1905, ii, 519; 1907, ii, 470). The apparatus used was similar to that of Schenck and Heller (A., 1905, ii, 519), and at first the ferrous oxide used was prepared by heating ferrous oxalate at 300° (compare Schenck and Heller, *loc. cit.*). It was found, however, that this was not satisfactory, since even at 700° gas is still evolved; consequently the results of Schenck and Heller are not trustworthy.

It was further found that the pressure set up when a mixture of 2 grams of ferrous oxide with 1·5 grams of iron (Kahlbaum) is heated at 530—660° is independent of the presence of sugar carbon; the ferrous oxide contained 0·5% of carbon, and before being used was heated in a vacuum for a long time at 650°.

Further experiments showed that the reaction between iron and carbon monoxide at 650° varies, according to whether the gas is led in a continuous current over the iron, or allowed to remain in contact with it in a closed vessel. In the former case, much carbon is deposited, whereas in the latter case, if, after equilibrium has been obtained, the iron is dissolved in hydrochloric acid, all the carbon is evolved as carbon dioxide, and none left behind as an insoluble residue. The way in which the carbon monoxide reacts in the latter case is uncertain.

The above results show that the reaction between iron and carbon monoxide is more complex than is generally assumed, and also that the conclusions and theories of Schenck and his co-workers (*loc. cit.*) are invalid, because based on inaccurate experimental evidence. The object of the author's investigation was thus not attained.

T. S. P.

Action of Sulphurous Acid on the Sulphides of Iron, Zinc, and Manganese. WILLIAM E. HENDERSON and HARRY B. WEISER (*J. Amer. Chem. Soc.*, 1913, **35**, 239—244).—It is well known that the freshly precipitated sulphides of iron, zinc, and manganese are readily soluble in sulphurous acid, whilst those of nickel and cobalt are only sparingly so. As conflicting statements have been made with regard to the nature of the reaction and the products formed, the present investigation was undertaken.

When freshly precipitated iron, zinc, or manganese sulphide is suspended in water and a current of sulphur dioxide introduced, the sulphide rapidly dissolves, and the sulphite of the metal is gradually deposited, the reaction being represented by the equation: $MS + H_2SO_3 = MSO_3 + H_2S$. On continuing to pass sulphur dioxide into the mixture, the sulphite dissolves to form the hydrogen sulphite. If the solution of the hydrogen sulphite is boiled, the sulphite is re-deposited. The solution now contains thiosulphate, which is produced by the action of sulphur, formed by the interaction of sulphurous acid and hydrogen sulphide, on the hydrogen sulphite, thus: $M(HSO_3)_2 + S = MS_2O_3 + H_2O + SO_2$. These and other experiments show that the reaction between sulphurous acid and the sulphides of zinc, iron, and manganese is a double decomposition of the usual type, and that, in so far as the conditions lead to the oxidation of the liberated hydrogen sulphide by the sulphurous acid, a certain amount of thiosulphate is produced by a secondary reaction. E. G.

Alloys of Cobalt with Chromium and Other Metals. ELWOOD HAYNES (*J. Ind. Eng. Chem.*, 1913, **5**, 189—191).—Tungsten alloys readily with chromium and cobalt in all proportions. Taking an alloy of chromium and cobalt as the basis, and keeping the proportion of chromium at 15% of the entire mixture, the alloy gradually increases in hardness with increasing percentage of tungsten. When the quantity of tungsten rises to 5%, the alloy becomes distinctly harder; 10% tungsten gives an alloy suitable for both cold chisels and wood-working tools; 15%, an alloy excellent for cold chisels; a 20% alloy makes good lathe tools for cutting steel and other metals at moderate speeds, etc. A 40% alloy is so hard that it readily scratches not only glass, but quartz, and can be used for turning cast-iron.

Very similar results are obtained when the tungsten is replaced by molybdenum. The 25% alloy has a magnificent colour and lustre. If carbon, boron, or silicon be added to any of the alloys, it renders them much harder, but they also become more brittle.

When the percentage of chromium is kept at 25% instead of 15%, the addition of either tungsten or molybdenum still increases the hardness of the alloy. T. S. P.

The Violet Chromium Sulphates. A. SÉNÉCHAL (*Compt. rend.*, 1913, **156**, 552—555).—Two violet chromium sulphates are at present known, namely, the hydrates having respectively $15H_2O$ and $17H_2O$ (compare Weinland and Krebs, A., 1906, ii, 453). A study of the vapour tension, rate of dehydration, and heat of solution of these hydrates now leads to the conclusion that there are five possible violet chromium sulphates, being the hydrates containing respectively 12, 14, 15, 16, and 17 H_2O. W. G.

The Reduction of Tungstic Acid and the Lower Oxidation Stages of Tungsten. I. OSCAR OLSSON (*Ber.*, 1913, **46**, 566—582). —All the reduction experiments were carried out with a solution of tungstic acid in concentrated hydrochloric acid, which was made

by adding gradually a solution of potassium tungstate to boiling hydrochloric acid. Success in obtaining such a solution is obtained only when the conditions given by the author are strictly observed. Double salts of tervalent tungsten can then be obtained from this solution as follows: The solution is reduced with tin at 40—60° until the colour is a deep green; it is then rapidly filtered through glass wool, and the filtrate saturated with hydrogen chloride, cooling meanwhile with a freezing mixture. A yellowish-green to yellowish-brown powder gradually separates; the current of hydrogen chloride is stopped after six to seven hours, and the crystals allowed to deposit for twenty-four hours, after which time they are collected, washed with alcohol and ether, dried in a current of carbon dioxide, and preserved in a carbon dioxide desiccator. The *potassium* salt thus obtained has the composition $K_3W_2Cl_9$, and by double decomposition in hydrochloric acid solutions of rubidium chloride, cæsium sulphate, and thallous chloride respectively, the *rubidium*, *cæsium*, and *thallium* salts were prepared. The *ammonium* salt was prepared similarly to the potassium salt, using a solution of ammonium metatungstate as the starting point. All these salts are anhydrous, have the general formula $M_3W_2Cl_9$, and crystallise in thin, hexagonal plates, which have a greenish-yellow colour in transmitted light. The concentrated aqueous solutions are green, becoming greenish-yellow on dilution. The solubility decreases as the atomic weight of the alkali metal increases. They can be preserved for several days when dry, but are rapidly oxidised when moist. The solutions show no characteristic absorption bands, but a general absorption at either end of the spectrum, the visible spectrum extending from $\lambda = 700$ to $\lambda = 520$ for a solution of 1 gram of the potassium salt in 100 c.c. of 3% hydrochloric acid, the thickness of the absorbing layer being 1 cm. For a solution containing 0·1 gram of the salt per 100 c.c., the spectrum extends from $\lambda = 700$ to $\lambda = 490$.

When the solution of tungstic acid aforementioned is reduced with tin at the ordinary temperature, it first becomes light blue in colour, the colour then gradually deepens, and finally suddenly changes to an intense reddish-violet colour, similar to that of permanganate. This colour persists for a long time, and a small quantity of a dark green powder deposits, consisting of quadratic, tabular crystals, which are red in transmitted light. These appear to be a *potassium double salt* of quadrivalent tungsten, having the empirical formula $K_2W(OH)Cl_5$. The salt is stable when dry, but oxidises rapidly when moist. The absorption spectrum of the hydrochloric acid solution is similar to that of the tervalent compounds, the visible spectrum for a solution of 1 gram in 150 c.c. of 4% hydrochloric acid and a thickness of 1 cm. extending from $\lambda = 730$ to $\lambda = 610$. T. S. P.

The Preparation of Metallic Vanadium. OTTO RUFF and WALTER MARTIN (*Zeitsch. anorg. Chem.*, 1913, **80**, 59—64. Compare A., ii, 166; Prandtl and Manz, this vol., ii, 142).—The authors' data refer to metal obtained free from slag by fusing in the arc under a vanadium electrode. C. H. D.

The System: Antimony Sulphide, Lead Sulphide. HENRI PÉLABON (*Compt. rend.*, 1913, **156**, 705—707).—A study of the melting-point curve of mixtures of the sulphides of lead and antimony. There is a eutectic at a temperature of 482°, corresponding with a mixture of 22 mols. of lead sulphide with 78 mols. of antimony sulphide. There are two transition points, one at 568°, and the other at 610°, where two compounds crystallise out corresponding in composition and appearance respectively with the minerals zinckenite, Sb_2S_3,PbS, and jamesonite, $Sb_2S_3,2PbS$. W. G.

Compounds of Bismuth and Iodine. H. S. VAN KLOOSTER (*Zeitsch. anorg. Chem.*, 1913, **80**, 104—112. Compare Marino and Becarelli, this vol., ii, 227).—Bismuth tri-iodide readily decomposes when heated, and must be prepared by heating the compounds together in a sealed tube. It then has m. p. 408°. The equilibrium diagram of mixtures of bismuth and iodine, also determined in closed tubes, shows that the tri-iodide forms a sharp maximum on the freezing-point curve, and that two liquid layers are formed at 339° between 38 and 96 atomic % Bi. The eutectic point lies very close to the bismuth end. A reaction at 281° possibly represents the formation of a compound BiI from BiI_3 and liquid. There is no evidence of the formation of a compound BiI_2 (Herz and Guttmann, A., 1908, ii, 199).

The mixtures have also been examined microscopically. The tri-iodide forms lamellæ, and a eutectic structure is well developed.
C. H. D.

The Sorption of Hydrogen by Palladium. ALFRED HOLT, EDWARD C. EDGAR, and JAMES B. FIRTH (*Zeitsch. physikal. Chem.*, 1913, **82**, 513—540).—From a series of experiments on the sorption (adsorption and absorption) of hydrogen, it is shown that palladium exists in an active and a passive form with respect to its action on hydrogen, and is only capable of occluding large volumes of hydrogen when in the active condition. The activity of palladium falls off rapidly after a time, but may be regained by heating. The authors come to the conclusion that the activity of the metal is due to the formation of a metastable modification. The rate at which hydrogen is occluded was studied, and it is shown that the velocity of occlusion falls off in proportion to the amount of hydrogen already present in the metal. From the experiments it is evident that hydrogen occluded by palladium is present in two forms: (1) as an adsorbed surface layer of high vapour pressure which can easily be removed by evacuating the containing vessel, and (2) as an absorbed layer which permeates the whole of the metal, but which is not of uniform concentration throughout the metal. The process of occlusion in this case is therefore shown to consist in an adsorption, which is then followed by a slow diffusion into the interior of the metal from the surface layer. The velocity of diffusion of hydrogen through palladium is studied, and shown to increase with the temperature, but it is not always the same, a fact which points to the diffusion being influenced by the condition

of the metal. The experiments show that it is unlikely that even after long periods the hydrogen has the same concentration throughout the whole of the metal. J. F. S.

Osmium Dioxide as a Hydrogen Carrier. FRANZ LEHMANN (*Arch. Pharm.*, 1913, **251**, 152—153. Compare Hofmann, this vol., ii, 62).—Osmium tetroxide in presence of oleic acid or liquid oils is converted into hydrated osmium dioxide, and the acid or oil is reduced to the corresponding saturated acid or glyceride; thus, a mixture of olive oil (10 grams) with 0·05 gram of osmium tetroxide, on heating and passing hydrogen during one hour, yielded a fat melting at 39°, and on further treatment gave a product melting at 45°. T. A. H.

Mineralogical Chemistry.

Chalcocite Deposition. ARTHUR COE SPENCER, (*J. Washington Acad. Sci.*, 1913, **3**, 70—75).—In the presence of oxygenated waters in the upper regions of ore-deposits, sulphides (iron-pyrites and copper-pyrites) are altered, with the formation of sulphates and free acid. Solutions of ferric sulphate percolating still farther are reduced to ferrous sulphate by contact with these sulphides; and at greater depths solutions of cupric sulphate react with the unaltered primary sulphides, giving rise to secondary chalcocite (Cu_2S). Sulphur dioxide is probably produced by these reactions, and its presence seems to favour the formation of chalcocite; further, copper-pyrites seems to have more effect in this direction than does iron-pyrites. Several equations are given to suggest the reactions which may take place under these conditions. L. J. S.

Immense Bloedite Crystals. WALDEMAR T. SCHALLER (*J. Washington Acad. Sci.*, 1913, **3**, 75—76).—A deposit of nearly pure sodium sulphate (containing 1·66% MgO) forms a crust on Soda Lake, in Carriso Plain, San Luis Obispo Co., California. In the black mud beneath this crust are found isolated crystals of bloedite, the largest of which measures $16\frac{1}{2} \times 10\frac{1}{2} \times 3\frac{1}{2}$ cm., and weighs 652 grams. The following analysis of this material agrees with the usual formula, $Na_2Mg(SO_4)_2,4H_2O$:

MgO.	Na_2O.	SO_3.	H_2O.	Total.
11·93	18·26	48·11	21·37	99·67

L. J. S.

Serpentines of the Central Coast Ranges of California. H. E. KRAMM (*Zeitsch. Kryst. Min.*, 1913, **52**, 78; from *Proc. Amer. Phil. Soc.*, 1910, **49**, 315—349).—A petrographical description is given of the serpentine rocks of this region. The primary minerals include

olivine, enstatite, bronzite, diallage, picotite, and chromite (anal. I, from Cedar Mountain, Alameda Co.), and those of secondary origin are serpentine, chrysotile, magnetite, tremolite, hydromagnesite (anal. II), calcite, dolomite, aragonite, epsomite, limonite, and hæmatite.

	Al_2O_3.	FeO.	CaO.	MgO.	Cr_2O_3.	NiO.	MnO.	$-H_2O$.	Total.
I.	18·79	16·99	trace	8·41	55·74	trace	trace	0·09	99·82

	SiO_2.	Fe_2O_3.	Al_2O_3.	CaO.	MgO.	CO_2.	H_2O.	Total.
II.	9·37	trace	trace	2·46	39·25	29·45	18·74	99·27

L. J. S.

Petrographical Investigations in the Mountains between the Septimer and Julier Passes. HANS PETER CORNELIUS (*Jahrb. Min.*, 1913, *Beil.-Bd.*, **35**, 374—498).—A detailed petrographical description of this district in Grisons, Switzerland, with several analyses of igneous and schistose rocks. The following mineral analyses are also given: I, riebeckite (or more exactly an amphibole containing 44·2% of the riebeckite molecule), isolated from a riebeckite-schist of contact-metamorphic origin; II, white diopside, forming platy masses with a porcellanous aspect, and occurring in veins in serpentine and contact-metamorphic limestone:

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO	CaO.	MgO.	K_2O.	Na_2O.	Loss on ignition.	Total.	Sp.gr.
I.	53·63	0·30	3·27	11·24	7·14	0·77	3·52	9·71	1·88	6·59	2·20	100·25	3·16
II.	52·52	—	—	1·16	1·10	0·11	26·68	17·59	—	—	0·93*	100·09	3·19

*CO_2.

L. J. S.

Analytical Chemistry.

Spectrophotometry in Analysis. CHARLES FÉRY and EUGÈNE TASSILLY (*Ann. Falsif.*, 1913, **6**, 73—78).—The quantity of metal in a solution may be estimated by determining the absorption-coefficient of the solution by means of the spectrophotometer. For the estimation of iron, the thiocyanate coloration is used, and in the presence of a large excess of thiocyanate the absorption is proportional to the quantity of iron present. In the case of copper, the metal is converted into its ferrocyanide before the solution is examined.

W. P. S.

Vegetable Indicator in Volumetric Analysis. M. EMMANUEL POZZI-ESCOT (*Ann. Chim. anal.*, 1913, **18**, 58—59).—An alcoholic infusion of crushed black pansy flower is recommended as indicator in volumetric work. Mineral acids change the colour to red, but it remains bluish-violet with weak acids (acetic, formic, etc.).

Alkalis even of the weakest description change the colour to green; it is particularly sensitive to ammonia. L. DE K.

A New Method for the Estimation of Hypochlorites. HERBERT G. WILLIAMS (*Chem. News*, 1913, **107**, 109).—See P., 1912, **28**, 327.

Further Observations on the New, Sensitive, and Characteristic Reactions of Bromine. III. ICILIO GUARESCHI (*Atti R. Accad. Sci. Torino*, 1913, **48**, 4—14. Compare A., 1912, ii, 989). —The author claims priority over Denigès (A., 1912, ii, 1208) for this reaction. The present paper mentions a number of other dyes which may be used instead of magenta, and also records the existence of traces of bromine in various pure salts and in the ashes of certain plants. The reaction may be used to distinguish the hydrobromides of organic bases from their other salts. The magenta reagent shows the presence of bromine in the dibromo-derivatives of the dicyanodialkylglutarimides. When a solution containing a trace of hypobromite is treated with acid, it gives the magenta reaction. The reaction may also be applied (in some cases as a convenient lecture experiment) to detect the bromine produced in such reactions as that between iodine and bromates, or the expulsion of bromine from some of its compounds by iodine. Some bromides (including those of potassium, barium, uranyl, sulphur, and lead) evolve traces of bromine when they are heated sufficiently; other bromides do so in presence of iodine, either with or without heating. Concentrated hydrobromic acid does not yield bromine, even when boiled with iodine. The decomposition of organic bromine derivatives can be recognised in the same way. Dibromo*iso*butane, $CMe_2Br\cdot CH_2Br$, tribromoethane, $CH_2Br\ CHBr_2$, and bromo*iso*pentane, $CHMe_2\cdot CH_2\cdot CH_2Br$, do not yield bromine when boiled with or without iodine. Bromoform evolves bromine when heated or exposed to light, and bromal hydrate behaves similarly. R. V. S.

An Application of the Electric Resistance Furnace to the Estimation of Oxygen in Iron and Steel. R. H. MCMILLEN (*J. Ind. Eng. Chem.*, 1913, **5**, 123—125).—Two electric furnaces capable of maintaining a temperature of 950°, and fitted with quartz tubes are connected up in series, a U-tube containing phosphoric oxide being placed between them. The first furnace is connected to the source of pure hydrogen, and the quartz tube contains several spirals of platinum gauze, so that any oxygen contained in the hydrogen is burnt up, the water produced being absorbed in the phosphoric oxide tube. The sample to be analysed (25 grams of drillings) is contained in a porcelain boat in the tube of the second furnace, and the water formed by the reduction of the oxides in the sample is absorbed in a weighed phosphoric oxide U-tube attached to the furnace. The latter U-tube is guarded by a sulphuric acid wash-bottle.

The usual precautions are taken for sweeping all air and moisture

out of the apparatus before the estimation is commenced It is advisable to run a blank experiment from time to time.

The results of the analyses of a number of irons and steels are given. T. S. P.

Direct Estimation of Oxygen in Organic Compounds. MAITLAND C. BOSWELL (*J. Amer. Chem. Soc.*, 1913, **35**, 284—290).—A method is described for the direct estimation of oxygen in carbon compounds. The substance, contained in a silica boat, is placed at one end of a quartz tube, 13 mm. in internal diameter and 980 mm. long, which is put into an ordinary combustion furnace. The substance is heated strongly in a current of pure hydrogen, and the products are passed over a long layer of fragments of charcoal, about 1 cu. mm. in size, maintained at a white heat. By this means all the oxygen in the compound is converted into water, carbon dioxide, and carbonic oxide. The water is absorbed in concentrated sulphuric acid, the carbon dioxide in soda-lime, and the carbonic oxide is estimated by passing the gas, freed from water and carbon dioxide, through iodine pentoxide, and absorbing the resulting carbon dioxide with soda-lime (compare Levy, A., 1912, ii, 203). Experiments are quoted which show that the method is capable of giving results of about the same degree of accuracy as the usual combustion method for estimating carbon and hydrogen.

E. G.

Iodometric Estimation of Persulphuric Acid. ERICH MÜLLER and HORST VON FERBER (*Zeitsch. anal. Chem.*, 1913, **52**, 195—197).—A stoppered flask holding 100—120 c.c. is filled with carbon dioxide gas, 5 grams of potassium iodide are added, and also 10 c.c. of ferrous sulphate solution (3 grams of crystals, 1 c.c. *N*/2-sulphuric acid up to 100 c.c. of water); any iodine liberated is removed with thiosulphate. After adding either the persulphate in powder or in solution and more water so as to leave about 30 c.c. space, the flask is closed and left for five minutes. The iodine liberated, which represents the persulphuric acid, is then titrated with standard thiosulphate. Towards the end, a current of carbon dioxide is passed and the titration continued. L. DE K.

Application of Devarda's Method in the Estimation of Nitrogen in Nitrocelluloses. KŒHLER, M. MARQUEYROL and JOVINET (*Ann. Chim. anal.*, 1913, **18**, 45—47).—A combination of the methods of Devarda and of Busch. 0·7 Gram of nitrocellulose is placed into a 700 c.c. flat-bottomed Jena flask, moistened with a little alcohol, and then treated with 30 c.c. of hydrogen peroxide (12 vols.), 60 c.c. of water, and 50 c.c. of aqueous potassium hydroxide, D 1·3; after placing on a small funnel, the flask is heated in a water-bath at 50—60° with frequent shaking. When the nitrocellulose has dissolved (the liquid should not turn yellow), the contents are boiled over the free flame until evolution of oxygen ceases.

When cold, 5 c.c. of alcohol and 2·5 grams of Devarda's alloy

(45% aluminium, 50% copper, 5% zinc) in fine powder are added. The flask is connected immediately with a Wagner distilling arrangement, the end of which, drawn to a point, dips into standardised sulphuric acid. When the evolution of hydrogen has diminished, the contents are heated just to boiling for twenty minutes, when a stronger heat is applied so as to distil half the liquid within thirty to thirty-five minutes.

The ammonia is then calculated as usual by titrating the excess of sulphuric acid in the receiver. L. DE K.

Methods of Estimating Nitrogen in Humus. CHARLES B. LIPMAN and H. F. PRESSEY (*J. Ind. Eng. Chem.*, 1913, **5**, 143—144).—The authors have compared the various methods for the estimation of nitrogen in humus. The humus extract was boiled with magnesium oxide until no more ammonia was evolved, and the nitrogen then estimated in the residue by the methods of Wilfarth, Gunning-Atterberg, and Hibbard, and the salicylic acid method. The Hibbard method was found to be the most satisfactory, giving the highest amounts of nitrogen, the best agreement between duplicates, and the least trouble in manipulation, as well as being the most speedy. It consists in heating the substance with 30 c.c. of concentrated sulphuric acid until fumes of sulphur trioxide are given off, and then adding 12 grams of a salt mixture made in the proportions of 10 grams of potassium sulphate, 1 gram of ferrous sulphate, and 0·5 gram of copper sulphate (compare *ibid.*, 1910, **2**, 463). The remainder of the estimation is as usual. T. S. P.

Colorimetric Estimations in Water Analysis by means of the Autenrieth-Koenigsberger Colorimeter. WILHELM AUTENRIETH and ALBERT FUNK (*Zeitsch. anal. Chem.*, 1913, **52**, 137—167).—The above colorimeter (A., 1910, ii, 910) is recommended for use in water analysis in the estimation of ammonia, nitrous and nitric acid (and their admixtures), iron, lead, and hydrogen sulphide. The usual reactions are employed. L. DE K.

Estimation of Ammonia in Effluents and Sewage. SERGIUS KRAPIVIN (*Zeitsch. anal. Chem.*, 1913. **52**, 198—199).—One hundred c.c. of the water are placed in a 200 c.c. flask, 10 c.c. of 10% barium chloride solution are added, and then 10 c.c. of $N/5$-sodium hydroxide and a few drops of phenolphthalein. After diluting to the mark and shaking, the solution is filtered, and 100 c.c. of the filtrate are neutralised with $N/10$-hydrochloric acid; 5 c.c. of 40% formaldehyde are added, and the liquid is titrated with $N/20$-sodium hydroxide until the colour remains pink. The acidity due to the formaldehyde itself is found by adding another 5 c.c. and titrating again.

The acidity liberated on adding formaldehyde represents the ammonia. L. DE K.

The Rate of Reaction of Nitrous Acid and Carbamide in Dilute Solutions. WALTER D. BONNER and EDWIN S. BISHOP (*J. Ind. Eng. Chem.*, 1913, **5**, 134—136).—It is shown that nitrous acid

and carbamide react at an appreciable rate, even when the initial concentrations are as low as 0·1 part of nitrite nitrogen per million, the carbamide being present in equivalent amount. If, however, the Griess reagent (sulphanilic acid–α-naphthylamine) is added to the solution, carbamide, even when present in excess, will not react with the nitrous acid, since the reaction between the nitrous acid and the Griess reagent is much quicker than that between the acid and carbamide.

The observation has been made that in very dilute solution carbamide and nitrous acid sometimes fail to react, for no apparent reason. T. S. P.

Soluble Silicic Acid in Basic Slag and its Effect on the Estimation of the Phosphoric Acid Soluble in Citric Acid. MAX POPP, J. CONTZEN, H. HOFER, and H. MENTZ (*Landw. Versuchs-Stat.*, 1913, **79–80**, 229—278).—The inconvenience caused by the presence of silica in estimating the soluble phosphoric acid in basic slag only occurs in the case of slags deficient in soluble iron. The following method gives satisfactory results: The citric acid extract (50 c.c.) is treated successively with 25 c.c. of iron citrate solution, 10 c.c. of 0·3% hydrogen peroxide, and 25 c.c. of magnesia mixture. The process is completed in the usual manner.

The iron citrate solution is prepared by adding 30 grams of ferric chloride dissolved in 50 c.c. of water to 1000 grams of citric acid; 4000 c.c. of 20% ammonia are then added slowly and carefully until all is dissolved. The volume of the mixture is made up to 5 litres, after which it is filtered.

The magnesia mixture is prepared by dissolving 550 grams of magnesium chloride and 700 grams of ammonium chloride in about 2 litres of water, adding 1750 c.c. of 20% ammonia, and diluting to 10 litres. It is filtered some days afterwards.

The total phosphoric acid in Wolter phosphate is estimated by dissolving 1 gram in 100 c.c. of 3% hydrochloric or nitric acid. The solution (not filtered) is treated with 2 c.c. of 3% hydrogen peroxide and 48 c.c. of iron citrate solution. It is then filtered, and 75 c.c. of the filtrate (=0·5 gram) treated with 25 c.c. of magnesia mixture. N. H. J. M.

The Test for Arsenic with Bettendorf's Reagent. LUDWIG W. WINKLER (*Zeitsch. angew. Chem.*, 1913, **26**, 143—144).—It is usually stated that Bettendorf's reagent, when testing for arsenic in solutions containing sulphuric acid, must be used in the cold, as otherwise the stannous chloride reduces the sulphuric acid to hydrogen sulphide, and stannous sulphide is precipitated. The author finds that this is not the case, and heat may be applied. The reagent is best made as follows: 100 grams of clear crystals of stannous chloride are dissolved in sufficient 36—38% commercial hydrochloric acid to give 1000 c.c. of solution. Traces of arsenic in the acid are deposited on keeping, the deposition being accelerated by shaking the solution with 1 gram of finely powdered glass. The clear, supernatant solution is used for the test. In testing

for arsenic one volume of the solution to be tested is heated to boiling with 5 volumes of the reagent, and then left for half-an-hour. Concentrated sulphuric acid must first be diluted with an equal volume of water.

The limit of sensitiveness of the test is 0·001 gram of arsenious oxide per litre. T. S. P.

An Internally Electrically Heated Combustion Tube for Organic Analysis. J. Marek (*J. pr. Chem.*, 1913, [ii], **87**, 287—288).—It has been shown previously (A., 1912, ii, 297) that the combustion of organic substances may be carried out without the use of an oxygen-carrier, provided that the combustion tube is strongly heated. In the present communication the author gives a sketch and description of an electrically heated combustion tube, in which the heating is effected internally by means of a spiral of platinum wire fused into the tube itself. F. B.

Gas Bubble and Washing Tube for Combustion Apparatus. H. E. Smith (*J. Ind. Eng. Chem.*, 1913, **5**, 150).—The part of the bubbler containing the sulphuric acid is modified in two ways: (1) a glass stopcock is fused on to the lower part of the bulb, so that the acid can be run out readily; (2) a side-tube containing glass beads is fused on, the top of this tube being closed with a rubber stopper, below which is fused another tube leading to the combustion apparatus. The apparatus can be recharged by taking out the rubber stopper and pouring in acid. T. S. P.

Modification of the Parr Total-carbon Apparatus. C. E. Millar (*J. Ind. Eng. Chem.*, 1913, **5**, 234—235).—The modification consists in the adaptation of a compensator for changes in temperature and pressure during the measurement of gas volumes, and may be applied to any gas burette. The principle is exactly the same as that applied to the ordinary nitrometer, where a third tube containing a fixed quantity of air is added and put into communication with the mercury of the levelling tube. In reading volumes of gas in the burette, the levelling tube is always raised until the mercury in the compensator stands at a fixed mark, whereby changes of pressure and temperature during the measurements are automatically compensated for. T. S. P.

A Method of Examination of Fermentation Gases. Walther Frieber (*Centr. Bakt. Par.*, 1913, ii, **36**, 438—443).—A modification of the method proposed by Burri and Düggeli (A., 1909, ii, 336). In the original method a shake culture with saccharine agar is prepared at the closed end of a long glass tube, the culture medium being covered by a layer of non-saccharine agar. By the formation of gas the latter is pushed towards the mouth of the tube, and the total gas production may be measured off. For the examination of the gases, the tube is filled with water, and the agar broken up by means of a bent wire; sodium hydroxide is then introduced, and the carbon dioxide absorbed.

This method is open to objection on account of the possibility of appreciable quantities of gas being absorbed or enclosed by the agar medium, and the author suggests (1) that mercury should be employed instead of water for filling the fermentation tube, and (2) that the culture tube filled with mercury should be heated for fifteen to thirty minutes in steam in order to melt the agar and to liberate the gases retained by it. On cooling, the volume of gas may be read off, and sodium hydroxide introduced in the usual manner. H. B. H.

A Comparison of Some Qualitative and Quantitative Methods for Carbonates in Soils. E. W. GAITHER (*J. Ind. Eng. Chem.*, 1913, **5**, 138—143).—The author confirms the method given by Marr (A., 1909, ii, 938) for the estimation of carbonates in soils.

If properly made, the litmus paper test is the best qualitative test for the presence or absence of native carbonates in soils from humid regions. Some soils may give alkaline aqueous solutions, because of the hydrolysis of minerals present in the soil. If there are no alkalis or basic materials in a soil which are capable of giving alkaline solutions, their absence will be indicated by the reddening of blue litmus paper. T. S. P.

Estimation of Hardness of Waters. PAUL ROHLAND (*Zeitsch. anal. Chem.*, 1913, **52**, 200—201).—The author explains the lathering of the soap solution after the calcium has been precipitated by the marked colloidal character of soap solutions. L. DE K.

Control of the Purification of Boiler Feed Water. GEORG WEISSENBERGER (*Zeitsch. angew. Chem.*, 1913, **26**, 140—143).—The author discusses the various methods which have been suggested for the control of the purification of boiler feed water, both from the point of view of accuracy and of time necessary for the analysis, and then proposes the following method: 100 c.c. of the water, at room temperature, are titrated with acid after the addition of 10 drops of a 20% solution of sodium chloride, using 2 drops of a phenolphthalein solution (1 gram in 100 c.c. of 95% alcohol) as indicator. The addition of the sodium chloride is to suppress the dissociation of the sodium carbonate, otherwise the end-point with phenolphthalein is affected. Two drops of methyl-orange (1 gram in 1 litre) are then added, and the water again titrated with acid. The neutral solution is then titrated with soap solution of such a strength that for 100 c.c. of water, 1 c.c. of the soap solution corresponds with 2° of hardness. A table is given from which, using the titration results, the quantities of lime water or sodium carbonate solution necessary for purification may be directly ascertained. T. S. P.

Estimation of Potassium by the Cobaltinitrite Method. J. L. M. VAN DER HORN VAN DEN BOS (*Chem. Weekblad*, 1913, **10**, 182—186).—A description of a method of estimating potassium volumetrically by means of sodium cobaltinitrite, applicable either

to an individual potassium salt, or to a mixture of potassium and sodium salts. The precipitate has the formula $K_2NaCo(NO_2)_6$.

A. J. W.

Estimation of the Carbonates and Hydroxides of Potassium and Sodium when together in Solution. W. A. BRADBURY and F. OWEN (*Chem. News*, 1913, **107**, 85—86).—A measured volume of the solution is titrated with sulphuric acid, using phenolphthalein as indicator. The acid used is equivalent to all the hydroxide and half the carbonate; methyl-orange is now added, and the titration completed; the additional amount of acid used is equivalent to half the carbonate, so that the amount of acid required for the carbonates and for the hydroxides can be calculated from these figures. The fully neutralised solution is evaporated to dryness, and the residue of sulphates weighed. The results obtained give all the data necessary for the calculation of the respective amounts of carbonates and hydroxides present.

Attempts to carry out the estimation by evaporating the solution to dryness and extracting the hydroxides with absolute alcohol gave unsatisfactory results.

T. S. P.

Estimation of Alkalis in Rocks. H. V. KRISHNAYYA (*Chem. News*, 1913, **107**, 100—101).—A suitable quantity of the powdered sample is heated in a platinum dish with hydrofluoric and sulphuric acids, and after expelling the excess of acid, the residue is dissolved in boiling dilute hydrochloric acid; any undissolved matter must be again submitted to the treatment with hydrofluoric and sulphuric acids. The mixed filtrate is then made up to a definite volume, and an aliquot part, representing 1 gram of the sample, is withdrawn. After evaporating to dryness and igniting the residue, thus rendering the iron and alumina insoluble, the alkali sulphates are extracted with boiling water, and, without filtering, converted into chlorides by adding barium chloride solution; some barium hydroxide is also added.

After removing the excess of barium with ammonium carbonate, the alkali chlorides are weighed jointly as usual. The potassium is then estimated as platinichloride in the ordinary manner.

L. DE K.

Estimation of the Absorbed Bases in Soils. DMITRI N. PRIANISCHNIKOV (*Landw. Versuchs-Stat.*, 1913, **79–80**, 667—680).—Kellner's method of estimating the absorbed bases in soils (displacing with ammonium chloride) is both slow and difficult, as the ammonium chloride is not easy to remove. Ammonium nitrite acts with greater vigour than the chloride, but has the disadvantage of being unstable. Both ammonium acetate and 3·2% ammonia are suitable for ascertaining the amount of absorbed potassium.

For estimating ammonia in soils, it was found that by digesting the soil (200 grams) ten times with 5% potassium chloride and distilling with magnesia, results were obtained which agree most nearly with those obtained by Boussingault's method and by

Schlœsing's hydrochloric acid method. The sodium hydroxide method of Schlœsing gives results which are evidently too high owing to the decomposition of amido-compounds.

Previous experiments showed that whilst plants can assimilate the potassium of biotite, nepheline, and muscovite, the potassium of orthoclase, sanidine, and leucite is not available, or only to a very slight extent. It was found that by extracting the minerals once with ammonium chloride, and estimating the potassium dissolved, similar indications were obtained.

Experiments with barley showed that the potassium of zeolites is almost completely unavailable when isolated. In contact with nutritive salts, and even with calcium carbonate, it is readily assimilated. N. H. J. M.

The Gay-Lussac Method of Silver Estimation. Frederic P. Dewey (*J. Ind. Eng. Chem.*, 1913, **5**, 209—214).—An account of the method used and the precautions taken in the United States Mint for the estimation of silver according to the method of Gay-Lussac. Very elaborate tests of the method have been made, and the conclusion arrived at is that two analysts, working on identical samples of standard silver and making four estimations each, may differ as much as 1 "fine" (0·1%) in their reports. T. S. P.

New Forms of Flask and Beaker for the Volumetric Estimation of Silver, Chlorine, Sulphuric Acid, etc. V. N. Ivanov (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 66—69*).—Volhard's method gives results which are about 0·4% too high (or too low) when used for the estimation of silver (or chlorine). This inaccuracy, which is due to adsorption of ammonium thiocyanate by the silver thiocyanate, may be avoided by using for the titration a beaker with vertical or slightly tapering sides, and a concave base. The central part of the base is blown into the form of a spherical bulb, which juts up into the body of the beaker, and leaves a distance of not more than 0·5 cm. between itself and the main wall of the beaker. The precipitate formed falls through this narrow space to the bottom of the beaker, where it remains even after rotation of the vessel. When the end-point is approached, the contents of the beaker are thoroughly mixed by vigorous shaking, the precipitate being allowed to settle again before the titration is continued. The final red coloration is found to persist for some hours, whereas that obtained in the ordinary way disappears in the course of a few minutes. The above procedure yields results identical with those given by Mohr's volumetric method or by the gravimetric method. T. H. P.

Purification of Barium Sulphate Precipitated in the Estimation of Barium. Frank A. Gooch and D. U. Hill (*Amer. J. Sci.*, 1913, [iv], **35**, 311—314).—When barium is estimated by precipitation of the sulphate in presence of alkali salts, considerable errors may be occasioned by the occlusion of foreign substances. These may be avoided by dissolving the precipitate in concentrated sulphuric acid and evaporating to dryness, when the barium sulphate

* and *Chem. Zeit.*, 1913, **37**, 427.

crystallises in more or less coarsely granular crystals, which can be readily washed free from the alkali metal sulphates.

The evaporation of the sulphuric acid solution can be effected in a platinum crucible heated by a Hempel burner, or by directing a small blow-pipe flame to the tip of a cone of fine platinum gauze, which is fitted into the mouth of the crucible. The use of this gauze cone is quite effective in preventing loss by sputtering.

H. M. D.

Estimation of Copper in White Metal Alloys. Frederick Ibbotson and L. Aitchison (*Chem. News*, 1913, **107**, 121).—0·5 Gram of drillings is dissolved in 10—15 c.c. of aqua regia, and an equal volume of water is added. Any lead chloride separating on cooling is filtered off. To the filtrate is added 1 gram of tartaric acid, and the bulk of the acids is neutralised with sodium hydroxide. The heated liquid is then poured slowly into a boiling solution composed of 20 grams of sodium hydroxide and 2—3 grams of hydrazine hydrochloride in 250—300 c.c. of water. After fifteen minutes the metallic copper is collected on paper pulp, washed with hot water, and then redissolved in dilute nitric acid (1 acid of D 1·2—1 water). The solution is evaporated to pasty constituency, and the residue is moistened with a few drops of nitric acid and dissolved in water; the solution should not be opalescent (absence of tin). After rendering alkaline with solution of sodium carbonate, acetic acid is added in slight excess, and the solution boiled. When cold, the copper is titrated in the usual way, iodometrically. L. de K.

The Thiocyanate Permanganate Method for Copper in Ores. D. J. Demorest (*J. Ind. Eng. Chem.*, 1913, **5**, 215—216).—Guess's method for the estimation of copper (compare Grossmann and Hölter, A., 1909, ii, 449) is modified by oxidising most of the thiocyanate with alkaline permanganate and completing the oxidation with acid permanganate; a correction factor is thereby avoided.

The weight of ore taken should contain from 0·05—0·3 gram of copper. It is heated for several minutes with 5 c.c. of concentrated hydrochloric acid, after which 10 c.c. of nitric acid are added, and the ore digested until completely decomposed; 10 c.c. of sulphuric acid (1 : 1) are added, and the whole evaporated until sulphuric acid fumes appear. It is then cooled, 50 c.c. of water containing 3 grams of tartaric acid added, and heated until all soluble salts are dissolved; again cooled, ammonia added until the liquid is a deep blue, and then acidified with sulphuric acid. After the addition of 1 gram of sodium sulphite, dissolved in 20 c.c. of water, the solution is heated nearly to boiling, and then a solution of 1 gram of potassium thiocyanate in 20 c.c. of water added, with vigorous stirring, to precipitate the copper. It is heated for some time to coagulate the precipitate and dissolve the tartaric acid, filtered through a Gooch crucible, washed well, and then 30 c.c. of a hot 10% solution of sodium hydroxide run through the crucible in order to decompose the cuprous thiocyanate; and again washed well. The filtrate is warmed to 50°, and the thiocyanate present titrated with

permanganate, spot-testing it from time to time with ferric chloride and hydrochloric acid. When the red colour in the spot-test becomes very faint, 30 c.c. of sulphuric acid (1 : 1) are added, all the manganese dioxide allowed to dissolve, and the titration finished with permanganate.

No elements interfere with the method except silver; any lead present is collected as sulphate after evaporating with sulphuric acid. The results are accurate. T. S. P.

Electrolytic Estimation of Copper in Ores containing Arsenic, Antimony, or Bismuth. D. J. DEMOREST (*J. Ind. Eng. Chem.*, 1913, **5**, 216).—Advantage is taken of the fact that copper is entirely precipitated as cuprous thiocyanate from a solution containing ammonium sulphate, ammonium tartrate, and tartaric acid. The ore (1 gram, or more if the sample is low in copper) is treated according to the method given in the preceding abstract, using, however, 7 c.c. each of hydrochloric acid and nitric acid, 5 c.c. of sulphuric acid, 30 c.c. of water, and 2 grams of sodium sulphite. The precipitate of cuprous thiocyanate, after being collected on a dense filter, is washed several times with a solution containing about 1% of potassium thiocyanate, and the same amount of tartaric acid. The precipitate is then dissolved in nitric acid (1: 2), using as little as possible, the solution boiled to destroy all the thiocyanate, the volume made up to 125 c.c., and the copper estimated electrolytically. T. S. P.

The Electro-analytical Separation of Copper from Tungsten and Molybdenum. W. D. TREADWELL (*Zeitsch. Elektrochem.*, 1913, **19**, 219—221).—It is shown that tungsten and molybdenum are not quantitatively separated from copper by electrolysis in potassium cyanide solution. Copper, existing as chloride, nitrate, sulphate, phosphate, or acetate, can be quantitatively separated from tungsten, which must be present as sodium tungstate, by the following process. The solution is treated with 15—20 c.c. of concentrated ammonia and 3—5 grams of ammonium sulphate, and electrolysed with current having an *E.M.F.* of 2 volts. Stationary or rotating cathodes may be used, and there is no deposition of tungsten if the current is allowed to pass for long periods after all the copper has been deposited. Copper can be separated from molybdenum, which must be present as ammonium molybdate by adding an alkali sulphite to the ammoniacal solution, and electrolysing with a current having an *E.M.F.* of 0·9 volt. In this process the current must not be allowed to flow for more than a few minutes after the blue colour has disappeared from the solution. Experiment shows that if it is allowed to flow for five minutes after the blue colour has vanished, all the copper will have been deposited, and no molybdenum hydroxide will have been precipitated. It is also stated that in the quantitative estimation of molybdenum as molybdenum trioxide, it must not be heated above 400—450°, and the operation must be carried out in a porcelain crucible, and not

in a platinum crucible. The reasons for these precautions are: (1) molybdenum trioxide is volatile above 450°, and (2) it is reduced in contact with platinum. J. F. S.

Estimation of Free Acid or Base in Aluminium Sulphate. V. N. IVANOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 57—66).—The method usually employed for the estimation of free acid in aluminium sulphate is that devised by Beilstein and Grosset, which consists in addition of ammonium sulphate to form ammonium alum, treatment with alcohol, evaporation of the filtrate to dryness, and titration of the dissolved residue with alkali in presence of methyl-orange. The author finds, however, that this method indicates about 0·22% of free sulphuric acid after addition to the aluminium sulphate of a quantity of alkali five times as large as should be sufficient to neutralise the free acid originally found. Further, the result obtained varies with the amount of water taken to dissolve the aluminium sulphate, and with the amount of alcohol used to wash the precipitated alum.

The following method is free from these defects. One gram of the sulphate is dissolved in a 100 c.c. Erlenmeyer flask in 50 c.c. of water, and into the liquid, heated to 85°, 12 c.c. of potassium ferrocyanide solution (1 : 12) are quickly added, with constant stirring, from a burette. Immediately afterwards 20 c.c. of barium chloride solution (1 : 10) are pipetted into the liquid, which is kept in vigorous movement. The whole of the liquid and precipitate is introduced into a 100 c.c. flask, and the volume made up to 100·25 c.c., 0·25 c.c. representing the volume displaced by the precipitate. When mixed, the contents are allowed to settle for an hour, 25 or 50 c.c. of the clear supernatant liquid being then titrated with decinormal sodium hydroxide solution in presence of 3 or 4 drops of methyl-orange solution (1 : 1000). The method has been tested by means of a solution of aluminium sulphate, to which different known proportions of sulphuric acid were added, and found to give satisfactory results. The reaction with the ferrocyanide is represented by the equation:

$$2K_4Fe(CN)_6 + 3H_2SO_4 = 6HCN + K_2Fe[Fe(CN)_6] + 3K_2SO_4.$$

When the clear liquid from the barium precipitate exhibits no acidity, the substance contains free base. In such case, to a solution of 1 gram of the aluminium sulphate in 50 c.c. of water are added 2 c.c. of seminormal hydrochloric acid, the liquid being then heated to 85°, and treated as described above. The difference between the amount of acid then found and that corresponding with 2 c.c. of seminormal acid is calculated as either aluminium hydroxide or sodium hydroxide.

If a rapid but not very accurate estimation of the acidity is desired, the aluminium sulphate solution may be titrated immediately with seminormal alkali hydroxide solution, a drop of the liquid being removed from time to time and placed on a filter paper previously soaked in methyl-orange solution (1 : 1000) and dried. When the red colour originally formed round the precipitate gives

place to an orange colour, the titration is complete. This procedure gives results about 0·2% too low. T. H. P.

Rapid Estimation of Manganese in the Presence of Iron. M. EMMANUEL POZZI-ESCOT (*Ann. Chim. anal.*, 1913, **18**, 56—58).—The solution containing the manganese is heated to boiling and precipitated with excess of sodium hydroxide and about 1 gram of persulphate. The precipitate, after being washed, is heated in a special apparatus (very much like that of Baubigny and Chauvanne; A., 1904, ii, 203) with hydrochloric acid, and the vapours are absorbed in a solution containing 3 grams of potassium iodide, 5 grams of sodium acetate, and 4—5 grams of zinc oxide in suspension. A slow current of carbon dioxide facilitates the elimination of the chlorine.

The iodine liberated is then titrated as usual with $N/10$-thiosulphate; 1 c.c. = 0·000275 gram of metallic manganese. L. DE K.

The Volumetric Estimation of Manganese in Rock, Slags, Ores, and Spiegels. FLOYD J. METZGER and L. E. MARRS (*J. Ind. Eng. Chem.*, 1913, **5**, 125—126).—The application of the authors' method for the estimation of manganese (A., 1912, ii, 94) to rock, slags, etc., is given.

Two to five grams of rock are boiled in a platinum dish with 5—15 c.c. of dilute sulphuric acid (1 : 2), and then with 5—15 c.c. of hydrofluoric acid until decomposition is complete; 5—10 c.c. of dilute nitric acid (1 : 1) and 2—3 c.c. of concentrated sulphuric acid are added, the flame removed, and about 1 gram of ammonium persulphate added in small portions at a time. When evolution of gas has ceased, the solution is evaporated until fumes of sulphur trioxide appear, cooled, 50 c.c. of water added, boiled and cooled. It is then transferred to a waxed beaker, and treated as described in the previous paper (*loc. cit.*). Slag is treated similarly to rock, 0·2—1·0 gram being taken. Ores (pyrolusite) are dissolved in 50% hydrochloric acid, the solution evaporated down with sulphuric acid, nitric acid then added, and afterwards ammonium persulphate, the remainder of the treatment being similar to that with rock. 0·5—1 Gram of the ore is taken. Ores, slags, etc., which are insoluble in hydrochloric or nitric acid, are treated in the same way as rock. Spiegels and ferromanganese are analysed according to the method already given (*loc. cit.*). T. S. P.

The Estimation of Small Quantities of Manganese and Chromium in Minerals and Rocks. MAX DITTRICH (*Zeitsch. anorg. Chem.*, 1913, **80**, 171—173).—The colorimetric estimation of manganese in rocks is often difficult, owing to the presence of chromium, which alters the colour of the permanganic acid solution. By adding ammonia to the mixed solution of permanganate and chromate and warming, all the manganese and iron are precipitated as hydroxides. The washed precipitate may be dissolved, warmed, and oxidised by means of ammonium persulphate as usual. The chromium may be estimated colorimetrically by comparison with a

standard solution of potassium chromate after removal of silver by sodium chloride, and concentration. The method is not accurate for chromium when the quantity of this falls below 2 mg.

C. H. D.

Volumetric Estimation of Chromium, Vanadium, and Iron in Presence of One Another. FREDERICK W. ATACK (*Analyst*, 1913, **38**, 99—102).—A solution of methylene-blue (4 grams per litre) is boiled with dilute hydrochloric acid in a current of carbon dioxide, and then decolorised with titanous chloride. A known quantity of the solution of the above metals is then run in, and the regenerated blue titrated with titanous chloride.

Chromium must be converted into chromate by boiling with sodium peroxide. If iron is also present, dilute sulphuric acid is added until the precipitate is redissolved; the result then will be chromate + ferric salt. By boiling another portion of the solution with hydrochloric acid, thus reducing the chromic acid, a second experiment will give the iron only. Vanadium, either alone or in presence of iron, is estimated as directed for chromium.

In a mixture of the three metals, one portion is titrated as directed, the result being the amount of chromate, vanadate, and ferric salt. A second portion is boiled with hydrochloric acid, thus, when titrated, giving the ferric salt only. A third portion is boiled with sulphur dioxide and then (partly) reoxidised with permanganate. The result of the methylene-blue titration is then vanadate + ferric salt.

In iron alloys the chromium may be determined directly by fusion with sodium hydroxide and peroxide. The chromate formed is then extracted with water.

L. DE K.

An Electrolytic Method for the Estimation of Tin in Canned Food Products. ALLERTON S. CUSHMAN and EVERETT B. WETTENGEL (*J. Ind. Eng. Chem.*, 1913, **5**, 217—218).—The usual method employed in the authors' laboratories was to destroy the organic matter with a mixture of sulphuric and nitric acids, neutralise the solution, from which all nitric acid had been expelled, with ammonia, acidify with hydrochloric acid, precipitate the tin as sulphide, and weigh as oxide. The great objections to this method are the time involved, the quantities of acid used, and the damage caused to the hoods and flues by the acid fumes. The method now adopted is as follows: 50 grams of the pulped material are brought to a slow boil with 50 c.c. of concentrated hydrochloric and 25 c.c. of nitric acid, using a 600 c.c. beaker. The boiling is continued for five minutes, stirring continuously, unless foaming occurs, when the flame is removed, and the material allowed to digest for ten minutes. The solution is then diluted with an equal volume of water, made alkaline with strong ammonia, and 25 c.c. of saturated ammonium sulphide, digested for a few minutes, and then filtered through a fluted filter. The residue is washed with boiling water containing a little

ammonium sulphide, and the tin in the filtrate (400 c.c.) is deposited on a rotating cathode. The deposition of tin is complete in one to four hours. 1·5 Amperes at 4 volts are used, but no details are given of the area of the cathode, which consists of a platinum crucible. T. S. P.

Estimation of Tin in Bronzes. FREDERICK IBBOTSON and L. AITCHISON (*Chem. News*, 1913, **107**, 109—110).—The tin is estimated directly in the precipitated metastannic acid, without any previous ignition or weighing.

For a bronze containing about 10% of tin, 1 gram of coarse drillings is taken and treated with 10—15 c.c. of nitric acid (D = 1·4). (The quantity of alloy taken should be such that it contains about 0·1 gram of tin.) When the action is complete, the solution is evaporated to a paste, 75 c.c. of water added, and boiled for a few minutes. The precipitate is allowed to settle, and washed by decantation through a tightly-packed filter of asbestos pulp, the hot wash-water containing a small quantity of nitric acid. It is washed finally with water until the free nitric acid is removed, and the whole of the filter and precipitate then transferred to the flask containing the greater portion of the metastannic acid, using as little water as possible in the transference (less than 20 c.c., if possible). Next a volume of concentrated sulphuric acid is added equal to that of the water used, and the solution boiled for three minutes, taking due precautions against bumping. Then 50 c.c. of concentrated hydrochloric acid are added and boiled for two minutes, when a clear solution should be obtained. About 1 gram of finely powdered antimony is added, boiled for about a minute, and then cooled rapidly under the tap in an atmosphere of carbon dioxide. When quite cold, it is titrated at once with $N/20$-iodine, using starch as indicator. The proportion of sulphuric acid to hydrochloric acid used should be about 3 : 5 by volume; a greater proportion of sulphuric acid interferes with the method. Dilution of the solution has no ill-effect on the titration, and the asbestos interferes in no way, the end-point being quite sharp.

The following method is based on the use of hydrazine for the precipitation of copper (compare Jannasch and Biedermann, A., 1900, ii, 315). 0·5 Gram of the drillings is dissolved in 10—15 c.c. of aqua regia, and the solution diluted with an equal volume of water, most of the free acid neutralised with a solution of sodium hydroxide, taking care that no precipitate is formed, and heated to boiling. In a large, conical flask a solution of 20 grams of sodium hydroxide in 300 c.c. of water is heated to boiling, 2—3 grams of hydrazine hydrochloride added (not sulphate), and then the solution of copper and stannic chlorides is run in drop by drop, shaking vigorously meanwhile. After digesting for fifteen minutes, the precipitated copper is collected, and washed with hot water. The filtrate is concentrated, acidified with hydrochloric acid, and the tin estimated either by the method above described, or gravimetrically. The copper can be estimated by any of the usual methods. T. S. P.

Volumetric Estimation of Tin by means of Potassium Bromate. FRITZ FICHTER and E. MÜLLER (*Chem. Zeit.*, 1913, **37**, 309).—Stannous chloride solutions may be titrated with potassium bromate solution, provided that the solution contains a sufficient quantity of free acid (compare A., 1902, ii, 12), the end-point of the titration being denoted by production of a yellow coloration due to the liberation of free bromine on the addition of bromate solution after all the stannous chloride has been oxidised. Twenty c.c. of a solution of a tin salt are treated with a small quantity of aluminium wire, and, when the aluminium has dissolved, 30 c.c. of concentrated hydrochloric acid and 20 c.c. of water are added, and the mixture is heated until the precipitated tin has re-dissolved. The solution is then cooled and titrated with a standardised potassium bromate solution. W. P. S.

[Assay of] Alloys of Tin and Antimony. PONTIO (*Ann. Chim. anal.*, 1913, **18**, 47—48).—In the practical absence of copper, 0·5 gram of the alloy is oxidised with nitric acid (D 1·3), the tin and antimony oxides are washed with acidified water, heated to bright redness, and weighed. The antimony is then estimated separately in another 0·5 gram of the sample by evaporation with nitric acid, moistening the residue with 1 c.c. of strong sodium hydroxide solution, and heating, short of boiling, with 60—75 c.c. of sodium monosulphide (D 1·15). From the solution obtained the antimony is then precipitated electrolytically (0·3 ampere, 4 volts) after first adding 20 c.c. of 20% potassium cyanide. The antimony is then removed from the platinum gauze cylinder with nitric acid, and finally converted by ignition into oxide.

In presence of copper, the joint oxides of tin and antimony are obtained pure as follows: 0·5 gram of the alloy is heated with hydrochloric acid and a sufficiency of nitric acid, the liquid is evaporated to 5 c.c., and after adding 50 c.c. of nitric acid (D 1·3) the whole is boiled until red fumes cease to be evolved. At short intervals a few grams of potassium chlorate are then added, and the whole is kept boiling for some twenty minutes. After adding an equal volume of water and allowing to deposit, the mixed oxides are collected, washed with acidified water, ignited, and weighed.

L. DE K.

Assay of Commercial Vanadic Acid. GABRIEL CHESNEAU (*Ann. Chim. anal.*, 1913, **18**, 108—111).—Moisture and loss on ignition are determined as usual; the latter is often negative. Vanadic acid, silica, iron, manganese, calcium, and magnesium are estimated by fusing 1 gram of the product with 2—3 grams of sodium carbonate containing 10% of nitre. On boiling with water, vanadic acid, silica, and alumina pass into solution, whilst the oxides of iron and manganese remain with the carbonates of calcium and magnesium. The insoluble matter is redissolved in hydrochloric acid, and the solution analysed as usual. Both the iron oxide obtained and the filtrate from the magnesium contain traces of vanadium; from the iron it may be recovered by fusion as directed, and the

aqueous extract may then be united with the magnesium filtrate and the vanadium estimated colorimetrically with hydrogen peroxide after concentration of the liquid and acidifying with nitric acid.

The alkaline solution is acidified with nitric acid and evaporated to dryness to render the silica insoluble. After treatment with dilute nitric acid, the silica is collected and the filtrate heated with slight excess of ammonia. The precipitate consists of alumina containing perhaps phosphoric or arsenic acid. After ignition and weighing, allowance is made for these acids, also for traces of vanadic acid, which may have co-precipitated. To the filtrate from the alumina is added barium nitrate, which yields a precipitate containing after ignition 37·24% of vanadic acid. Traces of vanadic acid in the filtrate may be estimated colorimetrically. The weight must, however, be corrected for phosphoric acid and arsenic acid, which also form insoluble barium compounds.

Sodium oxide is estimated by the Lawrence Smith method (fusion of 1 gram with 8 grams of calcium carbonate and 1 gram ammonium chloride; an extra addition of 3 grams of barium carbonate is recommended here).

Arsenic and phosphorus: 5 grams of the product are fused with 10 grams of sodium carbonate, the solution is acidified with hydrochloric acid, and the arsenic acid reduced with sulphur dioxide. After boiling, the arsenic is then precipitated as sulphide with hydrogen sulphide. The filtrate is evaporated with addition of 2—3 c.c. of pure sulphuric acid, and after dissolving in water and adding a few grams of ammonium nitrate the phosphoric acid is precipitated by heating for two hours at 40° with an equal volume of molybdate solution. It must be remembered that a portion of this phosphoric and arsenic acids may be contained in the alumina precipitate, and the remainder in the barium compound.

L. DE K.

Relationship of Cæsium and Rubidium Salts to the Heavy Metals. M. WAGENAAR (*Pharm. Weekblad*, 1913, **50**, 273—280).—The author recommends cæsium chloride for the microchemical detection of bismuth, cadmium, chromium, and zinc; and rubidium chloride for that of antimony, bismuth, aluminium, and chromium.

A. J. W.

Separation of Columbium and Tantalum by means of Potassium Chloride in Hydrofluoric Acid Solution. ENG. MEIMBERG and PAUL WINZER (*Zeitsch. angew. Chem.*, 1913, **26**, 157—158).—Thirty grams of the ore are decomposed by melting with potassium pyrosulphate. The residue is boiled with water and freed from any interfering metals. Of the purified acids, 5—10 grams are taken for the columbium estimation. This is dissolved in a sufficiency of hydrofluoric acid, and mixed with an excess of saturated solution of potassium chloride. The deposit of potassium tantalum fluoride is collected, heated with sulphuric acid to dryness, and again treated with hydrofluoric acid and potassium chloride. In both cases the deposit is washed with a cold solution of potassium chloride. The

compound is then decomposed by means of sulphuric acid, the tantalic acid is first boiled with water containing hydrochloric acid, then with ammonia, and finally weighed as pentoxide.

The columbium contained in the filtrate is recovered as usual; any titanium present should be estimated colorimetrically and allowed for. L. DE K.

The Estimation of Acetylenic and Ethylenic Hydrocarbons in Mixtures of Gaseous Hydrocarbons. PAUL LEBEAU and A. DAMIENS (*Compt. rend*, 1913, **156**, 557—559. Compare this vol., ii, 253).—The authors advocate two new reagents for use in gas analysis, one to absorb acetylenic hydrocarbons, and the other to absorb the olefines. The first is a solution containing 25 grams of mercuric iodide and 30 grams of potassium iodide in 100 c.c. of water. When being used, a small fragment of potassium hydroxide is introduced into the absorption tube. It is capable of absorbing twenty times its volume of acetylene, a white precipitate being deposited. The olefines are no more soluble in this reagent than in water.

The second reagent is a 1% solution of vanadium pentoxide in concentrated sulphuric acid, or a 6% solution of uranyl sulphate in the same acid. Either of these solutions can be employed, and will take up one hundred and fifty times their volume of ethylene, whilst being without action on carbon monoxide. The absorption is rapid, due to the presence of the catalyst. W. G.

Estimation of Alcohol in Very Dilute Solutions by means of Permanganate. H. P. BARENDRECHT (*Zeitsch. anal. Chem.*, 1913, **52**, 167—172).—Five c.c. of a fermented liquid (wine, beer, etc.), previously diluted so as to contain about 0·2% of alcohol, are poured into a mixture containing 100 c.c. of solution of potassium permanganate (39 grams in 4 litres) and 40 c.c. of aqueous sodium hydroxide (150 grams in 1 litre), which has been heated to boiling. After continuing the boiling for one minute, 100 c.c. of oxalic acid (80 grams in 4 litres) are added, followed by 40 c.c. of dilute sulphuric acid (2 : 5), and the solution is then titrated with permanganate (3·182 grams of potassium permanganate per litre). The result = excess of oxalic acid (*A* c.c.).

Meanwhile 5 c.c. of the liquid have been evaporated to dryness on the water-bath, and the residue dissolved in 5 c.c. of a solution of sucrose (1 gram in 250 c.c. of water), and the solution treated as before. Allowance is then made for the reduction caused by the sugar (28·05 c.c. permanganate), and the result (*B* c.c.) is deducted from *A*. Multiplied by 0·384, the number of mg. of alcohol, and multiplied by 0·483, the number of cm. of alcohol contained in the 5 c.c. operated on are obtained.

The addition of the sucrose improves the accuracy of the process.

Traces of alcohol in a liquid containing organic matters must be first recovered by distillation before applying the process. A little sucrose is added to the distillate and allowed for. L. DE K.

Potassium Permanganate in the Quantitative Estimation of Some Organic Compounds. C. M. Pence (*J. Ind. Eng. Chem.* 1913, **5**, 218—220).—Tocher's method for the estimation of phenol (A., 1901, ii, 353; compare also Donath and Ditz, A., 1900, i, 197) is open to the objection that the manganese dioxide formed in the oxidation with alkaline permanganate is not readily reduced in the subsequent operations. The method is modified as follows: 25 c.c. of the phenol solution (0·4 gram per litre) are added to 50 c.c. of $N/10$-permanganate and 3—4 grams of sodium hydrogen carbonate contained in a 500 c.c. glass-stoppered conical flask. It is boiled for five to ten minutes (with stopper removed), cooled to 60°, acidified with dilute sulphuric acid, and after keeping for two minutes cooled to room temperature. The solution is diluted, 5 c.c. of 20% potassium iodide added, and the liberated iodine titrated with $N/10$-thiosulphate in order to determine the excess of permanganate. The phenol is oxidised to carbon dioxide.

Pyrogallol, catechol, resorcinol, quinol, salicylic acid, and salol may be estimated similarly, but the cresols and benzoic acid do not give satisfactory results. T. S. P.

The Quantitative Estimation of the Oxidation Products of Cholesterol. Isaac Lifschütz (*Biochem. Zeitsch.*, 1913, **48**, 373—417).—A method is described by means of which oxycholesterol can be estimated in the unsaponifiable products obtained from tissues and other sources. This substance gives a colour reaction with a mixture of acetic and sulphuric acids, which is readily converted into a pure green colour by the addition of a few drops of 5% ferric chloride solution in acetic acid. Solutions obtained in this way give a spectrum with a well defined band in the red, the breadth of which is proportional to the amount of oxycholesterol in the solution. Three methods of spectroscopic estimation, by means of this band, are described, namely, (*a*) by a dilution method, in which the solution with unknown amount of oxycholesterol is diluted until it gives the same spectrum as a standard solution; (*b*) by alteration of the depth of layer of the solution used for absorption, until the spectrum is the same as that of a standard solution. This is the most accurate method, and an instrument constructed by Zeiss, with specially made vessels for altering the depth of the fluids, the absorption spectra of which are to be investigated, are described and figured in the text; (*c*) by ascertaining the dilution of the fluid necessary to produce the disappearance of the band. As the esters of oxycholesterol do not give the colour reaction, it is possible to estimate these by determining the amount of oxycholesterol present before and after hydrolysis. A method is given for preparing oxycholesterol for standard solutions, in which cholesterol in acetic acid solution is oxidised by benzoyl peroxide. Other oxidation products of acid character are obtained at the same time, of which a preliminary account is given by the author. The actual methods of carrying out the oxycholesterol estimations are given in full detail. S. B. S.

Influence of Ammonium Sulphate in the Polarimetric Estimation of Lactose. G. JAHNSON-BLOHM (*Zeitsch physiol. Chem.*, 1913, **83**, 441—443).—The presence of ammonium sulphate in such quantity as is used in the preparation of milk for polarimetric observation is shown to diminish the rotatory power of lactose very slightly. A correction of 0·1% is to be applied when the amount of lactose is from 4 to 6%. E. F. A.

Detection of Invert Sugar by means of β-Naphthol. FRANZ M. LITTERSCHEID (*Chem. Zeit.*, 1913, **37**, 321).—The test proposed depends on the fact that commercial invert sugar contains traces of furfuraldehyde compounds, which yield a red coloration with concentrated sulphuric acid and β-naphthol. For the detection of invert sugar in honey, 20 grams of the sample are rubbed down in a mortar with successive quantities of ether, the ethereal solutions are filtered, a small crystal of β-naphthol is added to the filtrate, and the ether is allowed to evaporate at the ordinary temperature. The residue is then treated with 5 c.c. of 88—90% sulphuric acid. Natural honey yields a dirty yellow coloration, a faint pink tint being observed in many cases, but if invert sugar is present a distinct red or bluish-violet coloration develops within thirty minutes. The test will readily detect the presence of 5% of invert sugar in honey. W. P. S.

The Soluble Nitrogenous Substances as a Factor for Valuing Flour. EUG. ROUSSEAUX and MAURICE SIROT (*Compt. rend.*, 1913, **156**, 723—725).—The authors have determined the total nitrogen, and the nitrogen in an aqueous extract of a number of flours, and find that the ratio, $\frac{\text{total nitrogen}}{\text{soluble nitrogen}}$, gives a useful indication as to the value of the flour for bread-making. In good flours the mean value of the ratio is 5·72; and if the value falls below 5·20 it is generally a sign of an unsatisfactory flour. This ratio has been found useful in the case of flours which, from ordinary analyses, appeared to be of the same value for bread-making, although differing in actual practice. W. G.

Estimation of Solid Fatty Acids by Hehner and Mitchell's Method. ALFRED HEIDUSCHKA and A. BURGER (*Zeitsch. öffentl. Chem.*, 1913, **19**, 87—89).—This method (A., 1897, ii, 289) was found to yield trustworthy results in the case of stearic acid, and also with palmitic acid and myristic acid, alcohol saturated with the respective acids being employed in the last two instances. The results found for palmitic acid are, however, too high if more than 0·5 gram of the acid is taken for the estimation. Whilst the presence of acids which are readily soluble in alcohol does not interfere with the estimation, it is essential that the particular acid under examination should not be mixed with other fatty acids only slightly soluble in alcohol. W. P. S.

Microchemical Analysis of Plants. III. Detection of Cinnamic Acid, Especially in Resins. OTTO TUNMANN (*Pharm. Zentr.-h.*, 1913, **54**, 133—136).—The micro-sublimation test described

previously by the author (A., 1912, ii, 104) affords a simple means of detecting and identifying cinnamic acid. When benzoic acid is also present in the substance under examination the sublimate will contain both acids, but it will usually be found that the benzoic acid sublimes before the cinnamic acid; if the sublimate is exposed to the atmosphere for a few days, the benzoic acid will volatilise completely. Cinnamic esters also yield a crystalline sublimate. The cinnamic acid may be distinguished from benzoic acid by several reactions, particularly that with bromine; by exposing the sublimate to bromine vapour, the cinnamic acid forms brownish-yellow droplets, and eventually yields crystals of dibromocinnamic acid. Under similar treatment benzoic acid remains colourless, but the crystals dissolved partially. W. P. S.

Estimation of Fat in Foods with Special Reference to Extraction with Trichloroethylene. R. NEUMANN (*Landw. Versuchs-stat.*, 1913, **79–80**, 701—736).—Fat can be estimated in all kinds of food by extracting with trichloroethylene; the usual shaking apparatus is employed. Ether dissolves non-fatty substances which are not extracted by shaking for a short time with trichloroethylene. This solvent has the advantages that the substance to be extracted need not be dried, and that it is not inflammable.

The disadvantages are the decomposition of trichloroethylene by light; it can only be used in diffused light, and must be kept in darkness. Owing to its characteristic taste, its removal with a pipette is unpleasant, although not injurious to health. An automatic apparatus is desirable. N. H. J. M.

Lecithin Preparations and the Estimation of Lecithin. ROBERT COHN (*Zeitsch. öffentl. Chem.*, 1913, **19**, 54—62).—Apart from pure lecithin, there are now on the market preparations, such as pills, tablets, powders, foods, etc., stated to contain definite amounts of lecithin; examination of these preparations shows that in a number of cases the proportion of lecithin present falls short of the amount guaranteed. The following method is recommended for the estimation of lecithin, and consists essentially of the extraction of the lecithin, the purification of the latter, and the estimation of the amount of phosphorus present. From 1 to 2 grams of a lecithin preparation, or from 5 to 20 grams of a food, are extracted with cold alcohol for some hours, then boiled twice for two hours with successive quantities of alcohol, and finally extracted for two hours with boiling chloroform. The alcoholic and chloroform solutions are evaporated, and the residue is boiled for two hours with chloroform, which dissolves the lecithin, whilst free phosphoric acid and glycero-phosphoric acid remain insoluble. The chloroform solution is then filtered and evaporated. For the estimation of the phosphorus, this residue may be oxidised by heating with a mixture of sulphuric and nitric acids, or ignited in the presence of magnesium oxide or of a mixture of sodium carbonate and potassium nitrate; the resulting phosphoric acid is then precipitated as

ammonium magnesium phosphate, and weighed as magnesium pyrophosphate. These methods yield equally trustworthy results. The quantity of phosphoric oxide found is multiplied by 11·36 to give lecithin. In the case of preparations which have been kept for a long time, or which have been maintained at a high temperature during manufacture, the above-mentioned method of extraction will not suffice to obtain all the lecithin in solution, and the alcohol extraction must be prolonged until the substance ceases to yield alcohol-soluble phosphorus compounds. W. P. S.

Detection of Preservatives in Fats (Butter, Margarine, Lard). E. VOLLHASE (*Chem. Zeit.*, 1913, **37**, 312)—Fifty grams of the fat are shaken with 100 c.c. of boiling water, two drops of 15% sodium hydroxide solution, and about 10 grams of solid paraffin. The mixture is then cooled, the aqueous layer is separated, and filtered. A portion of the filtrate is used for the detection of formaldehyde and sulphurous acid, the usual tests being employed. The remainder of the filtrate is now boiled after the addition of aluminium hydroxide, then cooled, and filtered. Separate portions of this filtrate are tested for the presence of salicylic acid, benzoic acid, fluorides, boric acid, and chlorates. W. P. S.

Estimation of Coumarin in Melitolus vulgaris and Officinalus. ERNST OBERMAYER (*Zeitsch. anal. Chem.*, 1913, 172—191).—Ten grams of the air-dried ground sample are extracted with ether in an extraction apparatus, and the ether is then evaporated in a 500 c.c. flask. The residue is submitted to distillation after introducing 300 c.c. of calcium chloride solution (1 kilo. in 3 litres) until the mass shows signs of solidifying. The heat should be regulated so that the operation lasts fully an hour.

The distillate is diluted to a definite mark, and then filtered. An aliquot part is taken for the estimation of the coumarin by titration with permanganate.

The neutral solution is mixed with zinc sulphate solution, then with standard permanganate, and boiled on an asbestos plate for ten minutes. When cold, the solution is passed through an asbestos filter, and the precipitate washed with water. The excess of permanganate is then found by titrating in the usual manner with oxalic acid, etc.

The titre of the permanganate is best verified by a check experiment with pure coumarin. L. DE K.

Miscibility Curves for the Estimation of Dissolved Substances; Camphorated Alcohol. HENRI ROSSET (*Ann. Chim. anal.*, 1913, **18**, 49—56).—When a camphorated alcohol of unknown strength has to be tested for content in camphor and alcoholic strength, two experiments are made, one with nitrobenzene and another with essence of turpentine. Nitrobenzene is very sensitive to alcoholic strength; turpentine very sensitive to amount of camphor. The critical temperature of mixing is determined with the usual precautions in the apparatus of Louise, and by consulting

the curves in the original paper the strength of the sample may be readily ascertained. L. DE K.

Reactions of the Digitalis Glucosides. Digitonin. C. REICHARD (*Pharm. Zentr.-h.*, 1913, **54**, 217—221).—The following three reactions may be employed for the identification of digitonin. Small quantities of ammonium vanadate, sodium tungstate, and potassium iodate are placed on separate microscope slides, a small quantity of digitonin is added to each, together with a drop of glacial acetic acid, and the mixtures are allowed to dry. The slide containing the vanadate exhibits a green colour after a few hours, but this change is not due to the presence of the glucoside; the other mixtures do not change in colour. Concentrated sulphuric acid is now added to the mixtures; a dark green coloration is obtained with the vanadate mixture, and, after moisture has been absorbed from the atmosphere, a faint violet coloration develops. The iodate mixture is coloured violet-black, and iodine is liberated. The tungstate mixture remains unaltered; even when the temperature is raised, the salt is not reduced, but the mixture becomes green or greenish-black in colour, changes which are due to the action of sulphuric acid on the glucoside. Another characteristic reaction consists in evaporating a drop of cobalt nitrate solution by the aid of a gentle heat until a deep blue-coloured residue is obtained; a small quantity of digitonin and a drop of glacial acetic acid are then added, and the mixture is exposed to the atmosphere for about thirty hours, when a mass of red crystals is obtained. In the case of digitoxin, this test yields a moist green residue, but no crystals form. Reactions of digitonin with several other reagents are described.

W. P. S.

Detection of Saponin. LEOPOLD ROSENTHALER (*Zeitsch. Nahr. Genussm.*. 1913, **25**, 154—158).—When saponin is hydrolysed with dilute acids an intermediate product is obtained, in which the sapogenin is still combined with a quantity of sugar; this product, termed prosapogenin, yields an orange-red coloration with concentrated sulphuric acid, the colour changing gradually to red, and then to violet. When shaken with an alkali solution, prosapogenin yields a persistent froth. The liquid under examination is treated with 2·5% of hydrochloric acid, filtered if necessary, and then heated on a boiling water-bath until the mixture ceases to froth when shaken. The mixture is now cooled slightly, shaken with ethyl acetate, the latter then separated, washed with water, and evaporated to dryness. Should the ethyl acetate solution be dark in colour, it may be treated with animal charcoal before evaporation. The residue is then tested with sulphuric acid and with alkali solution as described. In the case of beer, it is necessary to heat the liquid with its own volume of 95% alcohol until a flocculent precipitate separates; this is removed by filtration, and the filtrate then hydrolysed and tested; or the beer may be evaporated and the residue extracted with 70% alcohol. Methods which depend on the hæmo-

lytic action of saponin (A., 1912, ii, 819) are not always trustworthy, owing to the fact that certain saponins are devoid of this property.

W. P. S.

[Detection of] Antipyrine in Toxicological Analysis. G. DRUCE LANDER and H. W. WINTER (*Analyst*, 1913, **38**, 97—98).—Antipyrine may be isolated from viscera, etc., by means of the Stas-Otto process, the best final extraction medium being chloroform in the presence of ammonia.

The residue is then treated with 5 c.c. of Steensma's reagent and evaporated to dryness, when a beautiful rose-red colour is developed. It must be remarked that amyl alcohol, and also undenatured spirit, should be entirely absent, as they also yield a faint pink colour.

From urine, the antipyrine may be also isolated by simply shaking with chloroform, preferentially in the presence of ammonia.

Steensma's reagent is prepared by dissolving 1 gram of *p*-dimethylaminobenzaldehyde in 100 c.c. of a solution of 5 c.c. of 25% hydrochloric acid in 100 c.c. of absolute alcohol.

L. DE K.

Estimation of Morphine in Opium and its Preparations. GABRIEL GUÉRIN (*J. Pharm. Chim.*, 1913, [vii], **7**, 162—163).—Seven and a-half grams of opium, dried at 60°, are mixed with 3 grams of finely powdered lime and 30 c.c. of water to form a homogeneous fluid, which is placed in a 125 c.c. flask, using 45 c.c. of water in several portions to wash the mortar and pestle used in making the mixture. After remaining two hours with occasional agitation, the mixture is filtered, and 52 c.c. of the filtrate (=5 grams of opium) placed in a 110—120 c.c. flask with 5 c.c. of acetone and 1 gram of ammonium chloride. After the latter has dissolved, the liquid is set aside for twenty-four hours, and the morphine which has then crystallised out is separated by filtration and washed first with water and then with acetone, both solvents having been first saturated with morphine.

In the case of opium extract, 3 grams are dissolved in 75 grams of water and mixed with 3 grams of lime. After two hours 65 grams of the filtrate (=2·5 grams of extract) are treated as described above. For laudanum (tincture of opium) 75 grams are evaporated to dryness at 100°, and the residue dissolved as far as possible in 75 c.c. of water, mixed with 3 grams of lime, and after two hours 52 c.c. (=50 grams of laudanum) are treated as described above.

T. A. H.

Estimation of *l*-Tyrosine in Proteins. EMIL ABDERHALDEN and DIONYS FUCHS (*Zeitsch. physiol. Chem.*, 1913, **83**, 468—473).—See this vol., i, 409.

Nephelometry in the Study of Proteases. II. PHILIP A. KOBER (*J. Amer. Chem. Soc.*, 1913, **35**, 290—292).—In an earlier paper (this vol., ii, 260) a method has been described for studying proteases and nucleases by precipitating the substrate as a suspensoid by means of a suitable reagent, and estimating the amount of

suspended matter with the nephelometer. It is now shown that the nephelometer can be used for investigating the digestion of casein when a 3% solution of sulphosalicylic acid is used as precipitant. This reagent does not precipitate amino-acids, peptides, peptones, or urinary constituents under the conditions observed in the experiments. The nephelometric constant (*k*) for casein with this precipitant is 0·20. E. G.

Arnold's Nitroprusside Reaction in Urine. VINZENZ ARNOLD (*Zeitsch. physiol. Chem.*, 1913, **83**, 304—314. Compare A., 1907, ii, 115).—The violet coloration formed when a drop of 4% sodium nitroprusside solution, followed by alkali, is added to urine is produced, not only after taking meat or beef tea, but also, although relatively faintly, after taking pure carbohydrate or protein foods. The intensity of the reaction increases when the foods are taken in a prepared form so as to increase their digestibility. Beef tea causes the most marked reaction, which must accordingly be due to stimulating substances present among the substances in meat, to which it owes its flavour. The better flavoured the meat, the more intense is the violet reaction, which is entirely dependent on the intensity of the stimulus received. In cases of illness the reaction is entirely absent, but returns again during convalescence.

The chemical changes in the living cell receive a marked stimulus from the exciting substances in foods, particularly in meat. In a case of diabetes, when sufficient beef tea was administered with bread, so that a marked violet reaction in the urine was prolonged for two hours, no sugar was excreted. So long as the stimulus lasted the organs were able to utilise the sugar in the body.

The violet nitroprusside reaction is not confused with Weyl's creatinine reaction if only a single drop is added at first, and after waiting a few minutes when the violet colour has disappeared, more nitroprusside is added. E. F. A.

Estimation of Colloids in Effluents. PAUL ROHLAND (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 45—46).—A method of estimating the colloidal substances in factory effluents is described, which depends on the adsorption of dyes by the coagulated colloids. To 50 or 100 c.c. of the effluent, 1 c.c. of a 1% solution of aniline-blue is added, and the liquid evaporated to syrupy consistency on the water-bath. The coloured residue is then extracted with hot water, and after filtration the amount of unadsorbed aniline-blue is estimated colorimetrically. H. M. D.

A Rapid Method of Determining the Quality of Drinking Waters. B. GALLI-VALERIO and M. BORNAND (*Centr. Bakt. Par.*, 1913, ii, **36**, 567—573).—The use of Oldekop's neutral-red agar is recommended for the detection of contamination of the water by urea bacteria and especially *Bact. coli*. This is indicated by the appearance of fluorescence and the production of a canary-yellow colour when small quantities of the water to be tested are carried into slope tubes of the medium. H. B. H.

General and Physical Chemistry.

Refractive Index of Substances at their Critical Temperatures. EDMOND VAN AUBEL (*Physikal. Zeitsch.*, 1913, **14**, 302—303).—According to Smith (A., 1912, ii, 1013), the calculated refractive index of a large number of substances is equal to 1·126 at the critical temperature. The author finds that the calculated values for aniline, carbon disulphide, and water are 1·164, 1·189, and 1·102 respectively. The divergent values obtained for the last two substances indicate that anomalous refraction at the critical point is not confined to aromatic substances or halogen compounds. The calculated value for ethyl ether is 1·121, which agrees with the result obtained experimentally by Galitzin and Wilip (A., 1900, ii, 461). H. M. D.

Refraction and Dispersion of Gaseous Compounds and the Cause of the Divergence from Additive Relations. CLIVE CUTHBERTSON (*Phil. Mag.*, 1913, [vi], **25**, 592—604).—The deviations from the additive rule which are exhibited by gaseous compounds have been submitted to examination.

In the case of hydrogen chloride, bromide, iodide and sulphide, and sulphur dioxide, the refractivity of the compound is less than the sum of the refractivities of its constituents, whilst the dispersive power of the compound lies between those of the constituents.

On the other hand, the refractivity of nitrous oxide, nitric oxide, ammonia, and ozone is greater than the sum of the refractivities of the constituents, and the dispersivity is greater than that of either of the constituents.

In connexion with these relationships, it is pointed out that the spectra of chlorine, bromine, iodine, and sulphur, which occur in the first group, show strong absorption bands in the violet and ultra-violet regions which disappear in the compound; whereas nitrous oxide, nitric oxide, and ozone show absorption bands in the ultra-violet which are not present in the spectra of the elements.

In explanation of these facts, it is suggested that the refractivity of a gaseous element (excluding those which consist of monatomic molecules) or compound consists of two parts, which are distinguished as atomic and interatomic. The atomic refractivity is due to vibrations which are governed by forces resident in the atom, and may be assumed to remain nearly constant. The refractivity due to this mode of vibration is roughly 80 to 90% of the total refractivity measured in the visible region of the spectrum. The absorption connected with it is that which lies in the Schumann region. The interatomic refractivity is the result of the existence of free periods in the visible or neighbouring portions of the spectrum, and is due to forces which have their seat in more than one atom of the molecule. The absorption connected with these vibrations is that observed in the spectrum of these regions. The

interatomic refractivity of an atom varies according to the atom with which it is combined and with the nature of the linking.

The changes in refraction, dispersion, and absorption, which occur when two elements combine together, are due to the disappearance of the interatomic refractivity and the appearance of new interatomic frequencies.

The relations existing between the compounds examined and the constituent elements are shown to be in accord with this hypothesis.

H. M. D.

Refraction and Dispersion of the Halogens, Halogen Acids, Ozone, Steam, Oxides of Nitrogen and Ammonia. CLIVE CUTHBERTSON and (Mrs.) MAUDE CUTHBERTSON (*Phil. Trans.*, 1913, *A*, 213, 1—26).—It is well known that the refractivity of simple gaseous compounds is not in agreement with the additive law, and these measurements have been made in order to throw light on the cause of the anomalous behaviour. An account of the general results obtained, and of certain conclusions which have been drawn from them, has been published elsewhere (compare preceding abstract).

In most cases the refractivities have been measured with reference to the green mercury line (λ 5461), and in order to correct for the deviations from the ideal gas laws the refractivity ($\mu - 1$) is reduced to the value which it would have if the density of the gas or vapour were equal to that of hydrogen (at 0° and 76 cm.) multiplied by the molecular weight of the substance referred to that of hydrogen. If the density thus defined is D, and the density of the substance at 0° and 76 cm. is d, then the corrected refractivity is represented by $(\mu - 1)D/d$.

Except where otherwise stated, the following values refer to λ 5461: chlorine, 0·000784; bromine (λ 6438), 0·001157; iodine (λ 6438), 0·00210; hydrogen chloride, 0·000448; hydrogen bromide, 0·000615; hydrogen iodide, 0·0009258; water vapour, 0·0002527; ozone, 0·00052; ammonia, 0·0003786; nitric oxide, 0·0002955; nitrous oxide, 0·0005100.

From the values of the refraction at other wave-lengths, the authors have also obtained numbers representing the dispersion of the various substances. In general, the dispersion can be represented quite satisfactorily by a formula of the Sellmeyer type.

H. M. D.

Some Liquid Mixtures Specially Suitable for the Observation of Christiansen's Phenomenon. FERNAND BODROUX (*Compt. rend.*, 1913, **156**, 772—774).—The author has found certain mixtures of two liquids which exhibit Christiansen's phenomenon (compare *Ann. Phys. Chem.*, 1884, **23**, 298), and which are easier to prepare and work with than his mixtures of a liquid and a solid. One is prepared by the addition of 15 grams of ethyl acetate and 10 grams of water to 50 grams of a saturated aqueous solution of sodium chloride. This mixture is very sensitive to heat, that of the hand sufficing to modify the shadow colours. Another mixture is

prepared from a solution of 25 grams of sodium bromide in 35 grams of water by adding propyl alcohol drop by drop until the required effects are obtained. In repose the surface of separation of the liquids in these mixtures shows beautiful iridescences. W. G.

A Modified Hüfner Spectrophotometer. RICHARD VON ZEYNEK (*Zeitsch. physiol. Chem.*, 1913, **84**, 207—212).—Certain alterations in the Hüfner spectrophotometer are described in detail and figured. They have the object of simplifying and facilitating the use of the instrument. E. F. A.

Coloured Bunsen Flames. ERNST BECKMANN and H. LINDNER (*Zeitsch. physikal. Chem.*, 1913, **82**, 641—656).—A description is given of a modification of the apparatus of Beckmann and Waentig (A., 1910, ii, 1) for producing coloured Bunsen flames of constant intensity. The chief improvement in the apparatus lies in the method by which a constant supply of the salt solution is supplied to the rotating disk. This is achieved by allowing the liquid to flow through a jet 1·9 mm. diameter from a reservoir of constant level. The intensity of light measurements of sodium chloride flames produced by means of this apparatus were made by means of a König-Martens-Grünbaum photometer. It is shown that flames of very constant intensity can be obtained in this way, and that the addition of other salts does not affect the intensity of the sodium flame as measured by the *D*-line. It is also shown that the distance between the vessel, in which the spray is produced, and the burner has an influence on the intensity of the flame. Various sodium salts were used in the experiments, and it was shown that the salts which contain oxygen give a somewhat more intense flame than the others. The intensity of the sodium flame is proportional to the square root of the concentration of the solution used (compare Arrhenius, A., 1891, 515; Gouy, *Ann. Chim. Phys.*, 1879, [v], **18**, 5). Unsuccessful attempts were made to produce a constant potassium flame. In general it is shown that the electrical conductivity of sodium flames is increased by the addition of lithium salts. The addition of magnesium and calcium salts produces irregularities in the conductivity which are due to the non-volatile nature of the oxides of these metals. When these salts have been added, the conduction is unipolar and very considerable, and points to the existence of electrons. Quantitative analysis shows that the composition of the salt solution is the same in the flame as it is before the formation of the spray. J. F. S.

Doppler Effect of the Series Lines of Oxygen. HEINRICH WILSAR (*Physikal. Zeitsch.*, 1913, **14**, 308—310. Compare this vol., ii, 172).—Polemical against Stark (this vol., ii, 172). In support of the author's statement that the series lines of oxygen do not show the Doppler effect, curves are drawn which show the distribution of the light intensity for both longitudinal and transverse exposures. Although these records afford no evidence of a Doppler effect, it is pointed out that this does not prove its absence. If the effect

does occur in the case of the series lines, it is, however, quite certain that the intensity of the displaced line is very small in comparison with that of the stationary line. H. M. D.

Spectroscopic Study of the Electric Brush Discharge in Water and Salt Solutions. HAROLD SMITH (*Phil. Mag.*, 1913, [vi], **25**, 461—475).—The character of the brush and capillary discharge in water and aqueous solutions of lithium, sodium, potassium, and calcium salts has been investigated. The brush discharge was obtained by passing the current from a large induction coil between a platinum plate and an electrode constructed by sealing a platinum wire into a glass tube, and filing off the protruding end of the wire quite flush with the glass. In order to obtain the capillary form of discharge, this electrode was replaced by a quartz tube terminating below in a fine capillary, the actual electrode consisting of a platinum wire or plate supported in the upper wider portion of the quartz tube.

Under these conditions of discharge, the author has found the series and secondary spectrum of hydrogen, the series and elementary-line spectrum of oxygen, the spark lines of platinum, and also the spectra of the metals contained in the dissolved salts.

The series spectrum of hydrogen increases in intensity with increase in the current density, whilst the secondary spectrum is relatively less intense at higher densities. In the case of oxygen, the series spectrum is only observed at the higher current densities, whereas the elementary-line spectrum only appears with the feebler discharges.

The lines of the metal of the dissolved salt, which are observed in the brush discharge, appear to vary in relative intensity with the salt used and also with the current. In weak solutions these lines are destroyed when strong condensed discharges are passed between the electrodes. H. M. D.

The Spectrum of the Univalent and of the Bivalent Helium Ion in the Canal Rays. JOHANNES STARK, A. FISCHER, and H. KIRSCHBAUM (*Ann. Physik*, 1913, [iv], **40**, 499—541).—From electromagnetic and spectral observations on canal rays, Stark has previously drawn the conclusion (A., 1911, ii, 678) that the carriers of the series lines are positive ions. According to this view it may also be expected that ions of the same element, which carry different charges, will give rise to different spectra.

In order to obtain information in support of this theory, the authors have investigated the Doppler effect for the lines in the canal-ray spectrum of helium. In regard to the choice of helium as the element to be investigated, it is pointed out that Runge and Paschen (A., 1896, ii, 1) have already shown that the helium spectrum contains two distinct groups of line series which led these authors to suggest that helium consists of two different elements. It seemed possible that these two groups might be due to helium ions carrying one and two charges respectively.

The experiments consisted in the photometric determination of the

distribution of the light intensity along the wave-length scale for various helium lines, observations being made in pure helium and in helium admixed with oxygen or iodine vapour. In presence of these electro-negative gases, the intensity maximum corresponding with the displaced lines is very clearly developed, whereas in pure helium there is no sharp distinction between the intensity due to the displaced and the undisplaced line.

The observations lead to the conclusion that both singly and doubly charged positive ions are present in the helium canal rays; further, that the carriers corresponding with the principal and the two subsidiary series of doublets are the singly charged ions, whilst the principal and two subsidiary series of simple lines are due to carriers which consist of doubly charged positive ions. The relation between the numbers of the two kinds of carriers depends on the conditions of the discharge, namely, on the pressure of the gas, the magnitude of the cathode fall of potential, and the presence or absence of an electro-negative gas. H. M. D.

The Wave-lengths of the Rays of Krypton. HENRI BUISSON and CHARLES FABRY (*Compt. rend.*, 1913, **156**, 945—947).—The spectrum of krypton presents some very fine lines, and is therefore of great value, especially when the tube is cooled in liquid air, for the observance of interference phenomena of luminous waves. The authors have used it, comparing the two intense lines in the green and yellow with the red line of cadmium, using interferences produced by thicknesses of 2, 5, 15, 25, and 100 mm. This comparison of the orders of interference obtained with cadmium and krypton gives with great precision the wave-lengths of the krypton lines.

W. G.

Measurements in the Magnesium Spectrum with Reference to the International Normals. ANDREAS NACKEN (*Zeitsch. wiss. Photochem.*, 1913, **12**, 54—64).—Accurate wave-length measurements have been made in the arc and spark spectra of magnesium between $\lambda = 2630$ and $\lambda = 5710$. In general, the spark lines are found to be much less sharp than those furnished by the arc. The data are compared with those obtained by previous observers. H. M. D.

Systems of Series [Lines] in the Spectra of Zinc, Cadmium, and Mercury. FRIEDRICH PASCHEN (*Ann. Physik*, 1913, [iv], **40**, 602—605).—Further arguments are put forward in support of the author's contention that certain lines in the spectra of zinc, cadmium, and mercury form members of series which have not been previously described (compare A., 1910, ii, 3; 1911, ii, 833). H. M. D.

Spectral Investigation of the Arc Light between Carbons at Low Pressures. MICHELE LA ROSA (*Ann. Physik*, 1913, [iv], **40**, 542—550).—The changes in the arc light spectrum have been examined when the pressure of the surrounding gaseous atmosphere is reduced. As the pressure falls, the arc discharge approximates in its general characters to that form which is associated with the

passage of the current through ordinary discharge tubes. The transformation from the one form to the other is not accompanied by any sudden changes in the electrical factors, although the spectra obtained in the two conditions are appreciably different. The change in the spectrum with gradually falling pressure would seem to indicate that there are a number of distinct phases in the transition from the normal arc to the normal low pressure discharge.

H. M. D.

The Absorption of Light by Water Changed by the Presence of Strongly Hydrated Salts, as Shown by the Radiomicrometer. New Evidence for the Solvate Theory of Solution. J. SAM GUY, E. J. SCHAEFFER, and HARRY C. JONES (*Physikal. Zeitsch.*, 1913, **14**, 278—288; *Amer. Chem. J.*, 1913, **49**, 265—286. Compare A., 1912, ii, 711).—The radiomicrometer described in the previous paper has been employed in the investigation of the absorption of radiant energy by aqueous solutions of salts. The wave-length interval covered in the observations extended from about $\lambda = 700\mu\mu$ to $\lambda = 1400\mu\mu$.

When the radiomicrometer readings obtained with an aqueous solution of a certain thickness are compared with those of a water layer, the thickness of which is arranged so that it is equal to that which would be given by the water in the solution, it is found that the absorption of radiant energy by the solution is very frequently quite different from the absorption produced by an equivalent thickness of pure water. This is at any rate the case for solutions of strongly hydrated salts, such as calcium chloride, magnesium chloride, and aluminium sulphate. The data obtained in similar experiments with aqueous solutions of potassium chloride, ammonium chloride, and ammonium nitrate show, on the other hand, no appreciable difference between the absorbing powers of the solutions and the layers of pure water, which are of equivalent thickness.

It is supposed that the observations indicate that the water which enters into combination with the salts of the first group has a smaller capacity for absorbing the incident radiation than water which is in the free condition. The general results can therefore be interpreted quite satisfactorily in terms of the solvate theory.

Incidentally it has been found that the water absorption bands are displaced by the dissolved salt towards the region of greater wave-lengths, the extent of the displacement increasing with the concentration of the solution. This effect is obtained independently of the hydrate-forming capacity of the dissolved salt. H. M. D.

The Absorption of the Ultra-violet by Ozone, and the Extremity of the Solar Spectrum. CHARLES FABRY and HENRI BUISSON (*Compt. rend.*, 1913, **156**, 782—785).—A determination of the variation of α, the constant of absorption for ozone, as defined by the equation $I = I_0\ 10^{-\alpha d}$, where I and I_0 are the intensities of the light before and after absorption, and d the thickness in cm. of pure gaseous ozone, λ varying from 2300 to 3400. The maximum absorption takes place at λ 2550, is very high at this point, and

the absorption varies rapidly between λ 2900 and 3300, the value of a being given by $\log a = 17{\cdot}58 - 0{\cdot}00564\ \lambda$. From these results, combined with measurements made on the amount of sun's light transmitted by the atmosphere, the authors draw the conclusion that the ozone content of the atmosphere, if evenly distributed, would be equal to 0·6 c.c. per cub. metre of air. W. G.

Absorption of the Ultra-violet Rays by Acetone. JEAN BIELECKI and VICTOR HENRI (*Compt. rend.*, 1913, **156**, 884—886).—By photometric measurements of the spectrographs obtained from a condensed iron–cadmium spark, the light passing through either an aqueous or an alcoholic solution of acetone or through pure acetone, in layers of varying thickness, the authors have determined the values of the molecular constant of absorption, ϵ, in the formula $I = I_0{}^{\epsilon c d}$ for values of λ from 2144 to 3706. The results show that acetone, in solution or in the liquid state, possesses only one absorption band in the ultra-violet, the maximum being at λ 2706 for alcoholic solutions, and at λ 2648 for aqueous solutions, there being no indication of the second band mentioned by Gelbke (this vol., ii, 87). The absorption curve, between λ 2405 and 2981, can be very exactly represented by the Ketteler-Helmholtz-Reiff-Drude formula, $\epsilon = a\lambda^2/\{(\lambda^2 - \lambda^2{}_m)^2 + g^2\lambda^2\}$, where a, g^2, and λ_m are three constants. From calculation it is found that about one molecule in forty takes part in the absorption of the ultra-violet light by acetone. W. G.

Applications of the Electron Conception of Positive and Negative Valencies. V. Absorption Spectra and Dynamic Formulæ of Chloro-, Bromo-, and Iodo-benzene. HARRY S. FRY (*Zeitsch. physikal. Chem.*, 1913, **82**, 665—687. Compare A., 1911, i, 431; 1912, ii, 713).—The theory described in the previous papers is applied to the halogen mono-substitution products of benzene. Chloro- and bromo-benzene, since they both exhibit seven absorption bands, are stated to possess the same dynamic formulæ as benzene itself. The absorption spectra of these substances are discussed on the basis of the theory, and it is shown from the measurements of the absorption spectra (Baly, T., 1911, **99**, 856; Purvis, T., 1911, **99**, 811) that the frequencies of the absorption bands of a substance can be represented as a linear function of a series of even numbers, which represent the number of absorption changes ("contraplex-diplex" changes). The non-absorption of iodobenzene both in alcoholic solution and in thin layers of the pure substance is explained, in opposition to Purvis (T., 1912, **101**, 1821), as due to the unsaturated nature of the iodine, which prevents the nucleus taking up the centric form. J. F. S.

Ultra-violet Absorption Bands of the Reciprocal Linking of Carbon Atoms. JOHANNES STARK, WALTER STEUBING, CORNELIS J. ENKLAAR, and PETER LIPP (*Jahrb. Radioaktiv. Elektronik.*, 1913, **10**, 139—174).—A large number of hydrocarbons have been examined with reference to their behaviour towards ultra-violet rays of short

wave-length. By means of a fluorspar spectrograph, it has been possible to obtain satisfactory photographic records of the absorption spectrum as far as $\lambda = 185\mu\mu$, and in this way the region covered by previous investigators has been considerably extended. The hydrocarbons were examined in the form of vapour, the rays being caused to pass through a layer of constant thickness, whilst the pressure was reduced in a series of steps in order to obtain the spectrum for different concentrations. Curves are plotted from the photographs, the pressure of the vapour and the wave-length being adopted as the co-ordinates.

The experimental observations are interpreted in accordance with the view that the absorption of ultra-violet light is a specific property of the carbon atom. The seat of the absorption is supposed to be the valency electron, and the position of the absorption band is further supposed to depend on the linking with which the valency electron in question is associated.

The accumulated data indicate that the linkings C—H and C—C do not give rise to an absorption band at wave-lengths greater than λ 185; bands are found in this region, however, in the case of the linkings C=C and C≡C. Hydrocarbons which contain asymmetric double or triple linkings give rise to two broad bands, and it may therefore be supposed that the four or six valencies associated with the C=C and C≡C linkings respectively are approximately equivalent as regards their ultra-violet absorption, and the bands may therefore be regarded as peculiar to the linking as a whole.

The presence of two or more C=C or C≡C linkings in the molecule of a substance has an appreciable influence on the position as well as on the intensity of the absorption, and the nature of these effects is indicated by the curves obtained for different classes of hydrocarbons.

The C—C *Linking* (Hexane, *cyclo*Hexane, Camphane).—The data for these hydrocarbons indicate that the C—C linking, whether in an acyclic or a cyclic compound, does not give rise to selective absorption above λ 185. Although the observations do not show a fully developed band, it would appear that ring formation causes a shift towards the long-waved region.

The Single Non-cyclic C=C *Linking* (*iso*Butylene, β-Methyl-Δ^{β}-butylene, Hexylene, Octylene).—Two absorption bands are evident, the first and less intense band having its head in the region λ 230—λ 205, and the second at about λ 180. The heads appear to shift according to the nature of the groups associated with the carbon atoms.

Two Isolated Non-cyclic C=C *Linkings* (Diallyl, Geraniolene).—Two bands are also found in this case, the heads being situated at about the same positions as those found for the single linking. The intensity is, however, very much greater than that associated with the single linking.

Two Conjugated Non-cyclic C=C *Linkings of similar type* (β-Methylbutadiene, $\beta\gamma$-Dimethylbutadiene, δ-Methyl-$\Delta^{a\gamma}$-pentadiene, $\Delta^{a\delta}$-Hexadiene).—Compared with the single C=C linking, the head of the first band is shifted to λ 255—λ 235, and that of the second to about λ 210. The shift in both cases is about 20 to 30 $\mu\mu$, and at

the same time the intensity of the bands, particularly that of the first, becomes very much greater.

The Single C=C *Linking* (Camphene, Bornylene, α-Pinene).—The first band is not exhibited. On account of its small intensity, its appearance would probably require greater pressures than those employed in the observations. The head of the second band is at λ 204—λ 198, that is to say, the band is shifted towards greater wave-lengths as a result of the polycyclic linking.

Two or More Dissimilar C=C *Linkings* (Limonene, Sylvestrene, α- and β-Phellandrene, Dimethylfulvene).—In limonene and sylvestrene, the C=C linkings are isolated, and the head of the second band only is shown by the extinction curves. Its position is about λ 185. In the case of α- and β-phellandrene, both bands are clearly developed. The heads of the bands of the α-compound are at λ 258 and λ 210, those of the β-compound at λ 228 and λ 198. In both compounds the C=C linkings are conjugated. The shift resulting from the conjugation is much more marked in the case of α-phellandrene, which contains the two linkings in the six-C ring, whilst the β-compound has one linking outside the ring. Compared with the curves for limonene and sylvestrene, those for the two phellandrenes show very clearly the effect of conjugation.

Dimethylfulvene, which contains three C=C linkings, exhibits three well-developed broad bands with the heads at λ 370, λ 258, and λ 207 respectively. The middle band is the most intense. It is supposed that λ 207 belongs to the semicyclic C=C linking, the longer-waved band corresponding with this not having been developed at the pressures employed in the examination. The two other bands are attributed to the endo-cyclic linkings, displacement towards greater wave-lengths having occurred to a very large extent as a result of the double conjugation.

The Symmetrical C=C *Linking* (Ethylene).—Up to atmospheric pressure, ethylene shows only one band at about λ 195, and this is resolved into a series of narrow bands. It is therefore quite different in character from the short-waved bands attributed to the asymmetric C=C linkings in the hydrocarbons investigated above. Although only one band was found with ethylene, the authors consider that the longer-waved band would be found at higher pressures. Liquid ethylene was, in fact, found to absorb ultra-violet rays up to λ 235.

The above results show that the carbon valency associated with an asymmetric C=C linking, whether in a cyclic or an acyclic compound, gives rise to two broad bands in the ultra-violet region above λ 180. As compared with the position of the bands due to a single C=C linking, it appears that the bands are displaced towards greater wave-lengths, and at the same time intensified, if the C=C linking is endo- or semi-cyclic, or if the linking is conjugated with reference to a second C=C linking. H. M. D.

Ultra-violet Absorption Bands of the Reciprocal Linking of Carbon Atoms. II. Acetylene Linking. JOHANNES STARK and PETER LIPP (*Jahrb. Radioaktiv. Elektronik.*, 1913, **10**, 175—178. Compare preceding abstract).—The influence of the acetylene

linking on ultra-violet absorption has been investigated in reference to dipropargyl and acetylene. The extinction curve for dipropargyl shows two well-developed bands, the first of which has its head at $\lambda = 245\mu\mu$ and the second at $\lambda = 201\mu\mu$. The second band is much deeper than the first. It is supposed that the two bands correspond with the pair which have been found to be characteristic of the asymmetric ethylene linking. The absorption curve for acetylene exhibits a large number of narrow bands in the region of the second dipropargyl band, the intensity of which increases as the wave-length diminishes. As in the case of ethylene, these narrow bands are only obtained at comparatively high pressures, and it is probably on this account that the less intense absorption band, which would be expected at greater wave-lengths, has not been actually observed. H. M. D.

Ultra-violet Absorption Bands of the Reciprocal Linking of Carbon Atoms. III. Benzene Linking. JOHANNES STARK and P. LEVY (*Jahrb. Radioaktiv. Elektronik.*, 1913, **10**, 179—188. Compare preceding abstract).—In addition to the narrow group of bands between $\lambda = 270$ and $230\mu\mu$, the absorption spectrum of benzene shows a much more intense group of similar bands in the region $\lambda = 210$ to $\lambda = 190\mu\mu$. Naphthalene behaves in the same way, a group of narrow intense bands being found in the region $\lambda = 220$ to $\lambda = 190\mu\mu$ in addition to the less intense group situated between $\lambda = 310$ and $\lambda = 230\mu\mu$. Both the naphthalene bands are displaced towards the direction of greater wave-lengths relatively to the corresponding benzene bands.

The absorption spectra of *cyclo*hexene and $\Delta^{1:3}$-*cyclo*hexadiene, on the other hand, exhibit unresolved broad bands differing completely from the groups of narrow bands shown by benzene and naphthalene. The less intense band of *cyclo*hexene is situated in the neighbourhood of $\lambda = 220\mu\mu$, and the head of the second band lies at about $\lambda = 190\mu\mu$. The heads of the corresponding bands of $\Delta^{1:3}$-*cyclo*hexadiene are at $\lambda = 260$ and $\lambda = 213\mu\mu$ respectively. As a consequence of the conjugation of the ethylene linkings in this substance, the bands are displaced towards the visible region, and the intensity of the absorption, particularly that of the first band, is greatly increased.

From the totally different character of the benzene bands as compared with those of *cyclo*hexene and $\Delta^{1:3}$-*cyclo*hexadiene, the conclusion is drawn that the benzene ring contains no normal ethylene linkings. The relationships between the carbon atoms are of a specific kind, and this necessitates the assumption of a benzene linking.

Reference is made to the fact that the observed molecular refractivity of benzene agrees with that calculated on the assumption that benzene contains three normal linkings. This agreement does not, however, justify the conclusion that three such linkings are present. According to the author, the ultra-violet absorption of benzene would seem to show that the agreement is accidental and due to the circumstance that the refractivities of the actual linkings

are mutually affected by their close approximation (as in the case of conjugated ethylene linkings), and that the modified refractivity is practically equal to the refractivity of a normal ethylene linking.

H. M. D.

Absorption of Ethylbenzene in the Ultra-violet. GEORG WEIMER (*Zeitsch. wiss. Photochem.*, 1913, **12**, 33—53).—The absorption spectrum of ethylbenzene has been examined over the interval $\lambda = 2300$ to $\lambda = 2750$, observations being made on the vapour at temperatures between 20° and 80°, and on ethyl-alcoholic solutions containing from 0·02 to 50% of ethylbenzene. In both cases, the spectrum consists of a series of bands which are shaded off towards the red end of the spectrum. With rise of temperature, the vapour bands broaden out towards the red end, but the short-waved edges of the bands are unaltered in position by either change of temperature or of the thickness of the vapour column. In the case of the solution spectrum, on the other hand, it is found that the bands are displaced towards the red as the concentration is increased.

On comparing the ethylbenzene spectrum with that of toluene, it is seen that the two are identical except for the fact that the former is displaced towards the ultra-violet to the extent of $0·7\mu\mu$. The wave-length measurements in the vapour spectrum indicate that this consists of ten series of bands, which can be represented by means of Deslandres' formula. In the solution spectra the undivided bands become more or less merged together, but even in this case it is found that the wave-length data indicate the existence of a definite series.

H. M. D.

Absorption Spectra and Constitution of Benzene Derivatives. III. Phenols and Methoxy-, Aldehydo- and Nitrophenols in Alkaline Solutions. NICOLAI A. VALIASCHKO (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 199—239. Compare A., 1910, ii, 1015, and 1911, ii, 2).—The author has investigated the influence of sodium ethoxide on the absorption spectra in alcoholic solution of phenol (also in water with sodium hydroxide), *o*-, *m*-, and *p*-methoxyphenols, *o*-, *m*-, and *p*-hydroxybenzaldehydes, and *o*-, *m*-, and *p*-nitrophenols.

With phenol and the methoxyphenols, the spectrometric results show that replacement of the hydroxylic hydrogen by sodium is not accompanied by change in the structure or condition of the molecules, although the absorption spectra undergo intensification and also displacement towards the red portion of the spectrum.

The molecules of the isomeric hydroxybenzaldehydes and nitrophenols exist as salts in the same condition as in the free state, and retain their different peculiarities. In neutral solutions the ortho-isomerides form equilibrated systems of two forms of molecules, $\alpha \rightleftarrows \phi$, the former being intense, and the latter weaker modifications (*loc. cit.*); by formation of the corresponding sodium phenoxides, the α-form is strengthened considerably, and the ϕ-form slightly. Meta-isomerides also form equilibrated mixtures, the

α-form being here less, and the ϕ-form more, developed than with the ortho-compounds; replacement of the hydroxylic hydrogen by sodium intensifies both forms, the equilibrium being displaced towards the ϕ-modification. In neutral solution the para-isomerides exist in the phenolic condition, and when sodium replaces the hydroxylic hydrogen the ϕ-form is considerably intensified, and there appears a weak α-form, which may indeed be present, although ill-defined, in neutral solutions. The intensification which thus takes place in the form already existing in solution finds expression in increase of the region of absorption and its displacement towards the red end of the spectrum.

The bearing on these results of the views expressed by Baly, Tuck, and Marsden (T., 1910, **97**, 584) and by Hantzsch and Voigt (A., 1912, i, 151) is discussed. T. H. P.

Colour and Optical Activity. ERNESTO LONGOBARDI (*Anal. Soc. Quim. Argentina*, 1913, **1**, 58—66).—Attempts to resolve nitro-tyrosine and alkali-blue-6B by selective fixation on wool and silk gave negative results. G. D. L.

Processes Operative in Solutions. XXVI. Disturbance of the Equilibrium in Solutions of Lævulose by Salts and by Non-Electrolytes. E. E. WALKER (*Proc. Roy. Soc.*, 1913, *A*, **88**, 246—252).—If a solution of lævulose is heated and then quickly cooled to 25°, it is found that the optical rotatory power is altered, but that it gradually returns to the initial value in accordance with the formula for a unimolecular reaction. The same thing is observed if the lævulose solution is cooled and then rapidly warmed to 25°. This seems to show that the proportions in which the two isodynamic forms are present in the equilibrium condition vary considerably with the temperature. Evidence has been obtained that the change in rotatory power produced by the addition of ethyl alcohol is due to the same cause, this change being approximately proportional to the amount of alcohol which is added to a fixed quantity of water.

On the assumption that this is the cause of the change in the rotatory power, the author has investigated the influence of certain salts and non-electrolytes on the rotatory power of an aqueous solution of lævulose. The results indicate that methyl alcohol and its homologues, methylal and paracetaldehyde, favour the formation of α-lævulose, whereas phenol, sucrose, lævulose itself, and sodium and potassium chloride appear to have the opposite effect. In the case of the salts, it is suggested that the observed change in rotation may be in part due to the formation of compounds with the lævulose.

H. M. D.

Magnetic Rotatory Polarisation of Liquid Nitrogen and Oxygen. J. CHAUDIER (*Compt. rend.*, 1913, **156**, 1008—1010).—A study of the magnetic rotatory power and the rotatory dispersion of liquid nitrogen and oxygen. The magnetic rotation is proportional to the intensity of the field and the thickness traversed.

At 18° the magnetic rotatory power is positive in both cases, and the values found are: for nitrogen, $\rho_D = 0{\cdot}00415$; for oxygen, $\rho_D = 0{\cdot}00782$; and for carbon disulphide, $\rho_D = 0{\cdot}042$. The magnetic rotatory dispersion of nitrogen varies inversely as the square of the wave-length, and is very close to that of methyl chloride. Oxygen has a feeble rotatory dispersion, and does not obey the law of inverse squares, the values found being less than those calculated. The results obtained for the magnetic rotatory dispersion are analogous to those obtained by Becquerel for gaseous nitrogen and oxygen (compare *J. Physique*, 1880, **9**, 265). W. G.

Energy Absorbed in Photochemical Reactions. VICTOR HENRI and RENÉ WURMSER (*Compt. rend.*, 1913, **156**, 1012—1015).—The authors have measured the amount of energy necessary for the photochemical decomposition of a molecule in the case of hydrogen peroxide and acetone, and also the minimum of energy capable of provoking a luminous sensation in the eye, and in every case obtain values inferior to the "quantum of energy" according to Einstein. They suggest that the energy necessary for the decomposition of a molecule might serve as a measure of the degree of stability of the substance. W. G.

The Dissociation of Gaseous Compounds by Light; Gaseous Hydrogen Compounds of the Chlorine and Oxygen Groups. DANIEL BERTHELOT and HENRY GAUDECHON (*Compt. rend.*, 1913, **156**, 889—892. Compare A., 1910, ii, 606).—A study of the stability of the hydrogen compounds with the members of these two groups of elements towards light of different wave-length. As in the case of decomposition by heat, it holds good that, in the same family of elements, the stability of the hydrogen compounds with respect to light decreases as the atomic weight increases. Substances which are only dissociated at high temperatures are similarly only affected by the very rapid vibrations of the extreme ultra-violet light. Hydrogen chloride requires ultra-violet light ($\lambda < 0{\cdot}2\mu$) for decomposition, which even then is slow, whilst under similar conditions hydrogen bromide is rapidly and completely decomposed. Hydrogen iodide is decomposed by blue and violet light. A similar relationship is found in the case of water vapour, hydrogen sulphide, selenide, and telluride. W. G.

The Production of Light by Chemical Action. J. HERBERT VINCENT and J. MARLEY (*Chem. News*, 1913, **107**, 138).—The authors cannot find any effect on a photographic plate of the following reactions: Action of sulphuric acid on zinc; action of hydrochloric acid on sodium metasilicate; action of nitric acid on lead; hardening of plaster-of-Paris; electrolysis of water with platinum electrodes. These observations contradict those of Matuschek and Nenning (A., 1912, ii, 116), and it is difficult to account for the positive effects obtained by them. Experiments showed that the heat produced by chemical action does not give the effect. No experimental details are given. T. S. P.

Decomposition of Lactic Acid under the Influence of Sunlight. DOMENICO GANASSINI (*Chem. Zentr.*, 1913, i, 387; from *Giorn. Farm. Chim.*, 1912, **61**, 540—547).—The author upholds his statement that lactic acid decomposes into acetaldehyde, pyruvic acid, and carbon dioxide under the influence of sunlight and air (*Giorn. Pharm. Chim.*, 1910, **48**, 785), and explains Neuberg's contradictory conclusion (A., 1912, ii, 314) by the fact that the latter worker used sterilised solutions in hermetically sealed quartz vessels.

J. C. W.

Quantitative Investigation of the Photochemical Transformation of *o*-Nitrobenzaldehyde into *o*-Nitrosobenzoic Acid. FRITZ WEIGERT and LUDWIG KUMMERER (*Ber.*, 1913, **46**, 1207—1218).—The transformation of *o*-nitrobenzaldehyde into *o*-nitrosobenzoic acid under the influence of light (compare Ciamician and Silber, A., 1901, i, 390) is independent of air; it is a simple case of isomeric change, and may therefore be taken as a typical, specific light reaction. In order to study the process quantitatively, acetone had to be chosen as solvent, since the acid would be esterified by alcohol, and is only sparingly soluble in other media. A simple titration of the acid was found to be untrustworthy even with fluorescein or Hewitt's azo-dyes (A., 1908, ii, 269) as indicators. Samples of the solution were therefore diluted with water and submitted to conductivity measurements, a curve having been obtained empirically. The solutions were exposed in glass troughs to the rays from a quartz mercury lamp (compare Weigert, A., 1909, i, 219), being protected from heat rays by a tank of running water, and, as occasion required, filters of nitrosodimethylaniline in 0·0017% solution and quinine sulphate in 0·05% solution were interposed to cut off the violet and blue and ultra-violet light respectively. The light absorbed by the filters and by solutions of the two substances was photometrically determined by POHL and PRINGSHEIM.

Preliminary experiments showed that the same results were obtained under the same conditions, that it was unnecessary to stir the solutions, and that the amount of transformation was practically proportional to the time of illumination. In order to study the influence of the intensity of the light, the lamp was stopped down so as to make the source of light approximate to a point, and the solutions were placed at such distances that the intensities were in the ratio 4 : 2 : 1, and then illuminated for periods which varied as 1 : 2 : 4. It was found that slightly less transformation had occurred in the most remote vessel, thus showing that the Bunsen-Roscoe law, that the same quantity of light produces the same chemical effect, is not quite admissible.

In further experiments on the influence of the initial concentration of the solution, the light was filtered through the quinine sulphate or nitrosodimethylaniline solutions, when, after allowing for the amount of light absorbed by these filters, it was found that the sum of the quantities of *o*-nitrosobenzoic acid formed was practically equal to the amount produced, under otherwise similar conditions, by unfiltered light. In the case of ultra-violet light, the

effect is independent of the concentration, but for violet light the speed of transformation is, at first, proportional to the concentration. The order of the reaction therefore changes with the kind of light, so that no simple law can be deduced to express the quantitative course of the reaction. No proportion existed either between the speed of the reaction and the amount of light absorbed by the aldehyde, although they increased in the same direction. With mixed light, the chief work is done in dilute solutions by the ultra-violet rays, and in concentrated solutions by the violet.

Kailan (this vol., i, 51) has recently made similar experiments, but not with the same degree of refinement, and his results are criticised. J. C. W.

Physico-chemical Studies on Photographic Developers. (Correction.) NIKOLAI SCHILOV and S. FEDOTOV (*Zeitsch. Elektrochem.*, 1912, **19**, 268).—Reference is made to the paper by Leubner and Luther (A., 1912, i, 254), which confirms the conclusions of Schilov and Fedotov (A., 1912, i, 966). The authors correct printers' errors in the original paper (*loc. cit.*). J. F. S.

The Secondary Radiation Produced by α-Rays. B. BIANU (*Compt. rend.*, 1913, **156**, 785—788).—The author has studied the secondary radiation from α-rays by measuring the current produced in an ionisation chamber by the radiation from a metallic surface bombarded by α-rays. The results show the existence of a secondary radiation, easily absorbed, capable of ionising and carrying a negative charge, the velocity deduced for it being $1\cdot8 \times 10^9$ cm./sec. W. G.

Laws of Deflexion of α-Particles through Large Angles. HANS GEIGER and ERNEST MARSDEN (*Phil. Mag.*, 1913, [vi], **25**, 604).—From Rutherford's theory of the constitution of the atom it has been deduced that the single scattering of α-particles through large angles should occur according to a formula which has been made the subject of experimental test. (1) The number of α-particles emerging at an angle ϕ with the initial direction should vary as $\text{cosec.}^4\phi/2$. This was found to hold good for angles ϕ between 5° and 150°, in which range the number of α-particles varied from 250,000 to 1. (2) The number of α-particles scattered in any definite direction should be proportional to the thickness of the scattering foil. For small thickness this was found to be the case. For larger thicknesses the decrease in the velocity of the α-particle causes a rapid increase in the amount of scattering. (3) The scattering should vary approximately as the square of the atomic weight of the scattering material. This was found to be the case for materials of atomic weight between carbon and gold (Au, Pt, Sn, Ag, Cu, Al, C). (4) The amount of scattering varies approximately as the inverse fourth power of the velocity of the incident α-rays. This was verified over a range such that the number of α-particles scattered varied in the ratio of 1 : 10. (5) Quantitative measurements of the absolute fraction of α-particles of radium-*C*

scattered showed that, for $\phi = 45^\circ$ and a gold foil equivalent to 0·1 cm. of air ($2{\cdot}1 \times 10^{-5}$ cm. thick), $3{\cdot}7 \times 10^{-7}$ of the α-particles were counted on a screen 1 mm.^{2} area at a distance of 1 cm. from the foil. From this figure and the theoretical relation, it was deduced that the central charge of an atom consisted of a number of elementary charges equal to about one-half the number representing the atomic weight. Only single scattering is dealt with. Compound scattering, due to combination of a large number of deflections, in greater thicknesses of material is probably due, not only to the central charge of the atom, but to the electrons distributed through the volume of the atom. F. S.

Helium in Thermal Springs and Earth Gases. HERM. SIEVEKING and L. LAUTENSCHLÄGER (*Verh. Ges. deut. Naturforsch. Aerzte*, 1913, 62—64).—Nitrogen was separated from the purified gases by means of a mixture of magnesium powder, sodium, and calcium oxide. The helium was separated from the rare gases by freezing out the latter in the usual way. The activity of the gases, etc., expressed in volts/hours, was determined with an Engler-Sieveking fontaktoscope.

The results show that the stulm gases all show a higher percentage of helium than the water and sediment from the springs. The gases obtained directly from the springs contain considerably more helium than the stulm gases, since the latter communicate with the outside air.

There appears to be no numerical relation between the radioactivity and the content of radium. T. S. P.

Excitation of γ-Rays by the α-Rays of Ionium and Radiothorium. JAMES CHADWICK and ALEXANDER S. RUSSELL (*Proc. Roy. Soc.*, 1913, *A*, **88**, 217—229).—The source of α-rays consisted of 1·2 grams of thorium oxide containing the ionium in equilibrium with 3·6 mg. of radium. It was purified from all other radioactive substances before use by repeated precipitation of the hydroxides with ammonia, and, lastly, in nearly neutral solution with *m*-nitrobenzoic acid in excess. A small activity, due to β- and γ-rays, remained constant for ten days after purification, and can only be due to the ionium. Only 10% was due to β-rays, and part of this at least may be due to products of thorium. The remainder was not deviated by a magnetic field of 1000 gauss, when the preparation was spread over an area of 15 cm.^{2} at a distance of 9 cm. from the base of the electroscope. The conclusion was reached that it consists of a γ-radiation excited by the α-rays of ionium in the material itself (Chadwick, this vol., ii, 91).

By measurements of the absorption in aluminium the radiation was analysed into three types, each exponentially absorbed. The first is completely absorbed, after passage through 9 cm. of air, by 0·003 cm. of aluminium, and the value of μ/D was about 520 (cm.)$^{-1}$. From the whole preparation, 1·2 grams, disposed as stated, it contributed 32% of the ionisation, but in the form of a very thin film the effect produced by it is large compared with the other types.

The second type of medium penetrating power had a value for μ/D 9·4 (cm.)$^{-1}$, and contributed 60% of the ionisation; whilst the third and most penetrating type had a value of μ/D 0·17 (cm.)$^{-1}$, and contributed only 8% of the ionisation, which corresponded with less than one division per minute. Correcting for the obliquity of the beam, the values of μ/D are 400, 8·35, and 0·15 (cm.)$^{-1}$, and the relative energies of the beams, roughly evaluated, as 15 to 0·075 to 0·2. The second type of medium penetrating power corresponds with the characteristic X-radiation of thorium, and it is probable that the other two types correspond with still unknown X-radiations in different series.

Experiments with radiothorium showed that it also emitted a γ-radiation, which was too small and too quickly masked by the growth of products to be studied in detail. F. S.

Production of Fluorescent Röntgen Radiation. William H. Bragg (*Phil. Mag.*, 1913, [vi], **25**, 657—659).—A reply to J. Crosby Chapman (*ibid.*, 359), defending the hypothesis that the energy is conveyed from the primary X-ray to the homogeneous secondary X-ray by an intermediary cathode-ray, in which a preliminary account is given of work done in conjunction with Porter. The molybdenum X-rays have been compared with the selenium X-rays in their action on ethyl bromide and on sulphur dioxide. Bromine, being intermediate in atomic weight between selenium and molybdenum, the molybdenum X-rays, but not the selenium X-rays, can excite the bromine X-rays. Various expected effects have been looked for, and in some cases found. The cathode ray produced by the molybdenum X-ray, for example, should show deficiency in penetrating and ionising power in ethyl bromide, since its energy is being otherwise utilised. The same considerations apply, also, to the two kinds of X-rays. Also, secondary bromine X-rays should result by molybdenum cathode rays, but this has not yet been established. F. S.

Ionisation Accompanying Flame Gases. Henri Jacques Proumen (*Bull. Soc. chim. Belg.*, 1913, **27**, 80—90. Compare A., 1910, ii, 381, 479).—In extension of previous work, it is now shown that ionisation persists in the gases resulting from the flame of a candle, even when these have been kept for a considerable time after the extinction of the flame. Details of the methods of collecting the gases and measuring the degree of ionisation are given. The following conclusions are drawn: Gases from a candle flame show a residual ionisation, even after some hours of repose in a glass vessel, which may be due to persistence of initial ionisation or to the formation of ions by a change in state of the gases. This ionisation can be detected by obtaining current-potential curves. Ohm's law is followed at first, but eventually the current increases less rapidly than the potential. The gases collected exhibit an excess of negative charges, and show only slight mobility.

T. A. H.

Photo-electric Emission of Electrons by Calcium. ROBERT POHL and P. PRINGSHEIM (*Ber. Deut. physikal. Ges.*, 1913, **15**, 111—122. Compare A., 1912, ii, 317, 618, and previous papers).—The photoelectric properties of calcium have been examined by a method similar to that used in previous experiments with the alkali metals, magnesium, and aluminium. Over the wave-length interval $\lambda=230$ to $\lambda=700\mu\mu$, the emission is of normal character, being independent of the orientation of the direction of vibration of the incident light with reference to the plane of incidence. The number of electrons emitted per unit quantity of absorbed light energy varies with the wave-length, a maximum effect being obtained at about $\lambda=365\mu\mu$. This maximum becomes more pronounced as the angle of incidence of the exciting light diminishes; in the case of grazing incidence the maximum disappears, and the emissive effect then increases continuously as the wave-length falls. The observed dependence of the photo-electric emission on the angle of incidence is just the reverse of that which was found in the case of the selective photo-electric effect of the alkali metals.

H. M. D.

The Mechanism of Disintegration of Radioactive Substances. F. BUTAVAND (*Le Radium*, 1913, **10**, 75—80).—This purely theoretical and speculative paper is based on an analogy between the distance of the planets in the solar system and the type of atom postulated for radium and the radio-elements. F. S.

Preparation of Solid Therapeutically Active Compounds of Radium. EMANUEL MERCK and WILHELM EICHHOLZ (D.R.-P. 256666).—It has been previously shown by Wassermann (*Deut. med. Woch.*, 1911, 2389; *Berlin. Klin. Woch.*, 1912, **4**) that compounds of selenium and tellurium exert an electrical action on the cells of living organisms, and it is now found that the radium "adsorption" compounds of selenic, selenious, telluric, or tellurious acids, with salts of the alkalis, or alkaline earths, have an eminently specific action on tumour cells. *Radium barium selenate* is precipitated when radium barium chloride (0·4 mg.) in 0·16 c.c. of water is treated with 0·35 c.c. of *N*-barium chloride solution and 0·35 c.c. of *N*-sodium selenate; the filtrate is also radioactive. The preparation of *radium barium selenite, radium barium tellurate, radium barium tellurite,* and of *radium sodium selenate* is also described.

F. M. G. M.

The Radium Content of Pitchblendes. BERTA HEIMANN and WILHELM MARCKWALD (*Physikal. Zeitsch.*, 1913, **14**, 303—305).—In view of the results obtained by Gleditsch (A., 1911, ii, 845), according to which the ratio of radium to uranium varies quite appreciably in pitchblendes and related minerals, the authors have made a detailed examination of a number of pitchblendes from different sources. The method employed in the estimation of the radium content was similar to that described previously by Marckwald and Russell (A., 1911, ii, 360). The pitchblendes

examined were from East Africa, Norway (two samples), Joachimsthal, Marienberg, Freiberg, Pribram, Colorado, and Cornwall; and Bröggerite from Norway was also included in the series. The percentage of uranium in these minerals was found to vary from 9·01 in pitchblende from Cornwall to 71·2 in that from East Africa. The values obtained for the ratio of radium to uranium vary from 3·320 to $3·341 \times 10^{-7}$, the maximum deviation from the mean being less than 0·4%. The results are considered to prove conclusively that the ratio of the two elements in the primary minerals is quite constant, the mean value of the ratio being $3·329 \times 10^{-7}$.

In the case of six of the pitchblendes, the radium content was also estimated on the basis of their γ-ray activity, and in this way independent evidence was obtained in support of the constancy of the ratio.

On account of this relation, it is possible to make use of any pitchblende as a radium standard, and the employment of a mineral substance presents certain advantages over the use of an artificially prepared material. Apart from the question of impurities in the artificial standard, it is pointed out that the definition of the curie in terms of one gram of radium affords a unit which is much too large for convenient use in actual experimental work. As an alternative, the authors suggest that the curie should be defined as the quantity of radium emanation which is in equilibrium with one gram of uranium. H. M. D.

Chemical Properties of Thorium-*C* and Thorium-*D*. WALTHER METZENER (*Ber.*, 1913, **46**, 979—989).—Experimental investigations of the properties of thorium-*C* and -*D* have given results in complete agreement with the theoretical views of Fajans and others (A., 1913, ii, 276, 277). By the use of Strömholm and Svedberg's method of crystallising fairly soluble salts out of a solution of the active deposit and by other methods, it has been shown that thorium-*C* cannot be separated from bismuth, or thorium-*D* from thallium. The quantitative separation of thorium-*C* by means of nickel foil in a boiling hydrochloric acid solution is hindered by the presence of bismuth, but the fraction of the radio-element precipitated on the foil is the same as the fraction of the bismuth also precipitated. Similarly, the volatilisation is stopped if bismuth oxide is present. Precipitation of thorium-*C* by silver chloride or bromide is prevented by addition of bismuth. The proportion of thorium-*C* in the precipitate and filtrate is shown to be the same as that of the bismuth when the latter, in presence of thorium-*C*, is fractionally precipitated (1) as oxychloride, (2) as bismuth magnesium nitrate, (3) as basic bismuth nitrate. Thorium-*D*, separated by recoil, was dissolved and crystallised with thallium salts. The proportion of the radio-element in the crystals and mother liquor was the same as the proportion of thallium, no separation or concentration being effected. Thallous nitrate, thallous carbonate in dilute ammonia solution, and thallic ammonium sulphate were the salts crystallised. F. S.

Chemical Action of Thorium-X on Organic Substances, Especially on Uric Acid. WILHELM FALTA and L. ZEHNER (*Chem. Zentr.*, 1913, i, 639; from *Berlin. Klin. Woch.*, 1912, **44**, 2444—2446).—Thorium-X solution glows in the dark, reacts acidic, and 1 c.c. has an activity of 1000 electrostatic units. Its action on organic substances is entirely due to radiation, and since the disintegration of thorium-X compared with that of radium emanation is almost explosive in character, the effect is very considerable.

Easily oxidisable aniline dyes and arrowroot-starch-iodine solutions are bleached; alcoholic guaiacol solution becomes blue; aloin solution, red; permanganate is decomposed. Solutions of morphine and pilocarpine hydrochlorides, strychnine nitrate, atropine sulphate, sodium salicylate, and antipyrine become very dark in colour, and quinine sulphate becomes green; the solutions suffer in pharmacological value. Tyrosine solutions deposit a black precipitate; catechol solution becomes dark; homogentisic acid solution gives a brown colour and a black precipitate; solutions of resorcinol become yellow, and of adrenaline, red. Starch and albumin are hydrolysed, and uric acid salts are rendered more soluble, and are even chemically changed. J. C. W.

Apparatus for Study of the Activity of the Air of the Sub-soil. JOSÉ MUÑOZ DEL CASTILLO (*Anal. Fís. Quim.*, 1913, **11**, 165—166).—Porous cylinders surrounded by earthenware vessels, to which iron tubes of 10—12 mm. are sealed, are sunk at 0·5, 1, and 2 metres below the surface. G. D. L.

Activity of the Air of the Sub-soil in October, 1912. JOSÉ MUÑOZ DEL CASTILLO and JOSÉ BARRIO Y FERNÁNDEZ (*Anal. Fis. Quim.*, 1913, **11**, 225—234).—Numerical data over the period in question. At a depth of 0·5 metre the activity appears greater in a firm than in a loose soil, and up to 2 metres the activity increases with the depth. G. D. L.

Analytical Observation on the Activity of Rain Water. JOSÉ MUÑOZ DEL CASTILLO and JOSÉ BARRIO Y FERNÁNDEZ (*Anal. Fís. Quim.*, 1913, **11**, 167—168).—A certain sample of rain water contained a notable amount of emanation, which was extinguished according to Curie's law, and ions which disappeared after twelve days in a closed bottle. G. D. L.

The Electromotive Series of the Radioactive Elements. I. GEORG VON HEVESY (*Zeitsch. Elektrochem.*, 1913, **19**, 291—295; *Le Radium*, 1913, **10**, 65—69. Compare A., 1912, ii, 414).—The various methods which can be used for the determination of the positions of the radioactive elements in the electromotive force series are discussed, and it is shown that in the case of elements of short lives the only practicable method is the electrochemical one. This consists in the determination of the relation in which two radioactive elements (for example, Ra-A and Ra-B) are deposited from a solution on to an electrode at a constant potential. The knowledge

of the chemical characteristics of the elements Ra-*D* and Th-*B* enables the elements of short and long lives to be brought into the electromotive series. The electromotive series of the radioactive elements contains both strongly electro-positive and strongly electro-negative members just in the same way as the series for the commoner elements. It is shown that every radioactive change, whether it consists in the emission of an α- or a β-ray, leaves behind an atom the position of which in the electromotive series is far removed from that of the parent substance. From the last fact the author draws the conclusion that the chemical properties of the atoms depend to a large extent on the configuration of the electron rings in the atom, and he points out that in the radioactive elements we have "isomeric atoms," the different properties of which are due to the different special arrangement of the electron rings in the same way that the properties of isomeric molecules are conditioned by the different arrangements of the atoms in the molecules. J. F. S.

Influence of Temperature and Pressure on the Electrical Resistance of Metals. EDUARD GRÜNEISEN (*Ber. Deut. physikal. Ges.*, 1913, **15**, 186—200).—By reference to the data for copper, silver, platinum, gold, and lead, it is shown that the specific electrical resistance of the pure metals at low temperatures is a universal function of $T/\beta v_m$, where T is the absolute temperature, β the radiation constant, and v_m the characteristic frequency of vibration of the atoms of the metal.

It has also been found empirically that the ratio of the resistivity to the absolute temperature is at low temperatures proportional to the atomic heat. This relationship may be expressed in a different way, namely, that the rise of temperature produced in a thermally isolated metallic conductor during the time interval dt is proportional to the square of the current and to the absolute temperature of the metal.

Although Wien's theory does not satisfactorily represent the influence of temperature on the electrical resistance, it is shown that the variation of the resistance with pressure is in harmony with the view that the mean free path of the electrons is inversely proportional to the square of the amplitude of the vibrating atoms. The observed diminution of the resistivity on increase of pressure is found to agree quite well with that calculated on the basis of this theory in the case of aluminium, copper, silver, cadmium, and gold. For nickel, platinum, and lead, the agreement is not so good. The effect of pressure on alloys, which consist of solid solutions, is also expressed by Wien's formula. H. M. D.

The Selective Photo-electric Effect in Reference to Absorbed Light Energy. ROBERT POHL and P. PRINGSHEIM (*Ber. Deut. physikal. Ges.*, 1913, **15**, 173—185. Compare A., 1910, ii, 922; 1911, ii, 787; 1912, ii, 317).—If the photo-electric current emitted by the alkali metals when acted on by ultra-violet radiation is represented as a function of the wave-length, and the effect referred to unit quantity of absorbed energy instead of to unit quantity of

incident energy, it is found that the resonance maximum becomes much more sharply developed. The quantity of electricity which is set free when a quantity of energy equal to one calorie is absorbed in the middle of the resonance region amounts to 50×10^{-4} coulombs in the case of potassium, and 120×10^{-4} coulombs for sodium. Higher values for the electric discharge per unit of absorbed energy are obtained if the data for the coloured colloidal modifications of the alkali metals are employed in the calculation; for both potassium and sodium the observations indicate that the photo-electric discharge is of the order of 350×10^{-4} coulombs per calorie when the incident rays correspond with the middle of the resonance region.

From a comparison of the numbers representing the photo-electric effect referred to unit quantity of incident and absorbed energy respectively, it is found that the region of the selective effect is characterised by the fact that the metal has a high reflexion capacity towards rays of this wave-length. H. M. D.

Electrical Conductivity of Bromine Solutions of Iodine. VLADIMIR A. PLOTNIKOV and V. E. ROKOTJAN (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 193—199. Compare A., 1904, ii, 156).—The authors have measured the conductivities of solutions of iodine in bromine with concentrations of 0—44·5% of iodine (or 72·28% of BrI) at 25°, and of 44·5—59·48% of iodine at 40·6°. The specific conductivity at 25° increases continuously from $\chi_{25} . 10^6 = 0·32$ for 12% of iodine to 126 for 44·5% of iodine. The molecular conductivity diminishes uninterruptedly with increase of dilution. With rise of temperature the conductivity increases, the extent of the change being greater for dilute than for concentrated solutions.

These results are explained by the formation of an iodine bromide (compare Bruner and Bekier, A., 1912, ii, 732) and its dissociation into bromine and iodine ions.

The marked electrical conductivity of bromine solutions of iodine does not agree with the view that conductivity is conditioned by appreciable increase in the dielectric constant of the solvent.

Comparison of conducting solutions of iodine in bromine with non-conducting solutions of potassium bromide in bromine indicates the invalidity of the hypothesis which regards electrolytes as divisible into "good" or "typical," such as potassium bromide, and "bad." Electrical conductivity must, indeed, be considered as a consequence of the electrochemical relations of the solute with the solvent. T. H. P.

Electrical Conductivity and Fluidity of Strong Solutions. WILLIAM SANSOME TUCKER (*Proc. Physical Soc. London*, 1913, **25**, 111—122).—Measurements have been made of the viscosity and electrical conductivity of concentrated solutions of calcium chloride at temperatures between −50° and 85°.

At constant temperature (16·77°) the conductivity increases with the concentration, attains a maximum, and then diminishes. The maximum corresponds with a solution containing about 5 mols. of

calcium chloride per 100 mols. of water. If the ratio of the conductivity (C) to the fluidity (F) is plotted as a function of the concentration (n), expressed in mols. salt per mols. of water, a straight line is obtained which passes through the origin. In other words, the value of $C/n.F$ remains practically constant for values of n between 1 and 16·6. The data obtained by Bousfield and Lowry for concentrated solutions of sodium hydroxide (A., 1905, ii, 135) are shown to exhibit the same relationship.

The curves obtained by plotting the conductivity and the fluidity as a function of the temperature are found to exhibit considerable differences. It is also found that the curves obtained by plotting C/n as a function of the temperature vary considerably according to the value of n. When n is small, the curves are very nearly straight lines, but increasing curvature is developed as n increases. There is no evidence of the existence of a temperature at which the conductivity would become equal to zero, as has been suggested by Lyle and Hosking for sodium chloride solutions (A., 1902, ii, 440).

H. M. D.

The Dissociation Constants of Certain Very Weak Acids, Especially the Carbohydrates, Measured by Electrometric Methods. LEONOR MICHAELIS and PETER RONA (*Biochem. Zeitsch.*, 1913, **49**, 232—248).—If an acid is added to a given solution of a base, the hydroxyl ion concentration is diminished, which diminution can be readily measured electrometrically. The acid dissociation constant $K=[S'].[H]/S-S'$ when $[H^{\cdot}]=$ hydrogen ion concentration of the mixture, S' the concentration of the acid ions, $S=$ the total quantity of added acid. All these constants are readily measured, as S' is the difference of hydroxyl ion concentration of the alkali before and after the addition of acid. A correction, which is small in the case of weak acids, must be made for the dissociation of the sodium salts. If $\gamma=$ the dissociation grade, then $K=[S'].[H]/S-\frac{1}{\gamma}[S']$. To carry out the measurements, the concentration of the alkali should not exceed $0·03N$, and potassium chloride to the amount of $0·1N$ should be added, the interposed liquid between the electrodes being a saturated solution of this salt. The diffusion potential in this case is reduced to a minimum. The sodium hydroxide used must be quite free from carbonate, and the method is not available, owing to small changes produced on addition of the acid, when $K<10^{-15}$. By this method, the following values for K were obtained: Phenol, $5·8\times10^{-11}$; glycine k_a, $1·2\times10^{-10}$, and k_b, $1·9\times10^{-12}$; glycerol, $0·7\times10^{-14}$; sorbitol, $2·5\times10^{-14}$; mannitol, $3·4\times10^{-14}$; dulcitol, $3·5\times10^{-14}$; arabinose, $3·7\times10^{-13}$; dextrose, $6·6\times10^{-13}$; galactose, $5·3\times10^{-13}$; lævulose, $8·8\times10^{-13}$; mannose, $10·9\times10^{-13}$; sucrose, $2·40\times10^{-13}$; lactose, $6·0\times10^{-13}$; maltose, $18·0\times10^{-13}$; and raffinose, $1·8\times10^{-13}$.

S. B. S.

An Improved Method for the Electrometrical Measurement of the Reaction of Biological Liquids. KARL A. HASSELBALCH (*Biochem. Zeitsch.*, 1913, **49**, 451—457).—Liquids which contain dissociable oxygen compounds, or which are relatively poor in

"buffer" substances, cause certain difficulties when the reaction is electrometrically measured by the author's shaking method, as previously described (A., 1911, ii, 182). These can be overcome, however, by permanent shaking and constant washing of the electrodes by the liquid, by the use of a modified apparatus, which is described in detail and figured in the text. S. B. S.

The Conditions which Determine the Cathodic Overvoltage. JOHN N. PRING (*Zeitsch. Elektrochem.*, 1913, **19**, 255—262. Compare Pring and Curzon, *Trans. Faraday Soc.*, 1912, **7**, 237; Tafel, A., 1912, ii, 223).—The various theories concerning overvoltage on metallic surfaces are discussed, and a series of experiments is recorded showing the influence of various thicknesses of electrolytically deposited metals on various cathodes. The following cathodes and coatings were investigated: Copper coated with zinc; nickel coated with lead; nickel coated with zinc; nickel coated with tin; zinc coated with copper; platinum coated with copper; zinc coated with gold; copper coated with platinum. The potential measurements show that thin metallic layers on the cathode have a definite influence on the overvoltage, and that the influence depends on the thickness of the layer. For each metal there is a maximum thickness, above which an increase in thickness has no effect on the overvoltage. The maximum value is obtained whether the cathode itself has a higher or lower value than the surface layer. The thickness is the same as that to which the hydrogen penetrates the cathode at decomposition. The thickness for the various coatings are: platinum, 4×10^{-6} mm.; gold, $1{\cdot}6 \times 10^{-4}$ mm.; zinc, $4{\cdot}2 \times 10^{-4}$ mm.; copper, $3{\cdot}4 \times 10^{-3}$ mm.; tin, $5{\cdot}5 \times 10^{-3}$ mm.; nickel, $1{\cdot}6 \times 10^{-2}$ mm.; and lead, $6{\cdot}6 \times 10^{-2}$ mm. J. F. S.

Phenomena at the Anode in Discharge Through Gases. WALTER G. CADY (*Physikal. Zeitsch.*, 1913, **14**, 296—302).—Certain changes are described which have been found to take place in the positive column on the passage of the discharge through nitrogen in tubes provided with anodes of copper, mercury, iron, or silver. The phenomenon consists in a contraction of the positive glow in such a way that the discharge at the anode surface appears to be focussed in a number of centres. The effect is supposed to be due to the formation of small patches of oxide as a consequence of the presence of traces of oxygen in the tubes, but it is probable that other foreign substances on the anode surface may give rise to the same phenomenon. In this connexion the author discusses changes in the character of the discharge which have been noted by previous observers, and an attempt is made to correlate the phenomena.
H. M. D.

Transport Numbers in Antimony Trichloride as Solvent. KASIMIR FRYCZ and STANISLAS TOLLOCZKO (*Chem. Zentr.*, 1913, i, 91; from *Festschr. Univ. Lemberg*, 1912, **1**, 1—16).—In continuation of the study of antimony trichloride as an ionising solvent (Tolloczko, A., 1900, ii, 190; 1901, ii, 437; Klemensiewicz, A., 1908, ii, 1043), the

transport numbers of solutions of ammonium and potassium chloride have been measured at 99°. The results show that, with increasing dilution, the transport numbers increase much more rapidly than is the case in aqueous solution, and the general rule is confirmed that the ions which have the higher transport numbers are those that are common to the electrolyte and the solvent, in this case the chlorine ions. J. C. W.

The Magnetic Properties of Some Solid Hydrates of Copper and Chromium. (Mlle.) E. FEYTIS (*Compt. rend.*, 1913, **156**, 886—889. Compare A., 1911, ii, 1058).—A study of the coefficient of magnetisation of the hydrates of cupric chloride and its double chlorides with sodium, potassium, and ammonium shows that the molecular coefficients for the hydrates cannot be obtained additively from that of water and the anhydrous salt. The molecular coefficients of magnetisation of the anhydrous salts, having a brown colour, group themselves round the value 1230×10^{-6}, and those of the hydrates, green or blue, round 1400×10^{-6}.

In the case of the hydrates of chromium chloride and sulphate and the double sulphates of chromium and potassium, no difference is found between the specific coefficients of magnetisation of isomeric violet and green hydrates. With the exception of anhydrous chromic chloride, all the chromic salts have practically the same molecular coefficients of magnetisation. W. G.

The Magnetism of Anhydrous and Hydrated Salts. GRÉGOIRE WYROUBOFF (*Compt. rend.*, 1913, **156**, 1072—1074. Compare A., 1902, 565, 609).—A claim for priority over Feytis (preceding abstract). W. G.

[Magnetic] Susceptibility of Iron, Steel, Nickel, and Cobalt at Higher Temperatures. KÔTARÔ HONDA and HIROMU TAKAGI (*Sci. Reports Tôhoku Imp. Univ.*, 1913, **1**, 229—242).—The magnetic susceptibility was examined at temperatures up to about 1300°. The results are exhibited in the form of curves in which the reciprocal of the susceptibility is plotted as a function of the temperature. The general conclusion drawn from the data is that Curie's law is only applicable to definite and limited intervals of temperature.

In the case of nickel, the agreement is good above 500°, but slight deviations are found at lower temperatures. For cobalt the deviations from Curie's law are more marked. The curve is convex towards the temperature axis below 1240°, but above this the points lie on a straight line. In the case of β-iron, the law is only approximately satisfied, and for γ-iron the data diverge very widely from the theoretical requirements.

From the data for a number of steels containing different amounts of carbon, it appears that in the β-condition there is approximate agreement; the divergence from the law increases, however, with the carbon content, and the law is evidently not applicable to steels in the γ-condition. H. M. D.

Saturation Curves and the Law of the Corresponding States. EMILE H. AMAGAT (*Compt. rend.*, 1913, **156**, 843—848).—An extension of the work already published (compare this vol., ii, 188), the curves being given for very low pressures and also for other substances. The results obtained bear out the previous work and conclusions. W. G.

Adiabatic Expansion in Liquids. L. GAY (*Compt. rend.*, 1913, **156**, 1070—1072).—The author has determined the dilatation produced in liquids by adiabatic expansion from a pressure of two atmospheres to one in the case of mercury, water, and benzene, in an apparatus described in detail in the paper. From his results he has calculated the value of β, the isothermal coefficient of compressibility, by means of the formula $\beta=\gamma+T\alpha^2/41\cdot3c\mathrm{D}$, where γ is the adiabatic coefficient of compressibility, obtained experimentally, α the thermal coefficient of dilatation, c the specific heat at constant pressure, and D the density. The results obtained are in fairly close agreement with those already given by Amagat (compare A., 1909, ii, 549). W. G.

Method for Determining the Latent Heat of Evaporation of Metals. CR. MUSCELEANU (*Bull. Acad. Sci. Roumaine*, 1912/13, **1**, 145—151).—The principle of the method adopted consists in electrically heating the metal to its temperature of evaporation, and measurement of the heat employed and weight of metal volatilised. The following results were obtained: mercury, 63·66 cal.; cadmium, 181·0 cal.; zinc, 365·8 cal.; magnesium, 1700·0 cal.; bismuth, 161·5 cal., the pressure in each case being $2\cdot10^{-3}$ mm. of mercury. H. W.

A Relation between the Boiling Points and Molecular Weights of the Members of Homologous Series. SAMUEL SUGDEN (*Chem. News*, 1913, **107**, 135—136. Compare J. C. T., A., 1912, ii, 1136).—Starting with van der Waals' equation, and assuming that liquefaction will take place when the internal attraction of the particles for each other surpasses a critical value, that is, when $a/V^2=K$, the author deduces that $\alpha\sqrt{a}-\beta b=T$, where a and b are the constants in van der Waals' equation, T is the boiling point at constant pressure, and α and β are constants. Now a, the coefficient of attraction between the molecules, is proportional to their mass M, and b is probably also a function of M, and, for members of a homologous series, may be considered to vary as M. It follows therefore that the boiling points of the members of a homologous series should be connected by the relation: $T=A\sqrt{M}-BM$, where A and B are constants. If B is small compared with A, the relation reduces to the form $T/\sqrt{M}=$constant, which is that found by J. C. T. (*loc. cit.*), and this is found to hold in the case of the normal paraffins, the value of the constant being $37\cdot2\pm0\cdot04$. In the following series the value of A (given in brackets) is deduced from the relation $T=A\sqrt{M}-BM$, and found

to be constant: normal fatty acids ($66\cdot5 \pm 0\cdot2$); methyl esters of the fatty acids ($42\cdot8 \pm 0\cdot1$); alcohols, $C_nH_{2n+1}OH$ ($83\cdot3 \pm 0\cdot5$); ethers, $C_nH_{2n+2}O$ ($35\cdot9 \pm 0\cdot15$); aldehydes, $C_nH_{2n+1}\cdot CHO$ ($50\cdot3 \pm 0\cdot2$); ketones, $(C_nH_{2n+1})_2CO$ ($50\cdot4 \pm 0\cdot3$). T. S. P.

Vapour Pressures of the Alkali Metals. A. KRÖNER (*Ann. Physik*, 1913, [iv], **40**, 438—452).—The vapour pressures of potassium and cæsium have been determined at temperatures between 250° and 400° by a method involving the measurement of the change in volume which occurs when the heated metal is brought into communication with an indifferent gas and the total pressure is kept constant. When the data are combined with the vapour pressure values for sodium, which Gebhardt (A., 1906, ii, 9) obtained by measuring the boiling point at different pressures, it is found that the vapour pressure-temperature relationships are in agreement with the Ramsay-Young rule for closely related substances.

The method of vapour pressure measurement employed by the author can only be applied when the pressure is small, but by making use of the data for sodium, which extend over a much larger range of pressures, it is possible to calculate the vapour pressures of the other alkali metals over the corresponding range by making use of the boiling-point data for atmospheric pressure and the validity of the Ramsay-Young rule. H. M. D.

Ionic Size in Relation to Molecular Physics, Together with a New Law Relating to the Heats of Formation of Solid, Liquid, and Ionic Molecules. WILLIAM R. BOUSFIELD (*Proc. Roy. Soc.*, 1913, *A*, **88**, 147—169. Compare A., 1905, ii, 369; 1906, ii, 428).—By reference to the data for compounds containing hydrogen, potassium, sodium, or lithium in combination with chlorine, bromine, iodine, or the groups NO_3 or IO_3, it is shown that the heat of combination, in the liquid or solid state, of any of the electropositive elements with any of the electro-negative elements or radicles is approximately equal to the sum of certain constants peculiar to the two elements or radicles, together with $0\cdot875\delta V$, where δV is the change of atomic volume produced by the combination. This result may be expressed in the form $\Sigma = H_1 + H_2 + 0\cdot875\delta V$. In order to be able to assign definite values to H_1 and H_2, it is necessary to give an arbitrary value to some one element, but this makes no real difference to the additive nature of the relationships which are involved. The heats of formation of the halogen compounds of calcium, strontium, barium, zinc, and cadmium can be represented in a similar manner.

According to the data for the chlorides of lithium, sodium, and potassium, it appears that the heat of ionisation is similarly connected with the change in volume which occurs when the elements pass into the ionic condition. If n is the number of water molecules which are chemically combined with the dissolved salt, and if a calorific constant $1\cdot85$ is assigned to each molecule of combined water, then the heat of ionisation of the three salts can be represented by $\Sigma = 0\cdot875\delta V + 1\cdot85n + 46\cdot6$. This expression may be

modified and combined with the previous one, so as to obtain a formula which is applicable to the heats of formation of both solid salts and ionised salts.

In regard to the significance of the term $0.875\delta V$, it is supposed that this affords a measure of the diminution in the internal energy which results from the contraction occurring on combination.

An empirical relation between ionic volume and freezing-point depression has been found, which may be written in the form $1/D = p - qN(I_v - K)$, where D is the effective molecular freezing-point depression, N the number of mols. of solute per 1000 grams of water, I_v the ionic volume, and K the volume of the ionic nuclei, and p and q are constants. By combining this with the empirical relation $EV_s = a - bI_v$ (a and b being constants and EV_s the molecular solution volume of the electrolyte; see previous papers, *loc. cit.*), it is shown that numbers may be obtained which represent the molecular hydration of the dissolved salt. The values for lithium, sodium, and potassium chlorides, obtained in this way, are 21, 13, and 9 respectively. In combination with Washburn's data, obtained from transport measurements (A., 1908, ii, 1009), this leads to the following hydration values for the various ions: Cl, 4; K, 5 Na, 9; and Li, 17. H. M. D.

Heats of Combustion and Transformation of Some Elements. I. Diamond and Graphite. WALTER A. ROTH and H. WALLASCH (*Ber.*, 1913, **46**, 896—911).—The determinations were carried out in a bomb calorimeter, using liquid paraffin as the addition agent to bring about complete combustion. The graphite used was both natural and artificial (Acheson), and before use it was purified by treatment with two or more of the reagents: hydrochloric acid, nitric acid, hydrofluoric acid, chlorine. The purer it was, the greater was the heat of combustion.

The heat of combustion of one gram of diamond ($D^{18} = 3.50_3$) was found to be 7869 ± 3 gram-cal., in very good agreement with the corrected value (7869 ± 2) of Berthelot and Petit. For graphite, the value found was 7854 ± 1 gram-cal.; in most cases this value was independent of the source of the graphite, but with certain natural graphites a value 0.3% lower was obtained. The results for graphite are thus lower than for the diamond, in contradistinction to the results obtained by Berthelot and Petit with graphite obtained from a blast furnace.

The thermochemical measurements show that the distinction which has been made between graphite and graphitite cannot be maintained.

When finely divided graphite or lamp-black is mixed with liquid paraffin, there is a slight development of heat, which, however, is not sufficient to make any difference in the heats of combustion.

Purified graphite obtained from cast-iron or from the blast-furnace gave the values 7855—7865 gram-cal. per gram, in agreement with the numbers given above, and in disagreement with the value of Berthelot and Petit. T. S. P.

Calorimetric Study of the Iron–Carbon System. A. MEUTHEN (*Ferrum*, 1912, **10**, 1—21).—The total heat-content of a series of iron-carbon alloys between the limits 0·06 and 4·03% of carbon and 650° and 920° has been determined by means of the vacuum calorimeter. The heat of transformation of pearlite, containing 0·9% C, is 15·9 Cal. per gram, and that of β- into α-iron 5·6 Cal. per gram. One gram of α-iron separating from solid solution develops 14·1 Cal. per gram. The horizontal line in the equilibrium diagram, which represents the transformation of β- into α-iron, does not extend beyond 0·32% C. Within the limits 650—700°, the heat-content of the alloys is not directly proportional to the carbon concentration, but the curve consists of two straight lines, intersecting at a considerable angle at a concentration just above that of pearlite. C. H. D.

Heats of Combustion of Cyclic Compounds. II. PAVEL V. ZUBOV (*J. Russ. Phys. Chem., Soc.*, 1913, **45**, 240—251).—With reference to the data published in the author's first paper (A., 1902, i, 144), the following remarks are made: Methyl*cyclo*hexene (β) has been shown by Zelinski to be a mixture of isomeric hydrocarbons; methyl*cyclo*hexene (α) is 1-methyl-Δ^3-*cyclo*hexene; C_7H_{13}·CHMe·OH is probably methyl*cyclo*hexylmethylcarbinol; C_7H_{13}·COMe is probably methyl methyl*cyclo*hexyl ketone; 1 : 1 : 5-trimethyl*cyclo*-5-hexene-3-one is more correctly termed 1 : 1 : 3-trimethyl-Δ^3-*cyclo*-hexene-5-one (*iso*phorone).

The following new results have been obtained, the numbers referring to Cals. per gram-molecule:

Hydrocarbons.

		Constant volume.	Constant pressure.
C_5H_{10}	Methyl*cyclo*butane	790·5	792·0
	*cyclo*Pentane	789·9	791·4
C_6H_{12}	Methyl*cyclo*pentane	945·7	947·4
	*cyclo*Hexane	943·4	945·1
C_7H_{14}	1 : 3-Dimethyl*cyclo*pentane	1099·5	1101·5
	Methyl*cyclo*hexane	1100·8	1102·8
	*cyclo*Heptane	1096·3	1098·3
C_8H_{16}	1 : 2 : 4-Trimethyl*cyclo*pentane	1255·7	1258·0
	1 : 1-Dimethyl*cyclo*hexane	1252·8	1255·1
	1 : 3-Dimethyl*cyclo*hexane	1248·1	1250·4
	1 : 4-Dimethyl*cyclo*hexane	1238·9	1241·2
	Methyl*cyclo*heptane	1254·8	1257·1
C_9H_{18}	1-Methyl-3-propyl*cyclo*pentane	1412·9	1415·5
	1 : 2 : 3-Trimethyl*cyclo*hexane	1407·3	1409·9
	1 : 3 : 3-Trimethyl*cyclo*hexane	1406·0	1408·6
	Ethyl*cyclo*heptane	1418·3	1420·9
$C_{10}H_{20}$	1-Methyl-3-propyl*cyclo*hexane	1563·6	1566·5
	Carvomenthane	1527·0	1529·9
C_6H_{10}	Dimethylmethylene*cyclo*propane	905·6	907·1
	*cyclo*Hexene	898·9	900·4
C_7H_{12}	1-Methyl-Δ^1-*cyclo*hexene	1049·8	1051·5
	1-Methyl-Δ^3-*cyclo*hexene	1052·4	1054·1
	Methylene*cyclo*hexane	1052·9	1054·6
	Di*cyclo*heptane	1049·1	1050·8
	*cyclo*Heptene	1058·7	1060·4

Hydrocarbons (continued).

		Constant volume.	Constant pressure.
C_8H_{14}	1 : 1 : 2-Trimethyl-Δ^2-*cyclo*pentene (*iso*laurolene)	1203·4	1205·4
	Laurolene	1202·8	1204·8
	1 : 3-Dimethyl-Δ^3-*cyclo*hexene	1204·6	1206·6
$C_{10}H_{18}$	Fenchane	1515·3	1517·9
$C_{14}H_{26}$	Hexahydro-*m*-ditolyl	2123·5	2127·3
C_6H_8	$\Delta^{1:3}$-Dihydrobenzene	840·6	841·8
C_8H_{12}	1 : 3-Dimethyldihydrobenzene	1158·2	1159·9
$C_{10}H_{16}$	*l*-Limonene	1469·7	1472·0
	l-Pinene	1485·7	1488·0
	d-Pinene	1484·4	1486·7

Alcohols.

$C_5H_{10}O$	*cyclo*Butylcarbinol	754·2	755·4
$C_6H_{12}O$	1-Methyl-2-*cyclo*pentanol	895·1	896·6
	*cyclo*Hexanol	897·3	898·8
$C_7H_{14}O$	1-Ethyl-2-*cyclo*pentanol	1047·7	1049·4
	1 : 3-Dimethyl-2-*cyclo*pentanol	1039·2	1040·9
	1 : 3-Dimethyl-3-*cyclo*pentanol	1042·7	1044·4
	*cyclo*Hexylcarbinol	1056·0	1057·7
	1-Methyl-3-*cyclo*hexanol	1047·2	1048·9
	*cyclo*Heptanol	1059·0	1060·7
$C_8H_{16}O$	1 : 3-Dimethyl-2-*cyclo*hexanol	1206·0	1208·0
	1 : 3-Dimethyl-3-*cyclo*hexanol	1202·5	1204·5
	1 : 3-Dimethyl-5-*cyclo*hexanol	1193·1	1195·1
	1-Methyl-1-*cyclo*heptanol	1199·4	1201·4
$C_9H_{18}O$	Methyl*cyclo*hexylmethylcarbinol	1353·4	1355·7
	1-Methyl-3-ethyl-3-*cyclo*hexanol	1333·5	1335·8
$C_9H_{16}O$	1 : 3 : 5-Trimethyl-Δ^6-5-*cyclo*hexenol	1305·9	1307·9
$C_5H_{10}O_2$	1 : 1-Dimethylol*cyclo*propane	714·2	715·1

Ketones.

C_5H_8O	Acetyl*cyclo*propane	697·5	698·4
$C_6H_{10}O$	Acetyl*cyclo*butane	864·2	865·4
	1-Methyl-2-*cyclo*pentanone	840·7	841·9
$C_7H_{12}O$	1-Ethyl-2-*cyclo*pentanone	998·9	1000·4
	1 : 3-Dimethyl-2-*cyclo*pentanone	998·3	999·8
	1-Methyl-3-*cyclo*hexanone	1003·4	1004·9
	*cyclo*Heptanone	1005·1	1006·6
$C_8H_{14}O$	1 : 3-Dimethyl-2-*cyclo*hexanone	1139·5	1141·2
$C_9H_{16}O$	Ethyl *cyclo*hexyl ketone	1300·7	1302·7
	1-Methyl-4-acetyl*cyclo*hexane	1278·8	1280·8
	Methyl methyl*cyclo*hexyl ketone	1289·4	1291·4
$C_8H_{12}O$	1 : 3-Dimethyl-Δ^6-5-*cyclo*hexenone	1111·8	1113·3
$C_9H_{14}O$	1 : 1 : 3-Trimethyl-Δ^3-5-*cyclo*hexenone	1259·2	1260·9
$C_{10}H_{16}O$	Dihydrocarvone	1424·7	1426·7
	Carone	1409·2	1411·2

Acids.

$C_4H_6O_2$	*cyclo*Propanecarboxylic acid	488·3	488·6
$C_5H_8O_2$	*cyclo*Butanecarboxylic ,,	645·1	645·7
$C_7H_{12}O_2$	*cyclo*Hexanecarboxylic ,,	942·3	943·5
$C_8H_{14}O_2$	Hexahydro-*m*-toluic ,,	1095·6	1097·1
	A cyclic octoic acid from light petroleum (100—105°)	1098·6	1100·1
	Octoic acid from light petroleum (100—102°)	1091·1	1092·6
	*cyclo*Heptanecarboxylic acid	1096·3	1097·8

Esters.

		Constant volume.	Constant pressure.
$C_6H_{10}O_2$	Methyl *cyclo*butanecarboxylate	816·4	817·3
$C_{11}H_{18}O_3$	Ethyl 1-methyl-4-ethyl-3-*cyclo*butanone-4-carboxylate	1478·8	1480·5
$C_{15}H_{20}O_6$	Tri*cyclo*butyrin	1862·1	1863·3
$C_{18}H_{26}O_6$	Tri*cyclo*valerin	2329·8	2331·8

Furan Derivative.

$C_6H_{12}O$	4 : 4-Dimethyltetrahydrofuran	905·9	907·4

Nitrogen Compounds.

$C_5H_{11}N$	... ...	830·2	831·5
$C_7H_{15}N$	... ...	1128·0	1129·9
$C_9H_{19}N$	... ...	1440·1	1442·6
$C_9H_{17}ON$	... ...	1375·3	1377·2

The above numbers are based on Regnault's value of the specific heat of water at 20°. T. H. P.

The Chemical Interpretation of Special Points on Curves. L. GAY and F. DUCELLIEZ (*Bull. Soc. chim.*, 1913, [iv], **13**, 320—324). —It is pointed out that the commonly accepted idea that a maximum or minimum point in a curve representing the relationship between a physical property and the composition of a mixture represents a definite compound of the components of the mixture is often erroneous, and in illustration it is shown that a number of curves with different maxima may be drawn, representing the relationship between density and composition of mixtures of acetic acid and water. Maximal points in melting-point curves of mixtures generally represent definite compounds, but in other cases a number of other factors must be considered before it can be assumed that a special point in the curve implies chemical combination (compare Baud and Gay, A., 1909, ii, 558). T. A. H.

A Simple Method for Determining the Density of Mineral Powders. MAURICE BILLY (*Compt. rend.*, 1913, **156**, 1065—1067). —The density of the powder is determined by weighing it in an aqueous solution of potassium hydroxide, the pyknometer used being previously exhausted and then filled with carbon dioxide prior to the introduction of the powder. A slightly modified form of stopper is shown and described, by means of which the flask is evacuated, filled with carbon dioxide, and finally gradually filled with the alkali. It is claimed that this method is quicker, and gives a far higher order of accuracy than the methods usually employed. W. G.

A Modified Victor Meyer Apparatus. HAROLD CANNING CHAPIN (*J. Ind. Eng. Chem.*, 1912, **4**, 684).—A sketch with description of a modified Victor Meyer apparatus, in which the capsule containing the liquid (for the experiment) is made from a piece of 5 mm. glass tubing, sealed off at one end, and, after the liquid is

introduced, drawn into a capillary at the other, closed, and bent round twice at right angles; it is hung from the rod in the vaporising tube, a twist of which breaks the capillary and drops the capsule.

F. M. G. M.

The Expansion Pressure of Normal Fluids. L. GAY (*Compt. rend.*, 1913, **156**, 1015—1017).—A mathematical paper in which the author, using Young's values for the physical constants of chlorobenzene, *iso*pentane, di*iso*propyl, and *cyclo*hexane (compare T., 1889, **55**, 486), has verified his formula (compare A., 1911, ii, 1058) for the expansion pressure of liquids. For all the substances studied, the coefficient of compressibility is always less than $(V-b)/V(P+K)$, whence it follows that the internal pressure diminishes with the volume, the temperature remaining constant.

W. G.

A New Physico-chemical Volumetric Method. RENÉ DUBRISAY (*Compt. rend.*, 1913, **156**, 894—898).—An application of Donnan's work (compare A., 1900, ii, 201) and its extension by Lewis (A., 1908, ii, 357) on the emulsion of oils, to determining the acidity of solutions. The method consists in determining the number of drops formed by the flow of a given volume of standard alkali from a pipette immersed in a given volume of the solution, the acidity of which it is required to determine. By varying the total volume of alkali run in, the number of drops shows a very marked and sudden increase when the alkali added is just sufficient to neutralise the acid. Figures and curves are given in illustration of the method.

W. G.

A Simple Apparatus for the Absolute Measurement of the Coefficient of Viscosity of Gases and for the Demonstration of Maxwell's Law. H. PIWNIKIEWICZ (*Physikal. Zeitsch.*, 1913, **14**, 305—308. Compare Roberts, A., 1912, ii, 237).—A simple form of apparatus is described for the measurement of the viscosity of gases. It consists essentially of two small cylindrical gas reservoirs, connected by a capillary glass tube about 35 cm. long, the time required for the passage of a definite volume of gas through the tube being measured as well as the difference of pressure in the two reservoirs. The quantity of gas required is only a few c.c., and the measurement of the viscosity can be repeated as often as desired with the same material. The data obtained with air, carbon dioxide, and hydrogen show that the apparatus is capable of yielding accurate viscosity values.

It is also shown that the apparatus may be conveniently employed to demonstrate that the viscosity of a gas is independent of the pressure to which it is subjected.

H. M. D.

Viscosities of the Systems: Chloral–Water and Chloral–Ethyl Alcohol. NICOLAI S. KURNAKOV and N. N. EFREMOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 329—348).—For chloral the authors find D_4^{25} 1·5049 (Perkin, T., 1887, **51**, 809, gave 1·5060, and van Rossem, A., 1908, i, 501, 1·5030) and η_{25} 0·01263. Two preparations of chloral hydrate gave D_4^{50} 1·6193 and 1·6187 (Perkin, *loc. cit.*, found

1·6415 for the solid hydrate at 50°/4°), D_4^{60} 1·5966 and 1·5946, D_4^{90} 1·5148 and 1·5148, m. p. (slow heating) 48·1° (Perkin, *loc. cit.*, gave 57·7°, and van Rossem, *loc. cit.*, 47·4°).

The viscosity isotherms of liquid mixtures of chloral and water at 50°, 60°, 70°, 85°, and 90° are continuous curves exhibiting maxima, that of the 50° curve representing a viscosity nearly twenty times as great as that of the chloral, which is the more viscous constituent of the mixtures. The compositions at the maximal points are not constant for different temperatures, and do not correspond with rational proportions of the components; as the temperature is lowered, the molecular ratio 1 : 1 is indeed approached, but is not reached within the temperature limits of stable existence of the binary liquid phases. It is evident that the dynamic equilibrium of the system tends towards a limit depending on the formation of chloral monohydrate, which is accompanied by considerable development of heat.

These results are confirmed by the cryoscopic measurements of Beckmann (A., 1889, 11) and of Bruner (A., 1902, ii, 305), who found normal molecular weights for chloral hydrate in water, benzene, nitrobenzene, and *o*-toluidine, the values in acetic acid being less than the normal. At the solidifying temperatures of these solutions, below 0° to 5·7°, the dissociation of chloral hydrate is evidently so slight as to exert no appreciable influence on the magnitude of the molecular weight. Rise of temperature, however, increases the dissociation of the hydrate, and this is in agreement with the marked displacement of the viscosity maximum from the 50 mol. % point towards the water axis. The system chloral–water thus represents a typical example of the influence of hydration processes on the form of the viscosity diagram.

Similar relations hold for the temperature-coefficient of the viscosity. The curves showing the variation of this coefficient with composition for different ranges of temperature are of the same form as the viscosity isotherms, but the maxima are still more pronounced. The maxima correspond with 47·5 mol. % of chloral at 50—60° and with 45 mol. % for 60—70° and 70—85°; in the first case the coefficient is eighty-seven times as great as that for chloral. Here, too, the maximum never coincides with the molecular ratio 1 : 1, although this is approached as the temperature is lowered.

Chloral alcoholate, CCl_3·CHO,Et·OH, m. p. 45·2° (Leopold, A., 1909, ii, 472, found 46·6°), is highly hygroscopic, its specific gravity and viscosity being increased considerably by traces of water. For ethyl alcohol, the authors find D_4^{20} 0·7900, D_4^{30} 0·7818 (Doroshevski gave D_4^{20} 0·7893, D_4^{30} 0·7809), and η_{20} 0·01156 (Thorpe and Rodger, *Phil. Trans.*, 1894, **185**, *A*, 379, gave η_{20} 0·01192). Consequent on the smaller heat-effect of the reaction between the components, the viscosity maxima for chloral–alcohol mixtures are considerably flatter than with chloral–water, but here, too, the position of the maximum approaches the 50 mol. % point as the temperature falls. When small proportions of water are present, the maxima approach very closely the above point, and are then but slightly displaced by change of temperature. The temperature-coefficient curves for

different ranges of temperature are similar to those obtained for water–chloral. T. H. P.

Viscosity and Conductivity of Concentrated Solutions of Ferric Chloride. ENRIQUE MOLES, M. MARQUINA, and G. SANTOS (*Anal. Fis. Quim.*, 1913, **11**, 192—211).—Determinations of viscosity and conductivity of solutions of ferric chloride of from 0·025 to 8 molar strength at temperatures of 0°, 18°, 25°, and 35°. G. D. L.

Method for Determining the Surface Tension of Liquids for Biological Purposes. C. C. ERDMANN (*J. Biol. Chem.*, 1913, **14**, 141—147).—The apparatus described is based on that of Traube (A., 1911, ii, 328). A drop pipette of a few c.c. capacity is provided with a highly polished drop surface, ground so as to form the base of a cone. Ten, 20, or more drops are collected and weighed. The results are expressed as drop numbers corresponding with 5, 10, or 50 grams of substance. Small amounts of acid cause a pronounced change in the surface tension of serum; similar amounts of alkali have very much less effect. A modified form of the apparatus is described for surface tension determinations of less dilute solutions.

On heating serum the surface tension changes very slowly at low temperatures, but rapidly at the beginning of coagulation, from 65—70°. There is, however, a break in the curve at 38°. E. F. A.

Influence of Light on the Surface Tension of Various Solutions. N. A. MARENINE (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, *Phys. Part*, 28—30).—A number of aqueous solutions of measured surface tension were subjected for either two or three minutes to the action of the light from a high-tension arc between aluminium electrodes, their surface tensions being then re-measured. Water and 3% magenta solution showed no change; 30% resorcinol solution showed a decrease of 9·6%, this being probably due to chemical changes; whilst 10% solutions of eosin, sodium sulphite, and potassium permanganate, and also 1% methyl-violet and 20% potassium nitrate solution, showed increases in surface tension varying from 3·2 to 5·1%.

Further measurements demonstrate that the increase in surface tension reaches a maximum approximately 1·5 minutes after the action of the light ceases. The surface tension subsequently falls continuously to the original value, which is sometimes attained only after thirty minutes.

A quartz mercury lamp of great actinic power does not cause any such increase in the surface tension, and it seems likely that the phenomenon is due to an action of electrical character. T. H. P.

Independence of the Surface Tension of Light-sensitive Solutions on the Illumination. NICOLAI A. HESEHUS (*J. Russ. Phys. Chem., Soc.*, 1913, **45**, *Phys. Part*, 31—35).—The results of Marenine's experiments (compare preceding abstract) indicate that

the surface tension is not affected by the action of actinic rays. This conclusion is explained by assuming that these rays act solely on the stable nuclei of the electrons, and not on the external electrons of the atoms (compare Langevin, *J. Physique*, 1905). One of the consequences of Marenine's results is that actino-electric actions should be proportional to the concentrations of the solutions, and not, as G. C. Schmidt supposed from the results of his experiments with magenta solutions (*Ann. Physik.*, 1898, **64**, 708), to the square-roots of the concentrations. Schmidt's experimental data are, however, in good agreement with the hypothesis that the ionic dissociation increases in inverse proportion to the square root of the concentration. T. H. P.

Processes Operative in Solutions. XXV. Influence of Non-Electrolytes on Solubility. Nature of the Processes of Dissolution and Precipitation. HENRY E. ARMSTRONG and J. VARGAS EYRE (*Proc. Roy. Soc.*, 1913, *A*, **88**, 234—245).—Measurements have been made of the solubility of lead chloride, silver acetate, and potassium chloride in water at 25° in presence of various non-electrolytes. The results indicate that no distinction can be drawn between the influence of non-electrolytes on the solubility of slightly soluble salts and that exerted on the solubility of readily soluble salts. The action of non-electrolytes and electrolytes on solubility appears to be of the same kind; in both cases the solubility may be diminished or increased. The experimental data are discussed from the point of view of Armstrong's theory relating to the constitution of water and aqueous solutions.

H. M. D.

Estimation of the Solubility of Solids in Liquids. PETR KUSNETZOV (*Chem. Zentr.*, 1913, i, 765; from *Izvesta Don. Polytech. Inst. Novotscherkask*, 1912, **1**, ii, 399—410).—An improved form of Weimarn's apparatus (A., 1906, ii, 838) is described. By its means the solubility of manganese chloride, $MnCl_2,4H_2O$, was found to agree with the values of Dawson and William (A., 1900, ii, 210).

J. C. W.

The Formulation and Genetics of the Formation of Solid Solutions in the Dissociation of Oxides. SIEGFRIED BURGSTALLER (*Chem. Zentr.*, 1912, ii, 2005—2006; from *Abhandl. deut. naturwiss. med. Ver. Böhmen*, 1913, **3**, 147, 241).—The experiments of Wöhler (A., 1911, ii, 259), Milbauer (A., 1909, ii, 574, 889; 1910, ii, 294; 1911, ii, 113), and the author (this vol., ii, 57) lead to the assumption of solid solutions in the dissociation of oxides. According to the present views, a dissociating system, on the way towards equilibrium, passes from a system of three phases, gas, higher and lower oxide, by diffusion, into a system of gas and a solid phase composed of either a solution of the lower oxide or metal in the higher oxide or vice versa, or of two saturated solid solutions, according to whether the solids have the power of complete miscibility or form two series of mixed crystals. J. C. W.

Experimental Investigation into the Physical Conditions for the Crystallisation of Metals. EMILE GIURGEA (*Chem. Zentr.*, 1913, i, 677—678; from *Bul. Ṣoc., Ṣtiinṭe Bucureṣti*, 1912, **21**, 192—207).—When a porous pot containing a zinc rod is placed in a solution of copper sulphate, copper is deposited in the crystalline form on the outside of the cell. In the same way, lead may be deposited by zinc from lead acetate, and silver by copper from silver nitrate, in the form of crystals. The process has an application in the separation of one metal or another, as desired, from a mixture of different salts.

If a quantity of sand containing some metal powder or grains be moistened from below with copper sulphate solution, crystalline copper appears in the course of a few days, often with the accompaniment of copious gas evolution. This throws some light on the occurrence of metals with crystalline structure in the earth.

J. C. W.

Phenomena of Crystallisation in Ternary Systems. VI. Cases with a Gap of Miscibility in the Liquid and also in the Solid State. NICOLA PARRAVANO (*Gazzetta*, 1913, **43**, i, 220—237. Compare Parravano and Sirovich, A., 1912, ii, 836).—A continuation of this theoretical discussion. R. V. S.

Spontaneous Crystallisation and the Melting- and Freezing-point Curves of Two Substances which Form Mixed Crystals and the Freezing-point Curve of which Exhibits a Transition Point. Mixtures of *p*-Bromonitrobenzene and *p*-Chloronitrobenzene. (Miss) FLORENCE ISAAC (*Proc. Roy. Soc.*, 1913, *A*, **88**, 205—216).—The freezing points of mixtures of these substances are all situated between the freezing points of the pure components, but the freezing-point curve consists of two branches corresponding with the formation of two different kinds of mixed crystals. The transition temperature corresponding with the intersection of the two curves is 84·5°, the mixture at this point containing 27·5% by weight of *p*-bromonitrobenzene.

The melting-point curve also consists of two branches, which correspond with the two types of mixed crystals. At the transition temperature, two solid phases may exist in equilibrium with the liquid mixture containing 27·5% of *p*-bromonitrobenzene, the solid phases containing 30 and 60% of the bromo-compound respectively. The two branches of the melting-point curve are consequently intercepted by a horizontal line which extends from 30 to 60% on the composition axis. Variation of the composition of the liquid between these limits changes the relative proportion of the two solid phases without altering the composition of either.

The supersolubility or spontaneous crystallisation curve has also been determined, and it is found that for each mixture there is a definite temperature at which spontaneous crystallisation occurs. This curve lies almost completely between the freezing- and melting-point curves, and, like these, it shows a break in the neighbourhood of the transition point.

Microscopic observations relating to the pure substances and their mixtures are described. H. M. D.

The First Results of the Study of the Tables for Crystallo-chemical Analysis. EVGRAF S. FEDOROV (*Zeitsch. Kryst. Min.*, 1913, **52**, 97—136. Compare A., 1912, ii, 772; this vol., ii, 305—306).—Further examples are quoted from the author's tables. Not suitable for abstraction. L. J. S.

A New Theory of the Phenomenon of Allotropy. ANDREAS SMITS (*Zeitsch. physikal. Chem.*, 1913, **82**, 657—664).—Polemical against Tammann's "Theory of Polymorphism" (this vol., ii, 193) (compare also A., 1910, ii, 195, 400). It is shown that the phenomena of enantiotrophy and monotropy can be considered, logically and without undue hypotheses, from the same point of view. It is also held by the author that the theory of allotropy (*loc. cit.*) offers the first rational explanation of the fact that liquids, which are but little associated, separate monotropic forms, whilst liquids which are more strongly associated can separate enantiomorphic forms. The author states that the assumption of Tammann, that monotropic and enantiomorphic modifications are differently constituted, is contrary to experimental facts and theoretical conclusions. The author concludes by showing that the Tammann theory is based on a misunderstanding, and he shows that all the known facts are in agreement with his theory of allotropy. J. F. S.

New Method for the Preparation of Colloidal Solutions. A. PIERONI (*Gazzetta*, 1913, **43**, i, 197—200).—[With E. TONNIOLI.]—When a solution of silver nitrate in dry pyridine (3·5778 grams in 50 c.c.) is treated with half its volume of a solution of pyrogallol in dry pyridine (1·1424 grams in 50 c.c.), a slightly yellow solution is obtained, which on dilution with water yields colloidal silver solutions. These appear grey by reflected light, and from yellow to orange and finally violet by transmitted light, according to the concentration. Solutions containing 0·05 gram of silver per 100 c.c. of liquid are fairly stable, and by centrifugalisation the greater part of the colloid can be separated from them. When tannic acid is used instead of pyrogallol the result is similar, but the maximum stable concentration amounts to 0·064 gram per 100 c.c. of liquid. Analogous results are obtained with solutions of copper sulphate. In these cases the separation of the colloid is caused by hydrolytic action, but many substances can be prepared in colloidal solution without the intervention of water. In this way colloidal solutions of silver sulphide and of mercury sulphide are produced on mixing pyridine solutions of hydrogen sulphide with silver nitrate or mercuric acetate, whilst if silver acetate is taken a pyridine solution of colloidal silver is obtained. R. V. S.

Colloido-Chemical Studies of Protoplasm. WILLY RUHLAND (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 113—124).—A summary of

recent work on protoplasm and the protoplasmic membrane from the colloido-chemical standpoint. A bibliography is appended.
H. M. D.

A Fundamental Law of Dispersoidology. PETR P. VON WEIMARN (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 124—127).—According to the author's generalisation, every substance tends to change in that direction which is accompanied by a diminution in its free surface energy. It is pointed out that this is a special case of the law according to which any system tends to change in such a way that its free energy diminishes, and that, as such, it is of particular importance in the case of highly disperse systems in which the surface energy is probably the essential factor concerned. A number of changes, in which the law is supposed to operate, are cited. A case in point is presented by the transformation of a solid substance into an unstable, crystalline modification, or into a liquid, when the size of the particles is sufficiently reduced. The conversion of grey, metallic selenium into the red modification furnishes an example of this type of change, and the red and yellow modifications of mercuric oxide are supposed to be similarly related. The greater facility with which water is set free from hydrated crystalline substances when their degree of dispersity is sufficiently increased, is also supposed to be due to the operation of the surface energy law. Since ordinary aqueous solutions represent the limiting condition of a series of systems of continuously increasing dispersity, it seems probable that such solutions cannot contain chemically stable hydrates such as are formed in the crystalline condition. Ionisation of electrolytes is also supposed to be a consequence of the operation of the law, because the formation of an electrical double layer at the surface of the ion will result in the diminution of the free surface energy. H. M. D.

Regularities in the Hygroscopy of Chemical Compounds. C. REICHARD (*Pharm. Zentr.-h.*, 1913, **54**, 287—290).—After a review of the compounds which are hygroscopic in character, the author draws the conclusion that, at present, just as many reasons can be adduced against, as for, any scheme of classification. T. S. P.

Thermodynamic Functions of Mixtures with Reacting Components. PETRUS H. J. HOENEN (*Zeitsch. physikal. Chem.*, 1913, **82**, 695—742).—A theoretical mathematical paper in which the conditions for chemical equilibrium in the gaseous and liquid states are deduced from the second law of thermodynamics; the conditions arrived at are confirmed as far as the liquid state is concerned by other methods. The three thermodynamic functions η, ψ, and ζ are defined, and their properties are considered. It is shown that they embrace systems in which there is no chemical equilibrium. The theory is extended to systems of mixtures of any composition, and it is shown in this connexion that the functions for the equilibrium of such a system are identical with the usual thermodynamic functions. The method of determining equilibria in

heterogeneous systems, by means of the new functions, is indicated, and the conditions for the existence of an ideal liquid are put forward. J. F. S.

Chemical Equilibria in Gaseous Systems. UGO GRASSI (*Nuovo Cim.*, 1913, [vi], **5**, i, 85—96).—Two determinations of the constant of the reaction $COMe_2 + H_2 \rightleftarrows CHMe_2{\cdot}OH$ at 182° and 76 cm. pressure gave for the reaction constant the values $1{\cdot}48 \times 10^{-2}$ and $1{\cdot}45 \times 10^{-2}$, whilst a third experiment at 182° and 109 cm. pressure gave $1{\cdot}45 \times 10^{-2}$. In these cases acetone and hydrogen were taken; in an experiment starting with the alcohol and hydrogen at 182° and 76 cm. pressure, the value of the constant was $1{\cdot}40 \times 10^{-2}$. The experiments were conducted by leading purified electrolytic hydrogen through the organic substance contained in a weighed vessel kept in a thermostat. By altering the temperature of the thermostat, various mixtures of hydrogen with the vapour of the substance could be obtained. The mixture then passed through a copper tube, 180 cm. long, containing porous earth coated with reduced copper. The product of the reaction was retained in a condenser, and the excess of hydrogen escaping caught and measured. The apparatus was gas-tight, and its contents were kept at a known, constant pressure. The hydrogen was obtained by electrolysis in a cell comprising a nickel anode immersed in 25% sodium hydroxide in a porous pot; this pot in turn was placed in a second porous vessel containing a saturated solution of sodium sulphate, whilst outside this was an acid solution of copper sulphate containing a copper plate as anode. R. V. S.

Chemical Reactions in Strongly Compressed Gases. EMIL BRINER (*Zeitsch. Elektrochem.*, 1913, **19**, 301).—An answer to Trautz's criticism (*ibid.*, 150) of the paper of Briner and Wroczynski (A., 1911, ii, 705). J. F. S.

Chemical Equilibrium in the Action of Hydrogen Chloride Gas on Zinc Sulphate. CAMILLE MATIGNON (*Compt. rend.*, 1913, **156**, 788—791).—A study of the system zinc sulphate–hydrogen chloride, the reaction being:

$$(n+1)ZnSO_4 + 2HCl \rightleftarrows nZnSO_4,H_2SO_4 + ZnCl_2,$$

the dissociation pressure (387·6 mm.) being determined at 0°, has given the temperature of dissociation (12·3°) and the heat of formation (1·36 cals.) of the acid sulphate $ZnSO_4,H_2SO_4$. This crystalline acid sulphate completely decomposes zinc chloride at the ordinary temperature. W. G.

Landolt's Reaction as an Example for the Demonstration of the Foundations of Chemical Kinetics. ALFRED THIEL (*Chem. Zentr.*, 1912, ii, 2017—2018; from *Sitzungsber. Ges. Förd. Naturwiss. Marburg*, 1912, **2**, 11—35).—The influence of temperature, concentration, and catalysts on the time-reaction, oxidation of sulphurous acid by iodic acid, is described. An increase in the concentration of the iodic acid by five times makes the reaction

nineteen times as fast, and if the concentration of both reagents is increased by five, the speed becomes fifty-three times greater. The reaction becomes slower on cooling, but heating above 30° should be avoided. Acids accelerate the reaction, and the acceleration increases with the concentration of the catalyst. Hydriodic acid has the greatest effect, and the strong mineral acids arrange themselves in order of their strengths. Neutral iodides also accelerate the reaction.

In order to incorporate the catalytic influence of acids and iodides with the theory of reactions in steps, the following equations are given:

$$\text{I. } IO_3' + 5I' + 6H^{\cdot} \longrightarrow 3I_2 + 3H_2O.$$
$$\text{II. } SO_3'' + I_2 + 2OH' \longrightarrow SO_4'' + 2I' + H_2O.$$

According to this scheme, the sulphurous acid only reacts with free iodine, and the latter only appears when the former is completely oxidised. The second step is incomparably faster than the first. The scheme is supported by the fact that analogous reactions with oxidising agents which do not give up oxygen, for example, the oxidation of iodine ions by persulphate ions in presence of sulphurous acid, are uninfluenced by free acids.

The oxidation of sulphurous acid by ferric salts is considerably accelerated by iodides, but the influence of acids is not so simple as in Landolt's reaction, since the anion also plays a part. The addition of nitric acid sets back the ionisation of the sulphurous acid, and the reaction is slower.

The catalytic influence of iodides on some oxidations is seen in the reaction between ferric salts and stannous salts and in the reduction of arsenic acid by hydrogen sulphide, for the addition of potassium iodide causes remarkable acceleration in each case.

J. C. W.

The Nature of the Time Reaction between Carbonic Acid and Bases. ALFRED THIEL (*Ber.*, 1913, **46**, 867—874).—In a former paper (this vol., ii, 199) the author had no hesitation in subscribing to the explanation of the slow reaction between carbonic acid and bases (compare also this vol., ii, 198) as being due to the slow hydration of the carbonic acid, since ionic reactions, such as occurs in the neutralisation of an acid by a base, are practically instantaneous. If this explanation is correct, the time of neutralisation should be independent of the base when equivalent solutions are used. This is found to be the case when solutions of sodium hydroxide, either as such or containing equivalent quantities of strontium or barium chloride, and of barium hydroxide are used. In the case of a solution of sodium hydroxide and calcium chloride, the time of neutralisation is somewhat longer, the reason for this not being quite clear at present. With solutions of sodium hydroxide containing the equivalent amount of ammonium chloride, the times of neutralisation are considerably increased. The last fact cannot be due to a time reaction depending on the ammonia or ammonium hydroxide, since ammonia does not give a time reaction with any other acid. The author therefore draws the conclusion

that the rate of hydration of the carbon dioxide is not the deciding factor in the velocity of neutralisation, and puts forward the suggestion that the velocity depends on that of the reaction: $CO_2 + OH' \longrightarrow HCO_3'$. If it is further assumed that this reaction has a greater velocity than that of the hydration of the carbon dioxide, it would follow that if gradually increasing quantities of sodium hydroxide, or of sodium hydroxide and ammonium chloride, are added to successive and equal volumes of a solution of carbon dioxide, the rate of neutralisation should be practically instantaneous as long as the amount of alkali added does not exceed that necessary to neutralise the carbonic acid already present in solution, since this would be an ionic reaction. As soon as this quantity of alkali is exceeded, the reaction should begin to slow down, that is, there should be a sudden break in the curve showing the relation between volume of alkali used and time of neutralisation. Moreover, this break in the curve should occur at the same place, no matter whether sodium hydroxide or sodium hydroxide plus ammonium chloride be used. The experimental results agree with these deductions, and from them the author calculates that only about 2% of the total carbon dioxide present in solution exists as carbonic acid, from which it follows that the true dissociation constant of carbonic acid is approximately 2×10^{-5}, that is, carbonic acid is about as strong as acetic acid.

The behaviour of a solution of carbon dioxide is thus analogous to that of an aqueous solution of a γ-lactone, and by experiments with γ-valerolactone and sodium hydroxide the author shows that the boiling solution contains about 7% of corresponding acid; after this amount of acid has been neutralised instantaneously by the sodium hydroxide, the reaction between the lactone and the alkali is a time one.

Neutral salts retard, rather than accelerate, the reaction between an aqueous solution of carbon dioxide and bases. T. S. P.

Velocity of Formation of Precipitates. ALEXANDER FINDLAY (*Zeitsch. physikal. Chem.*, 1913, **82**, 743).—The author in reference to the paper of Jablczynski (this vol., ii, 203) calls attention to experiments of his own (A., 1900, ii, 716), in which he obtained results similar to those of Jablczynski. J. F. S.

Hydrolysis and Alcoholysis of Amides. SULO KILPI (*Chem. Zentr.*, 1913, i, 603; from *Suomalaisen Tiedeakatemian Toimituskia*, 1912, *A*, iii, No. 10, 3—30. Compare A., 1912, ii, 748).—The titrimetric method for estimating the ammonium salts produced by the hydrolysis of alkyloxy-amides has been extended to cases in which the reaction takes place in an aqueous-alcoholic medium. Experiments with acetamide and propionamide showed that the reactivity of the amide may be represented by the total velocity k of the hydrolysis and alcoholysis, and in solutions containing less than 50% of alcohol this value is found to coincide with the velocity of hydrolysis, k_1. J. C. W.

The Simultaneous Oxidation of Quinol and [Sodium] Sulphite by means of Atmospheric Oxygen. JOHANNES PINNOW (*Zeitsch. Elektrochem.*, 1913, **19**, 262—268. Compare A., 1912, i, 849; Schilov and Fedotov, A., 1912, i, 966).—The authors have investigated the atmospheric oxidation of quinol and sodium sulphite mixtures, together with the influence of cupric ions on the rate of oxidation of the mixture by atmospheric oxygen. It is shown that a small quantity of sodium quinoldisulphonate acts as an anti-catalyst, protecting the sulphide from oxidation by atmospheric oxygen, and that quinol disulphonate and glycerol act in the same way, and strengthen the action the one of the other. The presence of cupric ions increases the simultaneous oxidation, and at the same time changes the relation in which the two substances are oxidised in the sense that the quinol is used up more rapidly than the sulphite. The presence of the quinoldisulphonate retards the oxidation of the quinol sulphite mixture even in the presence of cupric ions, but it has no effect on the changed oxidation relationship brought about by the cupric ions. Not only the velocity of oxidation, but also the ratio in which the two substances are oxidised, are dependent on the hydroxyl ion concentration. The action of old quinol-sulphite mixture is due, not to the presence of sulphite in a complex, but rather to the presence of sodium quinolmonosulphonate. J. F. S.

The Transformation of Hydrazobenzene into Azobenzene and Aniline: A Reaction of the First Order. JULIUS STIEGLITZ and GEORGE O. CURME, jun. (*Ber.*, 1913, **46**, 911—920).—When an alcoholic solution of hydrazobenzene is heated in a sealed tnbe at 130°, transformation takes place according to the equation:

$$2Ph\cdot NH\cdot NH\cdot Ph \longrightarrow 2Ph\cdot NH_2 + Ph\cdot N_2\cdot Ph$$

(Biehringer and Busch, A., 1903, i, 296). If this is an intermolecular reaction, as supposed by Wieland (A., 1912, i, 902), it should be of the second order. According to the theory of Stieglitz (A., 1903, i, 235), however, it is probable that in such reactions phenylimide, $Ph\cdot N\colon$, is first formed according to the equation:

$$Ph\cdot N_2H_2\cdot Ph \longrightarrow Ph\cdot N\colon + Ph\cdot NH_2.$$

This reaction takes place slowly, and is followed by the instantaneous reaction: $2Ph\cdot N\colon \longrightarrow Ph\cdot N_2\cdot Ph$. The total reaction should therefore be one of the first order, as is found to be the case experimentally.

The velocity measurements were carried out at 140·3°, the alcoholic solutions being sealed up in glass tubes under a pressure of about 20 mm. The course of the reaction was followed by adding the contents of the tubes to excess of iodine solution, and titrating the excess with thiosulphate. The velocity constant has a mean value of 0·00156, and is independent of the dilution. When the reaction is about two-thirds complete there is a tendency for the constants to fall. T. S. P.

Surface Combustion. WILLIAM A. BONE (*Ber.*, 1913, **46**, 968—969).—A correction with respect to the author's reference to Nernst's theory of surface catalysis in his lecture to the German Chemical Society (this vol., ii, 204). T. S. P.

Catalytic Oxidation at High Temperatures. SERGIUS FOKIN (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 286—288).—Air saturated with methyl alcohol vapour was passed through heated tubes containing aluminium turnings, reduced nickel or cobalt, manganese, or platinum, copper, silver, or gold on asbestos, the temperature and the duration of heating being varied in different experiments. With cobalt, nickel, aluminium, manganese, and platinum the maximum yields of formaldehyde were small, but with copper, 43—47% was obtained, with silver 64—66%, with gold 71%, and with silver and copper together, 84%.

The results obtained with gold, copper, and silver indicate that the maximum catalytic activity must therefore be attributed to the metal with intermediate atomic weight, just as is the case with catalytic reduction, where palladium is the most effective metal.

It appears also that, in the catalytic oxidation of methyl alcohol, occluded oxygen plays a part similar to that of hydrogen occluded by the platinum metals in catalytic reduction; and that intermediate labile oxides are formed, so that atomic oxygen takes part in the change. T. H. P.

Catalytic Studies. III. Catalytic Deviation of a Reaction. EMIL ABEL and G. BAUM (*Monatsh.*, 1913, **34**, 425—515).—The principal results may be summarised as follows: In the presence of molybic acid the reaction between hydrogen peroxide and sodium thiosulphate in (acetic) acid solution gives not only tetrathionate, which is the ordinary product of reaction according to the equation (1) $H_2O_2 + 2S_2O_3'' + 2H^{\cdot} \longrightarrow S_4O_6'' + 2H_2O$ (Abel, A., 1908, ii, 26), but also sulphate, according to the reaction (2) $4H_2O_2 + S_2O_3'' \longrightarrow 2SO_4'' + 2H^{\cdot} + 3H_2O$. The relative proportions in which these two reactions take place, when molybdic acid is present only in traces of the order of 10^{-5} mol. of MoO_3 per litre, varies with the conditions of experiment between 1 : 1 and 1 : 8.

The tetrathionate reaction (1) is not influenced by the presence of molybdic acid; the sulphate reaction (2) does not proceed by way of tetrathionate, so that the course of the reaction is actually deviated by the catalytic action of the molybdic acid.

The velocity of the sulphate reaction (2) is independent of the concentration of the hydrogen peroxide, but proportional to the concentrations both of the thiosulphate and of the molybdic acid; hydrions have an accelerating effect, but the reaction also proceeds in their absence. The velocity equation is

$$-d[H_2O_2]/dt = 1500[MoO_3][Na_2S_2O_3]$$

at 25°, when $[H^{\cdot}]=0$, t is expressed in minutes, and the concentrations in gram-equivalents, that is, $(H_2O_2/2)$, $(Na_2S_2O_3)$, and (MoO_3) per litre.

The total velocity of reaction is expressed, at 25°, by the two simultaneous differential equations:

$$dx/dt = 1{\cdot}53[(H_2O_2) - x - y][(Na_2S_2O_3) - x - y/8]$$

and $dy/dt = 1500[MoO_3][(Na_2S_2O_3) - x - y/8]$, where the quantities in round brackets give the concentrations at the commencement of

the reaction, and x and y are the concentrations at the time t of the tetrathionate and sulphate respectively formed, and expressed in the appropriate units $\{x=(S_4O_6'')/2$ and $y=(SO_4'')/4\}$.

The mechanism of the reaction leading to the production of sulphate consists in the formation, with unmeasurable velocity, of a permolybdic acid, which then oxidises the thiosulphate to sulphate. This latter reaction takes place in stages, but the stage which regulates the velocity is bimolecular.

The analytical methods used in this investigation were based on previous work of Abel's (A., 1912, ii, 486).

The authors call attention to the analogy existing between this catalytic deviation of an inorganic reaction and the selective course pursued by ferment and enzyme reactions. T. S. P.

A Condenser in One Piece for the Kjeldahl Estimation of Nitrogen. ERNST PESCHECK (*Zeitsch. angew. Chem.*, 1913, **26**, 176).—The author describes a piece of apparatus in which the trap to check spray, the condenser, and the tube leading into the receiving flask form one piece of glass. The tube leading to the condenser is sloped downwards throughout its length towards the distilling flask, so that any alkali dissolved from the hot glass by the condensed steam is prevented from passing down the condenser.

D. F. T.

Inorganic Chemistry.

The Acidity of Water and of Hydrogen Peroxide and the Uniformity of Compounds. Preliminary Note. JOACHIM SPERBER (*Chem. Zentr.*, 1913, i, 502; from *Schweiz. Woch. Chem. Pharm.*, 1912, **50**, 741).—Since Merck's acid-free "perhydrol" liberates the acid from sodium silicate, borax, sodium metaphosphate, and potassium ferro- and ferri-cyanides, it is regarded as an acid, and since water sets free hydrogen peroxide from peroxides, it also is classed as an acid, "water acid." Oxides therefore become "aquates" and peroxides "hyperaquates," and hydrogen is assumed to be a metal. J. C. W.

Application of Hot Centrifugation to the Estimation of the Composition of Hydrates with Low Water Content. PETR KUSNETZOV (*Chem. Zentr.*, 1913, i, 765; from *Izvesta Don. Polytech. Inst. Novotscherkask*, 1912, **1**, ii, 389—398).—For the isolation of lower hydrates which are stable at higher temperatures it is recommended to surround the centrifuge with a mantle through which hot water may flow. By this means the *hydrates*, $MnBr_2,2H_2O$, $CaBr_2,2H_2O$, and $NiBr_2,2H_2O$, have been obtained. J. C. W.

Weight of a Normal Litre of Gaseous Chlorine and Silicon Tetrafluoride. Determination of the Atomic Weights of Chlorine and Fluorine. ADRIEN JAQUEROD and MELCON TOURPAIAN (*J. Chim. phys.*, 1913, **11**, 3—28. Compare A., 1911, ii, 189).—The authors' displacement method of measuring gaseous densities, which has the advantage that no mercury pump or greased stopcocks are necessary, has been applied to the corrosive gases chlorine and silicon tetrafluoride.

The weight of a normal litre of chlorine, liberated from hydrochloric acid by manganese dioxide or potassium permanganate, or by heating auric chloride, was found to be 3·214 grams. The values obtained by the displacement method and by means of a special form of Dumas bulb are in fair agreement.

Silicon tetrafluoride was prepared by the action of concentrated sulphuric acid on a mixture of calcium fluoride and quartz sand for the displacement experiments, and by heating barium silicofluoride for the Dumas bulb experiments, which gave a slightly higher value. The weight of a normal litre was found to be 4·693 grams.

When silicon tetrafluoride is passed over glass-wool at red heat to remove hydrogen fluoride according to Moissan's procedure, a subfluoride is apparently formed, since the normal litre weight increases to 4·820 grams.

In view of the uncertainty of the compressibility data used in the reduction of their experimental values, the authors' results cannot be employed at present to calculate the atomic weights of chlorine and fluorine. R. J. C.

Preparation of Perchloric Acid. FRANK C. MATHERS (*Chem. Zeit.*, 1913, **37**, 363).—One hundred grams of potassium perchlorate are distilled with 60 c.c. of concentrated sulphuric acid under a pressure of 10 cm.; meanwhile, water-vapour should be led into the distillation flask in such quantity that no crystals ($HClO_4,H_2O$) collect in the condenser. Only very little vapour is necessary, but an excess does not matter, as it only causes slight spirting and prolongs the distillation. The neck of the distilling flask should be lengthened in order to prevent the rubber stopper being attacked. Two hundred grams of potassium perchlorate are the most which can be used in a litre flask. The concentration of perchloric acid obtained varies from 88 to 98%.

If sodium perchlorate is used, 20 grams are treated with 30 c.c. of concentrated hydrochloric acid. The sodium chloride formed is insoluble, and the hydrochloric acid in the filtrate from it is driven off at 135°, whereby a 95% perchloric acid is obtained (compare Mathers, A., 1909, ii, 287). T. S. P.

The Finding of Iodine in the Waters of the Dead Sea, and the Detection of Iodine in Concentrated Solutions Rich in Magnesium Salts. HEINRICH FRESENIUS (*Verh. Ges. deut. Naturforsch. Aerzte.*, 1913, 118—120).—The water, which was

collected in the latter half of 1909, had D^{15} 1·1555 and the following composition, expressed in terms of grams per kilogram of water:

K.	Na.	Ca.	Mg.	Fe (ous).	Cl.	Br.	I.	SO_4.	HCO_3.
4·441	25·88	7·892	23·21	0·007586	124·1	2·124	0·000247	0·7319	0·06627

Magnesium chloride is present in by far the largest amount, then follow, in order, sodium chloride, calcium chloride, potassium chloride, sodium bromide. Sulphates are present to only a slight extent, hydrogen carbonates to a very slight extent, and iodides in traces. The presence of iodides has not previously been detected, probably owing to the fact that when the water is evaporated, hydrolysis of the magnesium iodide occurs, and the hydrogen iodide formed is driven off; this action takes place with the bromide also. In order to retain all the bromine and iodine in the solution during evaporation, it is necessary first to decompose all the magnesium compounds present with milk of lime.

The following method was used for the detection and estimation of bromine and iodine in such waters: 1090 grams of the water were diluted, heated to boiling, and then precipitated with an excess of milk of lime. After collecting the precipitate, the filtrate was evaporated, the residue powdered, and extracted four times with 96% alcohol. To the alcoholic extract were added a few drops of concentrated potassium hydroxide solution, the alcohol distilled off, and the residue heated until it glowed slightly, after which it was dissolved in water and the iodine liberated with nitrous acid. The iodine was extracted with carbon disulphide and estimated, after which the bromine (and some chlorine) was precipitated with silver nitrate and estimated by determining the loss in weight occurring on heating in a stream of chlorine. T. S. P.

Behaviour of Iodine towards Sulphur, Selenium, and Tellurium. Ernst Beckmann and Rudolf Hanslian (*Zeitsch. anorg. Chem.*, 1912, **80**, 221—234).—The molecular weight of selenium in iodine has been found (Olivari, A., 1909, ii, 39) to be Se_2 instead of Se_8, whilst there is no indication of the presence of a compound (Pellini and Pedrina, A., 1908, ii, 833). The low molecular weight is confirmed, and is almost the same at 184° as at 104°. Sulphur gives values falling little below S_8.

Anthraquinone (cryoscopic constant 148) gives S_8 and Se_8, whilst diphenyl (ebullioscopic constant 59·3) gives similar values. It is therefore a specific influence of the iodine, and not of high temperature, that causes the dissociation of the selenium molecule.

Tellurium reacts with iodine, and the cryoscopic and ebullioscopic results indicate a large proportion of single atoms. Red phosphorus in iodine gives P_1, a chemical reaction taking place. C. H. D.

Analysis and Preparation of Fuming Sulphuric Acid of Given Strength. Jose Prats Aymerich (*Anal. Fis. Quim.*, 1913, **11**, 118—136).—Formulæ and tables for use in the preparation of acid of a desired strength. G. D. L.

Selenium Oxybromide. R. TH. GLAUSER (*Zeitsch. anorg. Chem.*, 1913, **80**, 277—279).—When selenium oxychloride is distilled with sodium bromide, a dark red liquid is obtained, which solidifies, forming yellow needles, and has the composition $SeOBr_2$. The same compound has been obtained from selenium tetrabromide and selenium dioxide. The crystals melt between 30° and 40°, dissolve in sulphuric acid, and may be largely recovered after treatment with small quantities of water. C. H. D.

The Atomic Weight of Tellurium. PETR KUSNETZOV (*Chem. Zentr.*, 1913, i, 772—773; from *Izvesta Don. Polytech. Inst. Novotscherkask*, 1912, **1**, ii, 380—387).—When the differences between the atomic weights of the elements in the uneven periods are tabulated, they show a regular rise and fall within the separate groups. The negative difference between iodine and tellurium is in accordance with the other differences in the sixth group.
J. C. W.

The Oxidation of Nitrogen and Active Nitrogen. FRANZ RUSS (*Oesterr. Chem. Zeit.*, 1912, **15**, 316).—A discussion of the thermal and electrical principles which may account for the formation of active nitrogen (compare Ehrlich and Russ, A., 1912, ii, 41, and Strutt, A., 1911, ii, 482, 1056). F. M. G. M.

The Action of Ozone on Liquid Ammonia. WILHELM MANCHOT (*Ber.*, 1913, **46**, 1089—1093).—When ozone (10—11%) is passed into liquid ammonia at −70°, an orange-red colour is produced (compare A., 1908, ii, 101), which rapidly pales at −65° to −60°, when the current of ozone is stopped; above −60° the colour practically disappears. In the presence of a few drops of water, the colour is more stable, persisting to towards −50°. The addition of much water makes the colour less stable. If the ammonia is dissolved in anhydrous solvents like carbon tetrachloride, chloroform, etc., there is no formation of colour, neither do anhydrous trimethylamine and dimethylamine give rise to colour. However, the amines react similarly to ammonia (*loc. cit.*) in that, on acidifying after treatment with ozone, titanium sulphuric acid gives an intense reaction for hydrogen peroxide.

If liquid ammonia, contained in a U-tube, is cooled in liquid air, a layer of liquid ozone condensed over it, and then the U-tube allowed to warm up gradually to the temperature of the air, no explosion occurs. If the ammonia is replaced by di- or tri-methylamine, explosion occurs under the same conditions.

The colours obtained with ammonia are probably due to the presence of slight traces of water, which it is difficult to exclude. They are very similar to those obtained with ozone and potassium hydroxide (*loc. cit.*), and it would seem as if, in this respect, the ammonium hydroxide formed is more similar to the alkali hydroxides than di- and tri-methylammonium hydroxides. That the amines give no colour may, however, be due to the fact that at the low temperatures used the conditions are not favourable to the

formation of substituted ammonium hydroxides from the liquid amines. T. S. P.

Tension of Metal Ammine Compounds. WILHELM BILTZ (*Zeitsch. physikal. Chem.*, 1913, **82**, 688—694).—A criticism of Ephraim (this vol., ii, 129, 130). It is shown that Ephraim's statement, that the ammine salts split off ammonia one molecule at a time with the formation of all the possible ammines, is based on an error. The author demonstrates experimentally that only two ammines of nickel bromide exist, namely, the hexammine and the diammine. J. F. S.

The Allotropy of Phosphorus. WALTER A. WAHL (*Chem. Zentr.*, 1913, i, 774—776; from *Öfversigt Finska Vetens. Soc. Förhandl.*, 1911, **54**, *A*, 9, 22 pp. Compare Jolibois, A., 1909, ii, 726; 1910, ii, 846; Cohen and Olie, A., 1909, ii, 998).—When red phosphorus is heated in a strong capillary tube, it becomes almost black at 500°, and melts at 600° to a yellow, mobile liquid. On cooling, the colour deepens to a reddish-brown until solidification occurs. Purified, molten white phosphorus does not absorb light, but in the daylight the liquid becomes yellow, and then absorbs rays of $486\mu\mu$ and smaller. When a drop of white phosphorus, under water, is illuminated by a quartz mercury lamp, it immediately receives an elastic coating of red phosphorus.

From these experiments, the conclusion is drawn that molten red phosphorus is not identical with molten white phosphorus, but that at comparatively low temperatures it exists as a liquid of such high viscosity as to be vitreous. Between the two molten modifications, equilibria exist at different temperatures, but the pure molten white phosphorus is not an equilibrium mixture, since the speed of transformation into red phosphorus is extremely small below 250° in the dark. The fact that a labile substance can melt without passing into the stable form is seen in the case of benzophenone (this vol., i, 488). Above 250°, transformation proceeds apace, and the speed can be accelerated by catalysts. The colour of the red phosphorus which separates depends on the temperature, since devitrification occurs at high temperatures. Whether other modifications are produced in this process is uncertain, but Hittorf's crystallised phosphorus may be one of them. J. C. W.

Formation of Hydrogen Phosphide from Phosphorus and Potassium Hydroxide. E. LÖWENHARDT (*Zeitsch. physik-chem. Unterr.*, 1912, **25**, 368).—The author describes a simple method for preparing hydrogen phosphide without the presence of hydrogen or other inert gases.

The generating flask (a 125 c.c. Erlenmeyer) is filled to within 4 c.c. of the stopper with potassium hydroxide solution, and after adding the phosphorus gently warmed until the reaction starts; the delivery tube consists of a wide glass tube with a not too narrow outlet, and is dipped into warm water. As the action proceeds, the delivery tube becomes filled with white fumes of phosphoric oxide, and only a very slight or no explosion takes place. F. M. G. M.

The Action of Sulphur Trioxide on Silicon Tetrachloride. CHARLES R. SANGER and EMILE R. RIEGEL (*Zeitsch. anorg. Chem.*, 1913, **80**, 252—276. Compare A., 1912, ii, 752).—Molten sulphur trioxide and silicon tetrachloride mix at first without reacting, but the reaction, $2SiCl_4 + 2SO_3 = Si_2OCl_6 + S_2O_5Cl_2$, sets in very slowly in the cold, more rapidly at 50°, being then complete in six to ten hours. In presence of a large excess of sulphur trioxide, the further reaction occurs: $Si_2OCl_6 + 6SO_3 = 2SiO_2 + 3S_2O_5Cl_2$. Silicophosgen is not obtained. The two compounds, Si_2OCl_6 and $S_2O_5Cl_2$, appear to form a molecular compound on warming, which solidifies at −78°, whilst a simple mixture of the two substances solidifies at about −38°. In presence of water, chlorosulphonic acid, silica, and unaltered silicon tetrachloride are obtained, but not silicophosgen.
C. H. D.

The Alteration which takes place in Potassium Polysulphide. HENRI PECKER (*J. Pharm. Chim.*, 1913, [vii], **7**, 340—343).—Analysis of potassium polysulphide, which had been kept since 1906, showed that it had been completely decomposed; no trace of sulphide was present, the sulphur being either in the free state or as thiosulphate or sulphate. Only a trace of carbonate was present, so that the decomposition was not due to carbonation. The polysulphides disappear with the formation, chiefly, of thiosulphate, the oxidation being brought about by moist air.
T. S. P.

The Anhydrous Protosulphides of the Alkali Metals. ÉTIENNE RENGADE and N. COSTEANU (*Compt. rend.*, 1913, **156**, 791—793).—The authors have prepared the sulphides of sodium, potassium, rubidium, and cæsium in a pure anhydrous form by the direct action of sulphur vapour on an excess of the alkali metal at a temperature between 200° and 300°. On distilling off the excess of the metal, the sulphide crystallises out. They are all white, microcrystalline powders at the ordinary temperature, turning yellow as the temperature rises. The sulphides are less coloured and less soluble in their metals than the corresponding oxides, but the solubility increases with rise in atomic weight of the metal. They are more stable than the oxides, being unaltered by light, and are not decomposed by heat except at very high temperatures, when they give persulphides and vapours of the metals. W. G.

Acid Sulphates. VII. Acid Sulphates and Pyrosulphates of Sodium, Potassium, and Ammonium. JOHANNES D'ANS (*Zeitsch. anorg. Chem.*, 1913, **80**, 235—245).—The solubility isotherms of the three systems SO_3–H_2O–alkali sulphate have been determined at 25°, and the following solid phases have been observed in contact with the solution: $NaHSO_4$; $NaH_3(SO_4)_2,H_2O$; $Na_2SO_4,4{\cdot}5H_2SO_4$; $NaHS_2O_7$. $KHSO_4$; $KH_3(SO_4)_2,H_2O$; $KH_3(SO_4)_2$; KHS_2O_7. $(NH_4)_2HSO_4$; $(NH_4)H_3(SO_4)_2$; $(NH_4)HS_2O_7$. The data and triangular diagrams for the three ternary systems SO_3–H_2O–alkali oxide at 25° are also given. C. H. D.

A New Form of Potassium Dichromate. ALEXIS DUFFOUR (*Compt. rend.*, 1913, **156**, 1022—1024. Compare Wyrouboff, *Bull. Soc. franç. Min.*, 1890, **13**, 309).—By the addition of a considerable excess of aluminium sulphate to a solution of potassium chromate, the latter is partly converted into potassium dichromate, with the precipitation of aluminium hydroxide, and on concentration by heat the salt separates as a mixture of triclinic and monoclinic crystals. The latter are isomorphous with rubidium and ammonium dichromates, the optical figures for the crystals of the three substances being:

$K_2Cr_2O_7$	$a:b:c=1\cdot0167:1:1\cdot7716$;	$\beta=91°55'$
$Rb_2Cr_2O_7$	$a:b:c=1\cdot0202:1:1\cdot8081$;	$\beta=93°28\cdot5'$
$(NH_4)_2Cr_2O_7$........	$a:b:c=1\cdot0271:1:1\cdot7665$;	$\beta=93°42'$

Although they are the unstable form, the monoclinic crystals exhibit false equilibrium, and can be kept in contact with triclinic crystals in the cold without any appreciable change. They dissolve in a solution saturated with respect to triclinic crystals at 12·5°, whereas triclinic crystals are unaffected under the same conditions. On heating, the monoclinic crystals decrepitate, and then behave like the triclinic crystals (compare Le Bel, A., 1912, ii, 49).

W. G.

Sodium Silicate. Preparation and Recrystallisation of Sodium Silicate, $Na_2SiO_3,9H_2O$. ALBERT VESTERBERG (*Chem. Zentr.*, 1913, i, 777; from *Proc. VIII. Intern. Cong. Appl. Chem.*, 1912, **2**, 235—239).—When commercial water glass solution is mixed with sodium hydroxide and alcohol, the lower layer consists of a supersaturated solution of sodium silicate, and deposits orthorhombic crystals, $Na_2SiO_3,9H_2O$, m. p. 480° (approx.), in the course of time. The following solubilities are given; the figures refer to 100 c.c. of solution at 17·5°: In 0·5*N*-sodium hydroxide, 25·56 grams, D 1·129; in 0·5*N*-sodium chloride, 33·83 grams, D 1·150; in saturated brine containing 27·91 grams sodium chloride, 20·64 grams per 100 c.c. of solution. When kept over 50% potassium hydroxide or concentrated sulphuric acid, the crystals change into the *hydrate*, $Na_2SiO_3,3H_2O$, which soon absorbs water from sodium hydroxide of D 1·26 to form the *hydrate*, $Na_2SiO_3,6H_2O$. The ordinary hydrate speedily loses $6H_2O$ at 100°, but it must be strongly heated to remove the last traces of water. Anhydrous sodium silicate has m. p. 1007°.

J. C. W.

Hydrates of Calcium Oxide and their Molecular Compounds. II. Supersaturated Solutions of Hydrated Calcium Oxide. FEDOR FEDOROVITSCH SELIVANOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 252—257. Compare this vol., ii, 214).—Supersaturated solutions prepared by freezing solutions of hydrated calcium oxide under various conditions were found to contain 0·260—0·264 gram of CaO per 100 c.c. This concentration is in agreement with that obtained in Guthrie's first experiment, but the author was not able to prepare a solution containing 0·29 gram of CaO per 100 c.c., as indicated by Guthrie's second experiment (A., 1879, ii, 428). The

limiting concentration attained by freezing is hence 1 mol. CaO to 1184 mols. H_2O.

These supersaturated solutions are extremely sensitive to heat, and readily deposit crystals of the hydroxide, $Ca(OH)_2$, at the ordinary temperature. Even if the cold supersaturated solution is poured into a glass vessel at the ordinary temperature, the whole of the interior of the vessel becomes coated with the crystals. The formation of the crystals may, however, be retarded by keeping the solution vigorously agitated.

Presence of either of the crystalline hydrates, $2Ca(OH)_2,H_2O$ and $Ca(OH)_2$ (see following abstract), or of the amorphous hydroxide, $Ca(OH)_2$, produced no change in the supersaturated solutions, the excess of hydrate in the latter not being deposited. The crystalline hydrates are precipitated more readily on a glass vessel than on similar crystals.

The behaviour of the supersaturated solutions is similar to that shown by supersaturated gypsum solution (compare Potilitzin, A., 1894, ii, 39, 44), and it may be that supersaturated solutions of lime contain a stable hydrate, which is converted only with difficulty into hydrates of the compositions, $Ca(OH)_2$ and $2Ca(OH)_2,H_2O$. Such explanation is not, however, in good agreement with the properties of the known hydrates of lime, the sesquihydrate being highly unstable and easily transformable into the monohydrate; similar instability would be expected in hydrates containing more water than the sesquihydrate. T. H. P.

Hydrates of Calcium Oxide and their Molecular Compounds. III. Crystalline Hydrates. FEDOR F. SELIVANOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 257—266. Compare preceding abstract).—The monohydrate of calcium oxide, $Ca(OH)_2$, may be obtained in hexagonal plates or prisms by heating supersaturated solutions of lime or by evaporating aqueous lime solutions under diminished pressure at 28—30°. This crystalline hydrate is less soluble in water and in dilute sugar solutions than the amorphous hydrate having the same composition, the two hydrates hence being assumed to be in different physical conditions. Amorphous substances are regarded as highly supercooled liquids, the molecules of which would pass into solution less readily than those of crystalline substances. It may be, also, that the molecular weights of the two hydrates are different; indeed, the amorphous form cannot be transformed into the crystalline form either by heating with water or by prolonged storage over water.

The cryohydrate of lime gives, on solidification, absolutely transparent ice, but the solution formed when this ice melts deposits elongated hexagonal plates or small, rhombic plates of the sesquihydrate, $2Ca(OH)_2,H_2O$, which is very unstable, and decomposes when only slightly heated, giving the amorphous hydrate; it is less soluble in water than the monohydrate. T. H. P.

The System Lime, Phosphoric Oxide and Silica. OTTO NIELSEN (*Ferrum*, 1913, **10**, 97—112). — Tricalcium phosphate,

$Ca_3(PO_4)_2$, has m. p. 1550°, and is not reduced by carbon monoxide. Carbon begins to reduce it at 1400°. It is not decomposed by silica in a neutral atmosphere, but a chemical combination occurs at 1150°, and the product is completely reducible by carbon. This compound has the composition $3CaO,3SiO_2,P_2O_5$, a strong maximum being found on the freezing-point curve of mixtures of calcium phosphate and silicate at this composition and 1630°. Two compounds, $2SiO_2,P_2O_5$ and $3SiO_2,P_2O_5$, have also been found, the last of which melts without decomposition in the oxy-hydrogen flame.

C. H. D.

The Permeability of Glass for Water under the Influence of Electricity of High Tension. FRIEDRICH MEYER (*Ber.*, 1913, **46**, 1110—1115).—In contradistinction to Schützenberger (A., 1890, 1358), the author cannot find the least trace of permeability of glass towards water vapour under the influence of a high tension discharge.

T. S. P.

Ternary Alloys of Magnesium, Aluminium, and Zinc. GEORG EGER (*Intern. Zeitsch. Metallographie*, 1913, **4**, 29—128).—This complex system has been investigated fully by thermal and micrographic methods. The two compounds, Al_3Mg_4 and $MgZn_2$, form binary solid solutions, whilst the former also forms ternary solid solutions. There appears to be a ternary compound, $Al_3Mg_4,3MgZn_2$, which decomposes on melting, and forms solid solutions. The branch of the liquidus corresponding with this constituent ends in a eutectic point at 450°.

All the alloys are harder than aluminium, and most are brittle. All those containing free magnesium are attacked by moist air. The eutectic alloy, with Zn 93·5, Mg 3·3, Al 3·2, is tough, and takes a high polish.

C. H. D.

Influence of Thermal Treatment on the Solidification and Transformation of Cadmium-Tin Alloys. DOMENICO MAZZOTTO (*Intern. Zeitsch. Metallographie*, 1913, **4**, 13—28).—The heat-content of twelve alloys of tin and cadmium has been determined by comparing their rate of cooling with that of mercury under exactly the same conditions. The results obtained are in close agreement with those arrived at by Guertler (A., 1912, ii, 650) from theoretical considerations. The saturation point of the γ-tin solid solution at the eutectic temperature is 90% Sn, whilst the maximum heat effect of the transformation at 130° occurs at 94·5% Sn. It is therefore unlikely that any compound is formed, and the transformation consists in the separation of cadmium from solid solution in tin, a eutectoid alloy being formed. The solubility of cadmium in β-tin is about 1%. The heat of solution of cadmium in γ-tin is about 30 cal. per gram, or about twice the heat of fusion of cadmium. In such alloys, equilibrium is only obtained by quenching rapidly in order to obtain small crystals, and then annealing for long periods just below the eutectic or eutectoid point.

C. H. D.

Crystallisation in the Ternary System Cadmium-Potassium-Sodium Bromides. HERMANN BRAND (*Jahrb. Min.*, 1913, i, 9—27).—Binary mixtures of cadmium bromide (m. p. 567°) and potassium bromide (m. p. 735°), and of cadmium bromide and sodium bromide (m. p. 746°) in varying proportions were fused and the concentration-temperature diagrams given. With the former pair there are double salts, $CdBr_2,KCl$ (orthorhombic, m. p. 354°) and $CdBr_2,4KCl$ (rhombohedral, m. p. 324°), and also eutectics of these together and with the simple salts. The second pair yields no double salt, but only a eutectic mixture. For the ternary system of these salts five sections of the concentration-temperature diagram are given. L. J. S.

Compounds of Cerium Chloride with Ammonia. MAURICE BARRE (*Compt. rend.*, 1913, **156**, 1017—1019).—Cerium chloride readily forms additive compounds with ammonia. Gaseous ammonia, when introduced into a tube containing cerium chloride at −80°, combines with the chloride with the development of heat, and there is a considerable increase in the volume of the mass. By a study of the dissociation pressures, the author has established the existence of five different compounds of cerium chloride with ammonia, and has then prepared them in the form of white powders decomposable by water. The compounds are: $CeCl_3,20NH_3$; $CeCl_3,12NH_3$; $CeCl_3,8NH_3$; $CeCl_3,4NH_3$; and $CeCl_3,2NH_3$.
W. G.

A New Double Sulphate of Cerium and Silver. M. EMMANUEL POZZI-ESCOT (*Compt. rend.*, 1913, **156**, 1074).—By the addition of a warm concentrated solution of silver nitrate to a solution of ceric sulphate in warm concentrated sulphuric acid, deep orange-yellow, prismatic crystals are precipitated which, after filtering, washing, and drying in a current of air at 400°, give the bright orange-yellow *double sulphate*, $10Ce(SO_4)_2,6Ag_2SO_4$, which slowly takes up moisture, giving crystals containing $2H_2O$. The anhydrous double sulphate is only sparingly soluble in cold water, but readily soluble, with decomposition, in boiling water. W. G.

Solubility in Water of Lead as a Couple with and as an Alloy with Other Metals. ALBERTO SCALA (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 155—162).—The experiments deal with the solubility of lead in water in lead-zinc, lead-tin, lead-carbon, and lead-copper couples, and in various lead-tin alloys. The results indicate that the solubility is not increased in these circumstances.
R. V. S.

The Equilibrium between Lead Chloride and Ammonium Chloride in Aqueous Solution. (Mme.) N. DEMASSIEUX (*Compt. rend.*, 1913, **156**, 892—894).—A study of the equilibrium between lead chloride and ammonium chloride in aqueous solutions at three different temperatures, 17°, 50°, and 100°. Curves are given showing the ratio between the amounts of lead chloride and ammonium

chloride in solution, and the results show that the double chloride, $PbCl_2,2NH_4Cl$, can only exist in aqueous solution at temperatures above 70°. The two branches of the curves corresponding with $PbCl_2$ and $2PbCl_2,NH_4Cl$ are practically in the same direction, where they cut, at the eutectic. W. G.

Variations of the Physical and Chemical Properties of Red Lead. OLLIVER W. BROWN and A. R. NEES (*J. Ind. Eng. Chem.* 1912, **4**, 867—876).—A detailed account of numerous methods employed in the manufacture of red lead, with microphotographs showing the great variety of texture exhibited by commercial specimens, if it is prepared from different sources and by different processes. The following conclusions are drawn:

Red lead may be either crystalline or amorphous.

The crystalline modification has no definite form, but the crystals retain the form of the material from which the red lead was prepared.

The sp. gr. varies from 8·32 to 9·16. The variations in sp. gr. depend on (*a*) the temperature at which the oxide is formed, (*b*) the time of heating, (*c*) the chemical composition, and (*d*) the physical nature of the starting material.

The apparent density depends mainly on the fineness of the particles of the oxide, decreasing as the fineness increases up to a certain point. The temperature most suitable for the formation of red lead varies with the starting material used; about 425—430° is best for white lead, 450—470° for litharge and lead sponge; and about 450° for converting lead hydroxide and metallic lead into red lead, 450° being probably the temperature at which red lead can be most economically formed from any suitable starting material. Any red lead is rapidly and completely reduced to litharge at 525—530°.

Both "yellow" and "red" litharge are much more slowly roasted to red lead after being treated with water, showing that "air separation" of the litharge before roasting is to be preferred to "floating" in water. F. M. G. M.

Compound of Varying Composition in Alloys of Thallium and Bismuth. NIKOLAI S. KURNAKOV, SERGEI F. SHEMTSCHUSHNI, and V. TARARIN (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 300—329).—In the case of lead–thallium alloys, the distectic point is found to correspond with variable and irrational ratios between the atomic proportions of the constituent metals (compare Kurnakov and Puschin, A., 1907, ii, 262; Lewkonja, A., 1907, ii, 261; Kurnakov and Shemtschushni, A., 1909, ii, 855). A more marked example of this phenomenon is furnished by bismuth–thallium alloys, which give three irrational melting-point maxima, relating to three distinct phases.

The authors' investigation of these alloys extends to the thermal relations, the electrical conductivity and the temperature-coefficient of the resistance, the hardness and the pressure of efflux, and the micro-structure.

Analysis of the melting-point diagram indicates the existence of three phases of the compositions: (α) 0—5·8 atom. % Bi; (β) 5—33·0 atom. % Bi; and (γ) 55—64 atom. % Bi. Not one of the three corresponding maximal melting points accords with a rational atomic ratio between the constituent metals, and, as regards the first two maxima, there is general agreement between previous authors on this point. For the third maximum the authors find 62·8 atom. % Bi, which does not differ sufficiently from the 62·5% required for the compound Bi_5Tl_3 to admit of the existence of this compound being denied (compare Chikashigé, A., 1907, ii, 88), especially as the diagram for the γ-phase is exactly similar in form to many other curves with rational distectics.

With the curves of electrical conductivity and of temperature-coefficient of resistance at various temperatures, the maxima for the γ-phase correspond in all cases with one definite concentration, 64 atom. % Bi, giving irrational proportions of the two metals.

The existence of the compound Bi_5Tl_3 is therefore not in accord with the experimental data, and this conclusion is confirmed by the results of (1) measurements of the pressure of efflux and of the hardness, both by Brinell's ball test and by Ludwik's method (Baumaterialienkunde, 1907, **12**, 115, 147), and (2) micrographic examination.

The γ-phase cannot be regarded as conforming to any one of Roozeboom's four principal types of solid solutions. The microstructure and the melting-point diagram show that it possesses individual properties which in other systems correspond with typical chemical compounds, but the diagrams of the various properties exhibit no Dalton or singular point. It is therefore to be considered as belonging to the class of "indefinite compounds," the existence of which was defended by Berthollet in his dispute with Prout at the beginning of last century. T. H. P.

The Ternary System Copper–Cadmium–Antimony. ALADAR SCHLEICHER (*Intern. Zeitsch. Metallographie*, 1913, **3**, 102—126).—A considerable portion of this system has been investigated thermally and microscopically. The system $SbCu_2$–SbCd behaves as a pseudo-binary system, with a eutectic point. The great liability of antimony–cadmium alloys to undercooling, whereby the formation of the compound SbCd is suppressed, and only Sb_2Cd_3 is produced (Kurnakov and Konstantinov, A., 1908, ii, 391), is also observed in the ternary system. The compound $SbCu_2$ does not take up cadmium in solid solution, but SbCd takes up 8 atomic % of copper. The partial ternary system $SbCu_2$–SbCd–Sb has been examined in detail, and this portion of the space-model constructed.

The system Cu_2Cd_3–Sb_2Cd_3 is also pseudo-binary, and it is probable that $SbCu_2$ forms pseudo-binary systems with both Cu_2Cd_3 and Sb_2Cd_3. C. H. D.

The Changes in Dilute Mercuric Chloride Solutions. MARCEL DELEPINE (*Chem. Zentr.*, 1913, i, 49—50; from *Bull. Sci. Pharmacol.*, 1912, **19**, 610—622).—The changes which dilute solutions

of mercuric chloride suffer under the influence of light and air are chiefly due to the hydrogen carbonates in water, and the addition of sufficient acid to decompose these substances renders the solutions stable over a prolonged period. J. C. W.

The Action of Hydroxyl Ions on Colloidal Clay. PAUL ROHLAND (*Biochem. Zeitsch.*, 1913, **49**, 447—450).—Alkalis cause a colloidal chemical change in clays, which is associated with an increase of volume of the latter. The colloidal particles of the clay appear to undergo a coagulation, which is of reversible character. The concentration of the hydroxyl group does not undergo any change during the process, and different clays require different amounts of hydroxyl concentrations to produce the change. These amounts have not, up to the present, been correlated with the chemical composition of the clay. S. B. S.

The Formation of Temper-Carbon in Malleable Castings. A. SISSNER (*Ferrum*, 1912, **10**, 44—54).—The decomposition of cementite into iron and temper-carbon by heating below 1130° is accompanied by the development of heat. The inhibiting influence of 0·05% of sulphur on the decomposition is just neutralised by the presence of 0·28% of silicon. C. H. D.

The Theory of Undercooled Solid Solutions and the Nature of Austenite and Martensite. H. HANEMANN (*Intern. Zeitsch. Metallographie*, 1913, **3**, 127—141).—The effect of undercooling a solid metallic solution, followed by tempering, is not necessarily to produce the eutectoid, the formation of which was suppressed by undercooling. The nature of the crystallisation which takes place in an undercooled solid solution depends on the rate of formation of the different phases concerned, and on the extent of the undercooling with respect to each of these phases. A phase may even be produced which has no existence outside of the metastable region, and although this case may be exceptional, it is not legitimate to infer the structure of an undercooled alloy from a knowledge of the stable system alone.

Annealing either austenite or martensite at 650° causes resolution into ferrite and cementite, but the proportion of cementite produced is different in the two cases, and indicates that the needles of martensite contain only 0·3% of carbon. This suggests that martensite is a metastable solid solution of carbide in β-iron. Its transformation into the stable phases occurs at a much lower temperature than that of austenite. It is further shown that the change produced in austenite by cooling in liquid air consists in the crystallisation of a solid solution of low carbide content. This change takes place very rapidly. It is accompanied by expansion, and determinations with steel containing 1·79 and 1·50% of carbon respectively show that, whilst specimens quenched in different ways differ considerably in specific gravity, the differences become much less after quenching in liquid air. This gives a means of determining the proportion of austenite in a steel, and it is shown that

whilst autenite is only very slowly decomposed between 0° and 270°, it is rapidly decomposed above 270°. Martensite is very appreciably decomposed at 90°. All these observations are consistent with the supposition that martensite contains β-iron, and that its needle-like structure is due to its formation along the preexisting cleavage planes of austenite. C. H. D.

Formation of Iron Rust. GINO GALLO (*Gazzetta*, 1913, **43**, i, 288—298).—From experiments on the solution tension of iron immersed in various electrolytes, especially sulphates, the author finds that rusting takes place the more rapidly the greater the difference of potential existing between the iron and the solution with which it is in contact. He suggests that the presence of sulphides may be a cause (in consequence of electrolytic phenomena) of the rapid rusting of iron. This conclusion is supported by other facts, including the analysis of very resistive irons of ancient origin; these contain very little sulphur. R. V. S.

Formation of Rust under Protecting Paint [Coatings]. ERIK LIEBREICH and FRITZ SPITZER (*Zeitsch. Elektrochem.*, 1913, **19**, 295—301. Compare A., 1912, ii, 259).—The authors have investigated the causes of rust formation on iron coated with pigments containing zinc oxide, lead carbonate, red lead, and ferric oxide. It is shown that in every case the rusting is due to an electrochemical action represented generally by the element: iron | moisture | colour substance. The electromotive force of a series of cells compounded of iron and the colour materials was measured. The colour substances were compressed into rods, which were then used as electrodes; the following cells were measured at 20°: $ZnO \mid KCl,H_2SO_4 \mid Fe = +0{\cdot}150$ volt; $PbCO_3 \mid KCl,H_2SO_4 \mid Fe = +0{\cdot}095$ volt; $Pb_3O_4 \mid KCl,H_2SO_4 \mid Fe = +0{\cdot}075$ volt;

$$Fe_2O_3 \mid KCl,H_2SO_4 \mid Fe = +0{\cdot}090 \text{ volt.}$$

The iron used in these measurements was pure, whilst if technical iron was substituted the values were from 0·02 to 0·04 volt higher. The probable causes of the *E.M.F.* generated in each case are discussed, and hypotheses put forward as to the reason for the rusting. The hypotheses are tested by means of *E.M.F.* measurements of a series of elements made up of the various substances under discussion. J. F. S.

Uranyl Iodates. PAUL ARTMANN (*Zeitsch. anorg. Chem.*, 1913, **80**, 280).—The formula given for the potassium uranyl iodates (this vol., ii, 224) should be doubled, giving:

$$KIO_3{\cdot}IO_3{\cdot}UO_2{\cdot}IO_3{\cdot}IO_3{\cdot}UO_2{\cdot}IO_3{\cdot}KIO_3.$$ C. H. D.

Dehydration and Decomposition of the Hydrates of Uranyl Nitrate. Formation of a Monohydrate. ROBERT DE FORCRAND (*Compt. rend.*, 1913, **156**, 1044—1048).—Uranyl nitrate hexahydrate placed under a bell-jar with sulphuric acid in the cold at the ordinary pressure undergoes dehydration in two stages, as indicated by the rate of loss in weight. The first, lasting

for four to five days, corresponds with the formation of the trihydrate, and the second, complete at the end of one month, yields the dihydrate (compare Vasiliev, A., 1910, ii, 1072; Lebeau, A., **1911**, ii, 403). Reduction of the pressure only increases the rate of the two stages. Dehydration of the dihydrate in a current of carbon dioxide, containing no nitrous vapours, at 160° yields the anhydrous salt in four hours, there being, at the same time, a considerable amount of decomposition with formation of uranic acid. If the temperature is lowered to 125—130°, the velocity of reaction is diminished to one-twelfth, and there is a short first stage corresponding with the formation of a monohydrate. Dehydration under similar conditions at 98° yields an almost pure *monohydrate*, containing less than 1% of uranic acid. By the admixture of nitrous fumes with the carbon dioxide, the products of dehydration were in accord with those obtained by Marketos (compare A., 1912, ii, 848). W. G.

Synthesis of Borides in the Electric Vacuum Oven. EDGAR WEDEKIND (*Ber.* 1913, **46**, 1198—1207).—Electrodes were made by submitting mixtures of the finely powdered constituents (boron and metal) to hydraulic pressure. These electrodes were then fritted, and afterwards used in the vacuum electrical furnace of the author to form an arc between; the heat thus produced brought about the formation of boride, which either melted and dropped off the electrode into a proper receptacle, or was deposited as a powder, because of the disintegration of the electrode, on an asbestos sheath arranged round the electrodes.

Zirconium boride, Zr_3B_4, has a shining, silvery appearance; D = 4·98—5·00, the hardness being 7 (compare Tucker and Moody, T., 1902, **81**, 14). In the compact condition, it is only attacked by hydrofluoric acid, but when powdered, warm dilute hydrochloric acid dissolves it; nitric acid, dilute or strong, has very little action on the powder, and it is stable towards alkali hydroxides. It is attacked by fusion with sodium carbonate, and also by heating in a stream of chlorine.

[With C. HORST.]—*Vanadium boride*, VB, is metallic in appearance, and has a hardness greater than 7. It is stable towards alkalis and acids, with the exception of hydrofluoric and nitric acids, but is readily taken up by fused alkali hydroxide.

[With O. JOCHEM.]—*Uranium boride*, UB_2, has properties similar to those of vanadium boride. Molybdenum boride could not be obtained in a pure condition, although a product corresponding approximately with the formula Mo_2B was obtained. Tucker and Moody (*loc. cit.*) have described a boride having the composition Mo_3B_4, but a repetition of their experiments gave a product containing 88% Mo and 9·9% B. Mo_3B_4 requires Mo 86·7%, and since the product obtained is impure and nevertheless contains more than 86·7% Mo, it is improbable that it has the formula Mo_3B_4.

The results of Tucker and Moody with respect to tungsten boride, WB_2, were confirmed, but the density was 10·77 at 20°, as against 9·6 given by Tucker and Moody

Titanium boride was not fully investigated; it appears to be fusible with great difficulty. T. S. P.

Chinese Antimony Ores, Crude and Regulus. WALTER R. SCHOELLER (*J. Soc. Chem. Ind.*, 1913, **32**, 260—262).—The crude antimony investigated by the author is obtained at Chang-sha, in the province of Hu-nan, by liquation, 50 lb. of the ore being heated at a time in clay crucibles, and fired for two hours. The amount of sulphur found in the crude antimony does not correspond with that required by the formula Sb_2S_3, there being always a deficiency, which is probably caused by the presence of oxide of antimony (Sb_2O_5). Evidence for the presence of oxide is adduced by the fact that the liquated antimony sulphide is attacked by a solution of sodium hydrogen tartrate, whereby the antimony oxide is dissolved. Under like conditions stibnite is hardly attacked by the tartrate solution.

The antimony regulus obtained from the crude antimony apparently also contains oxide, but the amount of antimony dissolved by a solution of sodium hydrogen tartrate is much greater than the quantity of oxide assumed to be present.

In the sulphur assay of antimony sulphides the author finds that the most convenient method for eliminating the antimony is to precipitate it as antimonic acid by means of hot water. T. S. P.

The System Antimony–Selenium. NICOLA PARRAVANO (*Gazzetta*, 1913, **43**, i, 210—220. Compare Chrétien, A., 1906, ii, 550; Pélabon, A., 1911, ii, 575, 899).—The author has investigated this system both by thermal analysis and by microscopic examination of the alloys. From the curves it appears that there is only one antimony selenide, which does not mix in all proportions with antimony. The two liquid layers in equilibrium contain respectively, 11% and 35% of selenium. The two non-miscible liquids discussed by Pélabon and Chrétien exist, but the difference in their densities is so small that there is no complete separation of them during cooling. The discontinuity in the curve between 60% and 70% of selenium is to be explained, not by the existence of a compound Sb_2Se_7, but as being due to partial miscibility of the compound Sb_2Se_3 with selenium. Chrétien's selenides, SbSe, Sb_4Se_5, and Sb_3Se_4, do not appear on the curve, and are not indicated by the microscopical examination. The two alleged alloys, SbSe and Sb_4Se_5, are mixtures of antimony with Sb_2Se_3. R. V. S.

The System Bismuth–Selenium. NICOLA PARRAVANO (*Gazzetta*, 1913, **43**, i, 201—209).—The paper deals with the investigation of this system by the method of thermal analysis. The curve shows a discontinuity at about 73% of bismuth and 600—610°, and a maximum at about 63% of bismuth and 706°, which corresponds with the compound Bi_2Se_3. As the proportion of selenium is further increased, the curve falls, then remains horizontal, and finally descends to the m. p. of selenium. Various reasons are adduced, including arguments drawn from the microscopic appearance of the

alloys, to show that the thermal effect which mixtures containing 73—63% of bismuth show at 600—610° is due to the existence of the compound BiSe, which is of particular interest because in it bismuth is divalent. R. V. S.

Hydrolysis of Bismuth Nitrate. ALFREDO QUARTAROLI (*Gazzetta*, 1913, **43**, i, 97—124).—Measurements of the conductivity of solutions of bismuth nitrate containing excess of nitric acid show that strong hydrolysis occurs even in the presence of a considerable excess of nitric acid. The degree of hydrolysis under various conditions is shown by determinations of the concentration of the hydrogen ions, as indicated by the catalysis of methyl acetate. The dissociation constant of $Bi(NO_3)_3$ calculated from these results is 0·0230. The formation of the sparingly soluble product $Bi(OH)_2{\cdot}NO_3$ does not occur directly from $Bi(NO_3)_3$, but through an intermediate basic salt, probably $OH{\cdot}Bi(NO_3)_2$. The author shows by calculations from his experimental results how the phenomena observed on dilution of bismuth nitrate solutions may be explained, and the composition of the precipitates accounted for. R. V. S.

The Fluorides of the Noble Metals. OTTO RUFF (*Ber.*, 1913 **46**, 920—929).—If the fluorides of the noble metals could be obtained without having to use elementary fluorine, it would be possible to prepare fluorine by a chemical method by simply heating these fluorides.

[With WILLI JEROCH.]—Attempts to prepare the fluorides of gold and platinum by decomposing the chlorides of these metals with anhydrous hydrogen fluoride or by fusion with potassium hydrogen fluoride were, however, unsuccessful.

The compound of platinum and hydrofluosilicic acid ("kieselflussspatsäure Platinoxyd") described by Berzelius does not exist. Even solutions of platinum dioxide in concentrated hydrofluosilicic acid are strongly hydrolysed, and on evaporation give a residue of platinum dioxide hydrate, which contains only small quantities of platinum silicofluoride.

The addition of a solution of potassium fluoride to one of platinum tetrachloride gives an amorphous precipitate of *potassium pentachlorohydroplatinate*, $K_2(PtCl_5{\cdot}OH)$, there being no fluorine in the precipitate.

[With F. EISNER.]—The action of fluorine on various noble metals was studied by heating the metal, contained in a boat made of a mixture of cryolite and lithium fluoride, in a dry glass tube through which the gas was passed.

Ruthenium reacts with fluorine at 300°, but a sufficient quantity of the product formed could not be obtained for analysis. Iridium enters into reaction only at a dark red heat. Rhodium is scarcely attacked at a red heat. Palladium reacts slowly at a red heat. Osmium gives various fluorides (see next abstract). T. S. P.

Osmium Fluorides. OTTO RUFF and FRIEDRICH WILHELM TSCHIRCH (*Ber.*, 1913, **46**, 929—949).—Osmium forms three fluorides,

namely, the *tetrafluoride*, OsF_4, the *hexafluoride*, OsF_6, and the *octafluoride*, OsF_8. They are obtained by the action of fluorine on heated osmium, the composition of the product (mixture) formed depending on the temperature, on the strength of the current of fluorine, and on the activity of the osmium preparation used, which activity depends to a great extent on the temperature to which the osmium oxide, from which the osmium was obtained, was heated. It was necessary to use a platinum tube for the fluorination, since the osmium fluorides are very sensitive towards glass.

At about 250°, using an active osmium preparation, the product obtained consists of the octa- and hexa-fluorides only, the proportion of the latter increasing as the strength of the current of fluorine diminishes. At lower temperatures, or by using a less active osmium preparation, the product formed is mainly the tetrafluoride.

Osmium octafluoride is separated from the other fluorides by simply evacuating the platinum tube at ordinary temperature and collecting in a dry glass receiver cooled by liquid air. It is a lemon-yellow, crystalline substance, melting at 34·5° to a yellowish-red liquid. The vapour is colourless, has a peculiar odour, and vigorously attacks the mucous membrane of the nose and eyes. The vapour pressures determined at various temperatures by the method of Smith and Menzies (A., 1910, ii, 687) are: 38°, 552·5 mm.; 40·3°, 594·5 mm.; 42°, 634·2 mm.; 43·5°, 655·6 mm.; 47·3°, 757·5 mm. From these figures the latent heat of vaporisation per gram is calculated to be 20·6 cal., between the temperatures 38° and 54°, the molecular latent heat being 7101 cal. The mean vapour density, determined by V. Meyer's method, was 355 (theory = 343). When heated in a platinum tube, it begins to decompose at 225°, but the amount of decomposition is appreciable only above 400°. It attacks organic substances violently; the action on the various solid elements was also investigated. The aqueous solution is colourless, more or less hydrolysed, and has the odour of osmium tetroxide and not of the octafluoride. The solution in sodium hydroxide has the characteristic yellowish-red colour of the perosmic acids. With alkali fluorides it forms almost white salts (not investigated), which are decomposed by sodium hydroxide with evolution of ozonised oxygen.

The isolation of osmium octafluoride disposes of all doubts as to the octavalency of osmium.

Osmium hexafluoride is obtained, after removal of the octafluoride, by heating the platinum tube at 50° for one hour, the pressure being maintained at 20 mm. It sublimes, and condenses on the cool part of the tube as a light green, crystalline mass. It is difficult to obtain free from osmium dioxide and tetroxide, and a sufficient quantity of the pure compound could not be obtained to determine accurately its physical properties. The b. p. is about 202—205°; the m. p. is above 50° and below 120°, but could not be determined accurately, as the compound becomes black on heating in contact with glass. It is decomposed by water and sulphuric acid, giving the osmium oxides and hydrofluoric acid. It dissolves

in sodium hydroxide, giving a yellowish-red solution, similar to that of sodium osmichloride.

The way in which osmium tetrafluoride is obtained has been indicated; the small quantities of the higher fluorides formed at the same time are removed by heating the platinum tube at 100° and passing a current of nitrogen through it at low pressure. If the residue is extracted with water, the tetrafluoride dissolves. It was not isolated, but if hydrofluoric acid is added to the solution in the proportion of 2 mols. of acid to 1 mol. of fluoride, and the solution then neutralised with potassium hydroxide and evaporated, regular crystals are obtained, which are probably potassium osmifluoride. The fact that osmium is present in the aqueous extract in the quadrivalent condition was proved by titrating the sulphuric acid solution with permanganate, whereby oxidation takes place to the octavalent condition; the oxidised solution liberates iodine from potassium iodide, the osmium being reduced to the quadrivalent condition. The quantities of permanganate used and iodine liberated were equivalent. A similar method of analysis was also used with the hexafluoride.

The following vapour pressures of osmium tetroxide were determined: 95°, 275 mm.; 115°, 182 mm.; 125°, 640·4 mm.; 135°, 779 mm. The m. p. is 45°. T. S. P.

Mineralogical Chemistry.

A Danger to be Guarded Against in Making Mineral Separations by means of Heavy Solutions. WILLIAM F. HILLEBRAND (*Amer. J. Sci.*, 1913, [iv], **35**, 439—440).—It has long been known that certain minerals, especially metallic minerals, are acted on and decomposed by Sonstadt's (potassium-mercuric iodide) and Klein's (cadmium boro-tungstate) solutions. In the case now recorded there has been a replacement of calcium by an equivalent amount of potassium without the mineral being visibly affected. The material under examination was a canary-yellow, crystallised mineral, supposed to be carnotite, from Paradox Valley, Montrose Co., Colorado. It is a hydrous vanadate of calcium and uranium, differing from carnotite in containing calcium in place of potassium. This calcium carnotite is probably identical with the tuyamunite of Nenadkevich (*Bull. Acad. Sci. St. Pétersbourg*, 1912, 945). By the action of Sonstadt's solution it is converted into ordinary carnotite with a decrease in the optic axial angle of 25°. Anal. I is of the untreated mineral, and II of another portion which had been treated for eighteen hours with Sonstadt's solution:

	V_2O_5.	UO_3.	CaO.	K_2O.	CuO.*	SiO_2, P_2O_5, BaO, etc.	H_2O and loss.
I.	18·03	53·71	5·20	0·24	4·16	2·45	16·21
II.	18·31	55·37	1·72	6·08	4·22	1·91	12·39

* Copper, and possibly some of the calcium, present in an intermixed greenish vanadate.

L. J. S.

Helium in Glucinum Minerals. ARNALDO PIUTTI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 140—144).—The author has examined twenty-six minerals containing glucinum, but not radioactive, as to the amount of helium they contain. Taking into account the geological age of the various formations in which the specimens occurred, it is not possible to find any relationship between the amount of helium and the age of the mineral. Considerable variations also occur among the samples from the same locality. The beryls contain usually more helium than the chrysoberyls, whilst the phenacite (Gl_2SiO_4) examined did not contain any. This observation excludes the possibility of the derivation of helium from glucinum. R. V. S.

Natural Thio-salts. I. The Plagionite Group. FERRUCCIO ZAMBONINI (*Chem. Zentr.*, 1913, i, 739; from *Rev. Min. Crist. Italiana*, 1912, **41**, 1—38).—A new source of plagionite is the Veta purissima pit in Oruro, Bolivia, where it is accompanied by crystalline and massive pyrites and lead-coloured clusters of needles or fibrous aggregates of meneghinite (jamesonite ?), a transformation product of plagionite. The plagionite occurs in lead-coloured, lustrous lamellæ, and rarely in single crystals, with $a : b : c$ 1·1305 : 1 : 0·8422, $\beta = 107°15'$. It has D^{18} 5·54, and its analysis agrees with $5PbS,4Sb_2S_3$.

Spencer (*Min. Mag.*, 1909, **14**, 308) expected that plagionite, heteromorphite, and semseyite would form a morphotropic group in which the PbS content increased by two molecules from step to step. A consideration of the best analyses and of the crystallographic constants, densities, and molecular volumes of the extreme members, however, leads the author to consider the plagionite group as a series of solid solutions of the end salts $5PbS,4Sb_2S_3$, plagionite, and $5PbS,2Sb_2S_3$, samseyite. J. C. W.

Bauxite or Sporogelite? CORNELIUS DOELTER and EMIL DITTLER (*Centr. Min.*, 1913, 193—194. Compare A., 1912, ii, 357; 1913, ii, 230).—The name sporogelite has recently been proposed by Kišpatić (this vol., ii, 64, 69) for the colloidal aluminium hydroxide which forms an important constituent of bauxite. The present authors prefer, however, to retain the old name bauxite for this constituent, and to refer to the mixture of minerals (that is, a rock) as bauxitite. It is urged that a definite formula (Al_2O_3,H_2O) cannot be assigned to this mineral, but that, corresponding with the colloidal nature, the water may be variable in amount. L. J. S.

Delafossite, a Cuprous Metaferrite from Bisbee, Arizona. AUSTIN F. ROGERS [with analysis by G. S. BOHART] (*Amer. J. Sci.*, 1913, [iv], **35**, 290—294).—The mineral is found as indistinct, platy crystals on hæmatite, and occurs together with native copper and cuprite in clay at the lowest zone of oxidation in the Calumet and Arizona mine. The crystals are rhombohedral ($a : c = 1 : 1·94$), with a black colour and streak and a metallic lustre; $H = 5\frac{1}{2}$. They are non-magnetic and easily fusible, and readily soluble in hydrochloric acid and sulphuric acid, but not in nitric acid. A soft, black,

graphite-like form with lamellar structure also occurs. Analysis gave:

Cu.	Fe.	Insol. (hæmatite).	O.	Total.
41·32	37·26	0·21	[21·21]	100·00

The ratios are very closely Cu : Fe : O = 1 : 1 : 2, and the formula may be written as $Cu'Fe'''O_2$, cuprous metaferrite, or as $Cu''Fe''O_2$, cupric hypoferrite. Qualitative tests show the presence of both ferrous and ferric iron; but it is pointed out that mixed solutions of cupric sulphate and ferrous sulphate react in the same manner. The first formula is regarded as the more probable. The well-known metaferrites (magnetite, $FeFe_2O_4$, etc.) of the spinel group are cubic in crystallisation; but the artificial sodium metaferrite, $NaFeO_2$, is rhombohedral and perhaps isomorphous with delafossite. The mineral delafossite was first described from Siberia by Friedel in 1873, and it has hitherto been looked on as a doubtful species.

L. J. S.

Chromitite. MILORAD Z JOVITSCHITSCH (*Bull. Soc. franç. Min.*, 1912 [*i.e.* 1913], **35**, 511—516).—Analysis I. is of the black sand, to which the name chromitite was given (A., 1909, ii, 246), from the streams on the mountain Kopaonik, in Servia; and II—V of grains of the same mineral (II and III, dark brittle grains; IV and V, brighter and more resistant) isolated from a weathered mica-schist occurring in this district, and which is therefore to be regarded as the parent rock of the mineral chromitite:

	Fe_2O_3.	Al_2O_3.	Cr_2O_3.	CaO.	MgO.	Total.
I.	30·59	6·23	59·68	1·25	3·89	101·64
II.	26·39	6·47	61·58	1·45	3·34	99·23
III.	27·13	8·77	61·35	1·21	3·10	101·56
IV.	22·83	8·45	63 37	1·35	2·98	98·98
V.	25·14	10·77	61·36	1·04	3·65	101·96

These analyses give the formula $(Fe,Al)_2O_3,2Cr_2O_3$, differing from that previously given, namely, Fe_2O_3,Cr_2O_3.

Chrome iron-ores which contain some ferric oxide may be regarded as mixtures of chromite, $(Fe,Mg)(Cr,Fe,Al)_2O_4$, and chromitite, $Fe_2Cr_4O_9$.

L. J. S.

Titaniferous Magnetite in the Basalt of Eresztevény, Hungary. ALADÁR VENDL (*Foldt. Közl.*, 1912, **42**, 911—912, 958—959).—A mineral occurring in the basalt of Eresztevény in the Medves Mountains, as black grains with a bright metallic lustre on its conchoidal fracture, has been referred to as ilmenite ("Titaneisen"). It is, however, strongly magnetic, and the following analysis proves it to be really a titaniferous magnetite:

TiO_2.	SiO_2.	FeO.	Fe_2O_3.	Mn_3O_4.	Total.
6·58	trace	38·32	53·68	1·03	99·61

L. J. S.

Two Varieties of Calciovolborthite (?) from Utah. WILLIAM F. HILLEBRAND and HERBERT E. MERWIN (*Amer. J. Sci.*, 1913, [iv], **35**, 441—445).—The minerals described occur as thin encrustations,

together with other copper minerals, on sandstone near Richardson, in the canyon of Grand River, S.E. Utah. Both of them have the form of rosettes and patches of minute reticulated scales, and they are sometimes present together on the same hand-specimens. Only very limited amounts of impure material, consisting of scrapings from the sandstone surfaces, were available for examination. Analysis I (after deducting 30·6% of material insoluble in very dilute nitric acid) is of the yellowish-green variety. The optical characters of this indicate that the scales are probably monoclinic; and they show very strong inclined dispersion. Analysis II is of the greenish-yellow variety, which is probably pseudomorphous after the yellowish-green mineral. No definite formulæ can be deduced from these analyses. I is a hydrous vanadate of copper, and II a hydrous arseno-vanadate of copper and calcium:

	V_2O_5.	As_2O_5.	P_2O_5.	CuO.	CaO.	BaO.	MgO.	K_2O,Na_2O.	H_2O (105°).	H_2O (>105°).	CO_2.	SiO_2.	Fe_2O_3.	Total.
I.	30·6	1·1	0·3	48·4	3·9	2·7	0·3	0·7	1·8	6·4	2·4	0·6	0·8	100·0
II.*	16·0	17·2	0·8	37·1	15·3	2·3	0·5	0·2	1·0	4·3	0·9	0·7	0·5	100·0

* Also manganese, cobalt, and aluminium oxides, 3·2.

Very similar specimens have also been found in Paradox Valley, Montrose Co., Colorado. L. J. S.

Datolite from Mt. Mashuk, Caucasus. NIKOLAI A. ORLOV (*Jahrb. Min.*, 1913, i, Ref. 38; from *Ann. Géol. Min. Russie*, 1911, **13**, 146—148).—Previous analyses of the massive black mineral from this locality, near Pyatigorsk, did not lead to its correct identification, owing to the presence of impurities in considerable amount (A., 1912, ii, 950). Crystals of a black, grey (anal. I), and white (anal. II) colour have now been found, and the mineral is proved to be datolite. In the analyses, the boron was estimated by distilling the alkali fusion with methyl alcohol and hydrochloric or sulphuric acid, and collecting in a solution of potassium hydroxide:

	SiO_2.	TiO_2.	B_2O_3.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	Na_2O.	K_2O.	H_2O.	Total.
I.	42·41	0·14	16·18	1·45	1·78	32·90	0·12	0·21	0·01	5·02	100·22
II.	37·25	—	21·26	0·24	0·19	36·41	0·15	n.d.	n.d.	5·24	100·74

PETR N. TSCHIRVINSKI (*loc. cit.*, 166—174) also proves the identity of the massive mineral with datolite. It is rendered impure by intermixture with an amorphous, kaolin-like substance, hæmatite and other ores, clastic quartz and plagioclase, and calcite.

L. J. S.

Chemical Examination of Certain Minerals from Ceylon Gravel. GEORGII PROKOFEVITSCH TSCHERNIK (*Bull. Acad. Sci., St. Pétersbourg*, 1913, 163—174). — Gravel from the Sabaragamuwa Province of Ceylon contains small grey pebbles with a faint greenish tinge, the fresh fracture being almost pure black. The mineral gives a greenish-grey streak, and in thin sections permits a faint, bottle-green light to traverse it. It is not quite so hard as ortho-

clase, and D has 3·76. Thin sections are seen to be non-homogeneous. Chemical analysis gives the results:

SiO_2.	Ce_2O_3.	Y_2O_3.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	U_3O_8.
30·91	16·82	0·47	10·48	8·18	12·82	0·07	10·06	2·07	4·81

ThO_2.	H_2O.	K_2O.	Na_2O.	Quartz.	Total.
0·38	1·85	0·09	0·06	0·17	99·24

The mineral is hence an orthosilicate of the form:

$$(R^{II}O)_4(SiO_2)_3 + (R^{III}{}_2O_3)_2(SiO_2)_3 + H_2O,$$

and is similar, but not identical with, orthite, which has the composition, $6SiO_2,3R^{III}{}_2O_3,4R^{II}O,H_2O$. T. H. P.

Mineral Occurrences at Princeton, New Jersey. ALFRED C. HAWKINS (*Amer. J. Sci.*, 1913, [iv], **35**, 446—450).—Crystallographic descriptions are given of the various minerals (brookite, ilmenite, barite, chlorite, pyrite, calcite, and quartz), which are found as small, brilliant crystals in cavities and joints in brecciated sandstone in the neighbourhood of Princeton. Analysis, by A. H. Phillips, of the massive analcite, occurring together with crystals in the same district, gave:

SiO_2.	Al_2O_3.	Na_2O.	H_2O.	Total.
53·79	23·58	14·35	8·35	100·07

L. J. S.

Synthesis of Potassium-Nephelite. GEORGES FRIEDEL (*Bull. Soc. franç. Min.*, 1912 [*i.e.* 1913], **35**, 471—480). — Muscovite (anal. I) was heated with a solution of pure potassium hydroxide at 510—600° during forty to forty-five hours in a sealed steel tube with a copper lining. The copper was partly recrystallised, and the mica was transformed into a crystallised product identical with the mineral kaliophilite or potassium-nephelite. The crystals have the form of hexagonal prisms and plates, D 2·65; anal. II corresponds with the formula $K_2O,Al_2O_3,2SiO_2$, with some of the alumina replaced by ferric oxide. Previous experiments made under similar conditions (Friedel, A., 1890, 1080) showed that when more than 2% of sodium hydroxide is present in the solution the crystallised product contains a predominating amount of the sodium molecule, $Na_2O,Al_2O_3,2SiO_2$, as in natural nephelite. The potassium compound has been previously obtained by fusion with potassium fluoride, but in the form of orthorhombic crystals (Duboin, A., 1892, 1286).

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
I.	43·7	34·6	5·8	0·3	2·1	9·3	0·3	4·7	100·8
II.	37·2	26·2	6·6	—	—	29·6	0·9	—	100·5

It is therefore concluded that the potassium and sodium salts, $R_2O,Al_2O_3,2SiO_2$ may be isomorphous, and that the explanation of the composition of natural nephelite given by Morozewicz (A., 1908, ii, 201) does not apply. To account for the excess of silica the recent theories of Foote and Bradley, Schaller, and Bowen are more likely to be correct. L. J. S.

Viridine, a Variety of Andalusite. G. KLEMM (*Chem. Zentr.*, 1913, i, 54; from *Notiz. Ver. Erdk. Geol. Landesanst. Darmstadt*, 1911, 4—13).—A hornblende from the vicinity of Darmstadt contains a new mineral in the form of very small grains or columns of a green colour. It is rhombic, optically positive, and biaxial, has prismatic fracture, very strong pleochroism, double refraction (mean value 1·67), and considerable dispersion. Dittrich's analysis gave:

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	Mn_2O_3.	Total.
35·30	1·04	55·52	4·16	4·77	100·79

which agrees with the formula $(Al,Fe,Mn)_2(Si,Ti)O_5$. The mineral is therefore an andalusite in which aluminium has been partly replaced by iron and manganese, and is similar in constitution and pleochroism to Bäckström's manganandalusite (A., 1897, ii, 271).

J. C. W.

Minerals from the Ilmen Mtns., Urals. W. SILBERMÜNTZ (*Jahrb. Min.*, 1913, i, Ref. 51—52; from *Trav. Soc. Natur. St. Pétersbourg*, 1911, **35**, *Sect. Géol. et Min.*, 221—244).—Analysis I is of crystals of malacon; II, of brown ægirite; III, of green ægirite; and IV, of a felspar consisting of a perthitic intergrowth of albite and microcline, the former predominating. All these minerals were isolated from an ægirite-pegmatite from the Roshkov spring:

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.	CaO.	Na_2O.	K_2O.	Ign.	Total.	Sp. gr.
I.*	30·64	—	3·29	—	trace	—	—	—	—	0·95	100·55	4·54
II.	50·98	0·71	27·44	3·64	1·87	0·42	5·13	9·46	0·42	0·39	100·46	3·52
III.	54·14	1·12	28·21	1·76	1·68	0·19	2·80	8·93	1·10	0·88	100·81	3·39
IV.†	65·18	18·60	1·00	—	—	0·17	0·34	8·07	5·15	0·47	99·31	2·587

* Also ZrO_2, 65·67. † Also BaO, 0·33.

A mineral allied to parisite, from the Kyshtymsk district, and some other minerals are also described. L. J. S.

Alteration of Phyllite into a Compact Paragonite-rock. FR. KILLIG (*Centr. Min.*, 1913, 203—209).—The following series of analyses, all of material taken from the same hand-specimen, show the progressive replacement of potassium by sodium, the material having been transformed from a grey phyllite (anal. I) into white, shining scales of paragonite (anal. VI). The specimen came from the old emery mines on the Ochsenkopf, near Schwarzenberg, in Saxony. This alteration has taken place along crevices in the rocks of the district, and the paragonite is associated with corundum (emery) and metallic ores. The solutions which deposited the ores no doubt effected the change in composition of the rock. Several other analyses are given of the unaltered and partly altered phyllite:

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	Na_2O.	K_2O.	H_2O.	Total.
I.	43·09	0·57	38·03	0·83	1·90	0·82	1·11	1·12	7·31	5·33	100·11
II.	44·82	0·60	38·54	0·45	0·20	0·67	0·59	3·28	5·32	5·67	100·14
III.	44·54	0·62	38·79	0·41	0·15	0·79	0·36	4·87	3·88	5·58	99·99
IV.	43·86	0·57	37·21	0·73	1·90	0·78	0·28	5·23	3·62	5·80	99·98
V.	44·01	0·67	39·14	0·62	0·16	0·65	0·22	7·03	1·76	5·82	100·08
VI.	45·12	0·71	39·57	0·31	trace	0·49	0·11	7·94	0·47	5·50	100·22

L. J. S.

Composition of Volcanic Magmas. SANTIAGO PIÑA DE PUBIES (*Anal. Fis. Quim.*, 1913, **11**, 238—248).—Two volcanic magmas from the Canaries consisted respectively of phonolite and basalt.

G. D. L.

Meteoric Iron from Perryville, Missouri. GEORGE P. MERRILL (*Proc. U. S. Nat. Mus.*, 1912, **43**, 595—597).—This mass of iron, weighing about 17½ kilos., was found in 1906 near Perryville, in Perry Co., Missouri. The etched surface shows a very fine and somewhat irregular octahedral structure; and the metal is very hard and tough. Fragments showing no visible troilite have D 7·61. The bulk analysis is given under I, and that of the schreibersite under II:

	Fe.	Ni.	Co.	Cu.	Mn.	P.	S.	Si.	C.	Fe_2O_3.	Total.
I.	89·015	9·660	0·545	0·025	nil	0·365	0·002	0·003	0·015	0·370	100·00
I.	51·10	34·13	0·30	—	—	14·00	—	—	—	—	99·53

Rare metals (iridium, palladium, platinum, ruthenium) are present as traces, although in variable quantities. In one portion of 25 grams was found 0·004 gram of platinum, and in another of 100 grams only 0·002 gram. The precipitates of ammonium platinichloride were in all cases coloured faintly orange, indicating the presence of palladium. In another 100-gram portion of the iron were found 0·014 gram of ruthenium and 0·028 gram of iridium, while yet another 100-gram portion yielded 0·0009 gram of ruthenium and 0·0011 gram of iridium. This appears to be the first record of the presence of ruthenium in meteoric iron.

L. J. S.

Analytical Chemistry.

A New Form of Orsat Apparatus. LOUIS M. DENNIS (*J. Ind. Eng. Chem.*, 1912, **4**, 898—901).—The improvement in the Orsat apparatus (*Chem. News*, 1874, **29**, 176) for the rapid estimation of carbon dioxide consists essentially of a new form of spiral pipette, whilst comparative sketches demonstrate other devices for rendering absorption complete. F. M. G. M.

A New Dropping Apparatus for Use in Analyses. O. RUDOLPH (*Chem. Zeit.*, 1913, **37**, 427).—A bulb-shaped glass container terminates below in a nozzle bent nearly at right angles. To the neck are fused two horizontal glass rods bent down at the ends, by means of which it may be suspended from the wall of a beaker in which a mechanical stirring operation is taking place. The reagent need not be introduced into the apparatus until this has been placed in its proper position. L. DE K.

The Quantitative Handling of Small Quantities of Precipitates. JULIUS DONAU (*Monatsh.*, 1913, **34**, 553—560).—In the apparatus and methods previously described by the author (A., 1911, ii, 225) there is a possibility that small quantities of the

precipitate may remain behind on the walls of the tube used, and thus escape weighing. Modifications of the apparatus are now described, which do away with this error. Small platinum dishes are used to carry out the precipitation in, and these are tared, together with the filters used, both before and after the experiment, so that no part of the precipitate remains unweighed. Details are given of the results obtained in the gravimetric estimation of mercury, arsenic, iron, copper, chlorine, calcium, and sulphates.

It is claimed that there is a considerable saving of time when such micro-methods are used. For example, the estimation of chlorine in a soluble chloride is easily completed in half an hour.

T. S. P.

Application of New Results of the Investigation of Indicators to Quantitative Studies. ALFRED THIEL (*Chem. Zentr.*, 1913, i, 653; from *Sitzungsber. Ges. Beförd. ges. Naturwiss. Marburg*, 1912, **6**, 54 pp.).—An attempt has been made to combine Hantzsch's conception of the colour change of indicators as being due to chemical rearrangements with Ostwald's theory of indicators, which employs the ionic theory and the law of mass action. By means of calculations from measurements on the sensitiveness of methyl-orange and phenolphthalein culled from the literature, a further attempt has been made to provide a clear idea of the adaptability of these indicators to common titrations. A strong acid (hydrochloric) and a strong base (sodium hydroxide) were chosen as standard solutions, and strong, weak, and very weak acids and bases (hydrochloric acid, acetic acid, and phenol; sodium hydroxide, ammonia, and *p*-chloroaniline) were titrated, the dilution being such that all the involved substances could be considered as completely dissociated. "Titration curves" are given connecting the initial hydrogen-ion concentration with the volume of standard solution added, and the influence of dilution and temperature on these curves is shown.

J. C. W.

Ferrous Sulphate Monohydrate and its Use in Volumetric Analysis. DANIEL FLORENTIN (*Bull. Soc. chim.*, 1913, [iv], **13**, 362—366).—It is pointed out that the monohydrated form of ferrous sulphate is readily obtained pure, is not hygroscopic, and can be kept for long periods without change, so that it is suitable for use in standardising oxidising solutions such as potassium permanganate solution.

The salt is prepared by dissolving 400 grams of ferrous sulphate, previously crystallised several times, in 200 c.c. of 50% sulphuric acid by warming gently on a water-bath. Almost as soon as solution is complete, the monohydrate begins to separate as a colourless, crystalline powder, which is collected on a Büchner filter, washed with alcohol or dry acetone, then with dry ether, and is finally dried under reduced pressure over sulphuric acid. The yield is about 40 grams.

T. A. H.

New Colour Reactions of Hydrogen. ANGEL DEL CAMPO Y CERDÁN (*Anal. Fis. Quim.*, 1913, **11**, 172—178).—Polemical against

Giral (this vol., ii, 147). The author points out that numerous colour reactions of reduction, for example, with molybdic, arsenomolybdic, vanadic, phosphovanadic, tungstic, phosphotungstic, and silicotungstic acids, may be obtained by the aid of Zengelis' platinum method (A., 1910, ii, 1106). G. D. L.

Direct Estimation of Water in Food-stuffs and Other Articles by Distillation. FRANZ MICHEL (*Chem. Zeit.*, 1913, **37**, 353—355).—The principle of the method is as follows: The substance in which the water is to be estimated is distilled with an excess of an indifferent liquid, which is insoluble in and lighter than water, and has a higher boiling point than water. The indifferent liquid used is a mixture of pure toluene and commercially pure xylene in the proportion of 1 : 2 by volume. The vapours from the distilling flask are condensed in a condenser which opens on to a funnel connected with a graduated tube. When the distillation is complete, the contents of the tube are left until the water has settled to the bottom, when its volume may be read off, making appropriate corrections for the effect of the toluene-xylene mixture on the meniscus. It is an advantage to centrifugalise the contents of the tube in order to bring about rapid separation.

The method was tested on honey, butter, and milk, and found to give good results. T. S. P.

The Estimation of Chlorine in Urine and Blood. K. O. LARSSON (*Biochem. Zeitsch.*, 1913, **49**, 479—485).—Chlorine can be directly estimated in urine by direct titration with silver nitrate and the use of potassium chromate as an indicator, if the urine (diluted if necessary so that the sp. gr. is not higher than 1025) is first treated with pure animal charcoal (1 gram to 20 c.c. urine). By this means the purine substances which interfere with the titration are removed. A similar method is applicable to the estimation of chlorine in blood; 5—10 c.c. of blood are treated with 50 c.c. of hot 2% magnesium sulphate solution and a little acetic acid, and the mixture is heated on a water-bath until the coagulation of proteins is complete. After cooling, the liquid is diluted to 100 c.c., and then treated with about 3 grams of charcoal. The chlorine titration is then carried out with 50 c.c. of the filtrate. S. B. S.

Estimation of Chloride and Bromide in Organic Fluids. STEFAN VON BOGDÁNDY (*Zeitsch. physiol. Chem.*, 1913, **84**, 11—14).—An apparatus for the estimation of the halogens in blood and similar organic fluids is described and figured. The fluid is heated in a Jena flask in a stream of air with concentrated sulphuric acid, copper sulphate, and potassium sulphate. The escaping vapours pass through a spiral wash-bottle containing silver nitrate and provided with a glass stopper at the bottom, which can be removed. A second such wash-bottle is attached for safety. The precipitate of mixed silver haloids is collected in a filter tube, and after weighing a stream of chlorine is passed through to convert the whole into silver chloride. E. F. A.

Guareschi's New Bromine Reaction for the Detection of Bromate in Potassium Chlorate. FRANCESCO NICOLA (*Chem. Zentr.*, 1913, i, 461; from *Giorn. Farm. Chim.*, 1912, **61**, 538—541. Compare Guareschi, A., 1912, ii, 989; this vol., ii, 333).—The author describes the successful application of Guareschi's reaction to the detection of small traces of potassium bromate in potassium bromide. When testing for bromates in potassium chlorate, it is best to ignite the sample and to apply the test to the chloride.

J. C. W.

Detection of Iodine in Concentrated Solutions Rich in Magnesium Salts. HEINRICH FRESENIUS (*Verh. Ges. deut. Naturforsch. Aerzte*, 1913, 118—120).—See this vol., ii, 401.

Detection and Estimation of Fluorine in Wines. F. COMA Y ROCA (*Anal. Fis. Quim.*, 1912, **10**, 469—477).—The uncorrected error in Fresenius's method for the determination of fluorine amounts, according to the author, to +2·1, and after correction to −4·4%. More accurate results were obtained by using all-glass apparatus and boiled sulphuric acid. In application to the estimation in wines the errors, both by gravimetric and volumetric methods, are considerable (in the latter about 8%). Qualitatively, 1 mg. of sodium fluoride in 300 c.c. of wine may be detected.

G. D. L.

Estimation of Oxygen in Iron and Steel by Reduction in an Electric Vacuum Furnace. W. H. WALKER and WALTER A. PATRICK (*J. Ind. Eng. Chem.*, 1912, **4**, 799—801. Compare A., 1912, ii, 995).—A sketch of the apparatus employed with a preliminary account of the procedure whereby the oxygen in iron and steel can be estimated by conversion of the metallic oxides into carbides by heating with an excess of carbon in an electric furnace, with the quantitative formation of carbon monoxide.

The metal (20—25 grams) is mixed with powdered graphite in a graphite crucible, placed in an electric vacuum furnace of the Arsen type, the pressure reduced to 0·01 mm., and the crucible heated at 500—600° during fifteen minutes, allowed to cool, and any adhering oxygen washed out with perfectly dry nitrogen, this process being repeated until the absence of oxygen is ensured.

A current of about 300 amperes is passed; the metal fuses, when violent ebullition often occurs, which must be moderated by opening the circuit; after about twenty minutes' heating, the furnace is cooled, dry nitrogen admitted, and the gas removed in convenient volumes into an apparatus, where the carbon monoxide is estimated by passing it over iodine pentoxide at 130° (Kinnicut and Sanford, A., 1900, ii, 314). By heating at 130° (instead of 150°) oxidation to carbon dioxide is complete, and the decomposition of the iodine pentoxide is reduced to a minimum, which was a difficulty previously experienced in this method (*loc. cit.*).

F. M. G. M.

Sulphur and its Variations in the Biological Treatment of Sewage Water. LUCIEN CAVEL (*Compt. rend.*, 1913, **156**, 1099—1101).—A determination of the amount of sulphur combined in the form of organic matter in the sewage effluent gives a measure of its purification. The examination is conducted as follows: The effluent is allowed to remain for three hours, when the heavier particles settle, and then to it is added zinc chloride, followed by sodium carbonate in suitable quantity. The precipitate, which carries down with it all suspended matter, is collected, dried, and extracted with carbon disulphide, thus giving the free sulphur. The residue is washed with benzene and decomposed by hydrochloric acid, the hydrogen sulphide liberated being weighed as silver sulphide, which gives the sulphur in the form of sulphide. To the residue, sodium hydroxide is added, and the whole is heated at 80° for six hours, after which chlorine is passed through the liquid. The combined sulphur, now converted into sulphate, is weighed as barium sulphate, thus giving a measure of the purity of the effluent.

W. G.

Assay of Hyposulphites. EMIL BOSSHARD and W. GROB (*Chem. Zeit.*, 1913, **37**, 423—426, 437—439).—*By Means of Ammoniacal Copper Sulphate.*—About 0·1 gram of the sample is placed in a corner of the bottom of a flask, and while slightly inclining the flask an ammoniacal solution of copper sulphate (4·469 grams of crystallised copper sulphate per litre) is added from a burette in quantity sufficient to complete the reaction within a few c.c. The liquid is now allowed to come in contact with the solid, and after shaking 2 drops of indigo-carmin (1 gram per litre) are added. The titration is continued until the yellow colour changes to a clear blue. Two mols. of copper = 1 mol. of sodium hyposulphite. All the operations are carried out in the author's special apparatus in a current of oxygen-free nitrogen or hydrogen. The usual impurities present in commercial samples do not appreciably affect the result.

By Acidimetry.—The sample is oxidised by atmospheric oxygen, and the acidity is then estimated as usual, preferably with standard barium hydroxide; allowance should be made for any pre-existing acidity, which must be determined in a current of hydrogen.

By Means of Mercuric Chloride.—To 300 c.c. of a saturated solution of mercuric chloride is added 1 gram of sodium hydrogen carbonate. A weighed quantity of the sample is then added, and the precipitate consisting of mercury and mercurous chloride is collected on an asbestos Gooch crucible, and washed first with dilute hydrochloric acid and then with water. The whole is then placed in a beaker and treated with 5 grams of potassium iodide and 5 c.c. of water, followed by 5 c.c. of $N/10$-iodine. After ten minutes with frequent stirring, the excess of iodine is titrated with thiosulphate.

If the number of c.c. of iodine absorbed is represented by x, and the weight of the sample taken by a, the percentage will be according to the formula $x = 174 \cdot 14t/200a = 0 \cdot 8707t/a$.

L. DE K.

The Quantitative Estimation of Sulphuric, Nitric, and Nitrous Acids in Mixed and Waste Acids. GEORGE FINCH (*Zeitsch. ges. Schiess-Sprengstoffwesen*, 1912, **7**, 337—339. Compare Telle, A., 1906, ii, 578).—A modification of the method previously described (A., 1912, ii, 991), in which, after titrating the total acidity with barium hydroxide and separating the barium sulphate, the neutral mixture of barium nitrate–nitrite is titrated with a neutral solution of $N/5$-potassium chromate:

$$H_2SO_4 + 2HNO_3 + 2OHSO_2{\cdot}ONO + 5Ba(OH)_2 = 3BaSO_4 + Ba(NO_3)_2 + Ba(NO_2)_2 + 8H_2O.$$

$$Ba(NO_2)_2 + Ba(NO_3)_2 + 2K_2CrO_4 = 2BaCrO_4 + 2KNO_2 + 2KNO_3.$$

Experimental results demonstrating the accuracy of the method are tabulated in the original. F. M. G. M.

Apparatus for Fumeless Kjeldahl Nitrogen Digestion. ALBERT P. SY (*J. Ind. Eng. Chem.*, 1912, **4**, 680).—A group of four of the ordinary long-necked Kjeldahl flasks supported in a line on iron rings are closed by loosely fitting bulb-tubes consisting of a tube with two large bulbs with an elbow bend; each of these are connected by rubber tubing with a suction pump, having four branches. These bulbs act as air condensers for the acid fumes, and prevent the liquid in the flasks from evaporating as rapidly as if the fumes are allowed to escape. F. M. G. M.

Estimation of Nitrites in Potable Water. MAURICE LOMBARD (*Bull. Soc. chim.*, 1913, [iv], **13**, 304—309).—The estimation of nitrites in potable water by means of *m*-phenylenediamine or of sulphanilic acid and α-naphthylamine is rendered tedious by the somewhat fugitive nature of the colorations obtained and the necessity of preparing a new scale of tints for each series of tests. The author proposes the use of the following reagent, the tints obtained with which very closely resemble those given by suitably diluted solutions of potassium dichromate which form the scale of comparison: sulphanilic acid (1 gram) is dissolved in a saturated solution of ammonium chloride (100 c.c.); phenol (1·5 gram) is then added, followed by approximately $2N$-hydrochloric acid (100 c.c.). In practice, the reagent (1 c.c.) is added to the water (50 c.c.), which, after the lapse of at least fifteen minutes, is rendered alkaline by addition of an excess of ammonia. The coloration obtained is then compared with those of previously standardised solutions of potassium dichromate. By this method, 0·1 mg. of sodium nitrite per litre could be estimated, which is regarded by the author as the limit of useful accuracy. If, however, traces of nitrites are to be detected, he prefers to use sulphanilic acid and α-naphthylamine. If the reagent is to be preserved during considerable periods, replacement of the acid by water is recommended. Immediately prior to use, it is then acidified with an equal volume of hydrochloric acid. H. W.

Estimation of Phosphorus in Iron and Steel. PAUL ARTMANN [and J. PREISINGER] (*Zeitsch. angew. Chem.*, 1913, **26**, 203—208).—A review and criticism by the first author of the various methods used for the above estimation. A new method has been worked out by the authors, which is, briefly, as follows.

The sample (about 1 gram for pig-iron, 2—4 grams for steels) is dissolved in nitric acid; any graphite is removed by filtration. The phosphorus is fully oxidised by means of permanganate, and then precipitated with molybdate solution.

The filter and precipitate after being carefully washed are replaced in the flask, 10 c.c. of standardised hypobromite solution are added, and then 7 grams of sodium hydrogen phosphate. After diluting to 80 c.c., 0·5 gram of potassium iodide is added, and then 15 c.c. of $4N$-sulphuric acid. The iodine liberated is then titrated with $N/20$-thiosulphate solution.

The difference between the blank check and the result obtained represents the ammonia in the yellow precipitate, and hence the phosphorus.

The hypobromite is conveniently prepared by pouring 1400 c.c. of saturated bromine water into 500 c.c. of $4N$-sodium hydroxide.

L. DE K.

Estimation of Phosphorus in Commercial Acetylene. LOUIS M. DENNIS and W. J. O'BRIEN (*J. Ind. Eng. Chem.*, 1912, **4**, 834—836).—A modification of the method described by Lunge and Cedercreutz (A., 1898, ii, 54) for estimating the gaseous compounds of phosphorus present in acetylene which has been prepared from calcium carbide. The acetylene is generated in a Kipps apparatus with a saturated solution of sodium chloride, and obtained without any appreciable rise of temperature; a Friedrich's gas-washing bottle is considered a more efficient absorption apparatus than the ten bulb-tubes employed by Lunge (*loc. cit.*), and the hydrogen phosphide after absorption by sodium hypochlorite is estimated as magnesium pyrophosphate.

F. M. G. M.

The Assay of Hypophosphorous Acid. HORACE NORTH (*Amer. J. Pharm.*, 1913, **85**, 147—148).—Samples containing excessive amounts of foreign acids (sulphuric, oxalic, tartaric, phosphoric, phosphorous) are readily recognised by their excessive barium number, which the author states should not exceed 5.

The details are as follows: Weigh 1 c.c. of the sample in a carefully tared, stoppered Erlenmeyer flask. Add 20 c.c. of water free from carbon dioxide, and titrate with $N/5$-barium hydroxide with phenolphthalein as indicator. When the precipitate has subsided it is collected, well washed, dried, and ignited. The corrected weight in milligrams divided by the weight in grams of absolute acid as indicated by the titration is called by the author the "barium number."

L. DE K.

[Estimation of] Arsenic in Zinc. SIDNEY CROOK (*Chem. News*, 1913, **107**, 149).—The granulated sample is sieved through a

24-hole sieve. The Marsh's apparatus should be fitted with a half-inch glass tube containing a roll of lead acetate paper, and about 6 inches of fused calcium chloride, and also with a mirror tube. The hole of the inlet tap of the apparatus should be about one-eighth of an inch in diameter, so as to admit the granulated sample. The apparatus is charged in the usual way with arsenic-free zinc (20 grams) and sulphuric acid (30 c.c. of recently boiled and cooled dilute acid), and when free from air and the action almost ceased, 20 c.c. of recently boiled distilled water and 0·5 gram of the sample are put in the thistle funnel. The hydrogen flame is then put out, a small Bunsen burner placed beneath the mirror tube, and when the tube is nearly red-hot its outlet is stopped up with the thumb in order to cause a gentle back pressure. On opening the tap of the thistle funnel, the whole of the sample of zinc can be caused to fall into the apparatus, without air entering. The tap is then closed, the water withdrawn from the funnel and replaced by 30 c.c. of dilute sulphuric acid, sufficient of which is then run into the flask to keep the hydrogen flame not more than $\frac{1}{4}$ inch in height. The reaction should be continued for half-an-hour, after which the mirror of arsenic obtained is compared with a set of standard mirrors. The sample should be so arranged as to give not more than 0·1 mg. of arsenic. T. S. P.

Rapid Estimation of Boric Acid in Milk and Cream. FREDERIC W. RICHARDSON and WILLIAM KEIGHLY WALTON (*Analyst*, 1913, **38**, 140—141).—To 50 c.c. of milk or 10 grams of cream diluted with 40 c.c. of water are added 5 c.c. of 5% copper sulphate solution, and after heating to boiling the casein-copper precipitate, which carries down the fat, is collected and washed several times with boiling water. The filtrate is then used for the estimation of the boric acid as follows:

Two c.c. of a 1% alcoholic solution of phenolphthalein are added, and then $N/10$-sodium hydroxide until a certain blue shade appears. About one-third of the volume of glycerol is now added, and the titration is repeated until the blue shade again appears. Under these conditions 1 c.c. of $N/10$-alkali = 0·0071 gram of crystallised boric acid. L. DE K.

Combined Estimation of Boric Acid and Fat in Cream. FREDERIC W. RICHARDSON (*Analyst*, 1913, **38**, 141—142).—The fat in cream (see preceding abstract) may be readily recovered from the "casein precipitate" by drying the filter and contents in the mouth of a short-necked counterpoised flask in a water-oven. The filter is then lifted out, and placed in a Soxhlet tube, which is attached to the flask, into which most of the fat has already collected. Light petroleum (of low b. p.) is then used for the extraction as usual. L. DE K.

Estimation of Total Carbon in Steel and Ferro-Alloys by Combustion in Oxygen under Pressure. W. G. VON JOHN (*Chem. Zeit.*, 1913, **37**, 426—427).—The sample is placed in a

crucible made of asbestos, or preferably of magnesia, and burnt at 1 atmospheric pressure in an atmosphere of purified oxygen in the special apparatus devised by the author. The combustion is started by electrical contrivance.

The products of combustion find their way into a solution of sodium hydroxide (4 grams per litre), the excess of which is then titrated with standard sulphuric acid (4·083 grams per litre), using phenolphthalein as indicator; 1 c.c. of acid=1 mg. of carbon. When dealing with alloys, the combustion should be assisted by means of lead peroxide. L. DE K.

The Estimation of Carbon by Combustion in Moist Oxygen. SIEGFRIED HILPERT (*Ber.*, 1913, **46**, 949—952).—In the estimation of carbon in steels, by combustion in dry oxygen, it is necessary to heat to a temperature of about 1200°. If moist oxygen is used, a temperature of 950° is sufficient in the case of ordinary, chrome, and chrome-tungsten steels; for 80% ferromanganese, containing 6·16% C, a temperature of 1050° is necessary.

In the case of certain organic compounds, such as aluminium phenyl, hippuric acid, glycine, alanine, carbazole, phenyl dihydrogen phosphate, etc., which are difficult to burn satisfactorily, accurate results are obtained with moist oxygen at lower temperatures than ordinarily used.

When using moist oxygen, a 5 cm. long, straight, phosphoric oxide tube should be inserted between the calcium chloride tube and the potassium hydroxide bulbs. If the hydrogen also is to be estimated, the combustion should be carried out in the ordinary way until carbonisation is complete, after which the calcium chloride tube is changed and the combustion finished with moist oxygen.

T. S. P.

Estimation of Carbon Dioxide in Carbonates. FRANK S. SINNATT (*Analyst*, 1913, **38**, 136—140).—A complicated apparatus, being in part that described previously (A., 1912, ii, 679), is used. The carbonate is decomposed by means of dilute hydrochloric acid, and the gases evolved are passed over calcium chloride and silver sulphate, and find their way into an exhausted flask; before starting, the whole of the apparatus has been swept by a current of purified air.

The last traces of carbon dioxide in the liquid are expelled by heating. Finally, a known volume of standard barium hydroxide is admitted into the flask, purified air is transmitted until normal pressure is restored, and the excess of barium hydroxide is then titrated as usual. L. DE K.

A New Apparatus for the Estimation of Carbon Dioxide. E. W. GAITHER (*J. Ind. Eng. Chem.*, 1912, **4**, 611—612).— A description, with sketch, of an apparatus for the estimation of carbon dioxide in soils by the double titration method; the advantages claimed are: that it does not require to be taken apart for any of the operations involved; it contains no delicate, easily broken

parts; it can be employed at atmospheric pressure or under a diminished pressure of 70 cm., and that one person can simultaneously keep six experiments working, and complete thirty-six estimations in an eight hours' day. F. M. G. M.

A New Apparatus for the Volumetric Estimation of Carbon Dioxide. HOWARD W. BRUBAKER (*J. Ind. Eng. Chem.*, 1912, **4**, 599).—A criticism of the apparatus previously described for this purpose by Bowser (A., 1912, ii, 995), with a sketch of one the author considers more easily manipulated. The carbon dioxide is passed into a closed graduated conical flask containing potassium hydroxide, the air aperture in which consists of a glass tube with a widened base, filled with glass beads and resting on the bottom of the flask. The subsequent titration is carried out without transferring the distillate. F. M. G. M.

A Carbon Dioxide Absorption Bottle. W. A. KOENIG (*J. Ind. Eng. Chem.*, 1912, **4**, 844).—The bottle, which is 12 cm. high and 3·5 cm. wide, is fitted at the neck with an inlet-tube and at the base with an outlet-tube, each of which are furnished with a mercury "trap." The interior of the bottle is packed with soda-lime at the top and calcium chloride at the bottom, and the weight when thus prepared does not exceed 50—60 grams; it can be employed for about one hundred estimations of carbon dioxide in steel drillings without re-charging. F. M. G. M.

Estimation of Colloids in Arable Soils. MARYAN GÓRSKI (*Zeitsch. landw. Vers. Wesen. Oesterr.*, 1912, **15**, 1201—1216).—From the result of numerous experiments on the absorption of colloids in soils by crystal-violet, the formula suggested by Freundlich (A., 1907, ii, 155, 534, 939) is considered correctly to represent this reaction; the author is also in agreement with the results of König, Hasenbäumer, and Hassler (A., 1911, ii, 1033). F. M. G. M.

New Methods of Soil Analysis and the Estimation of Colloids in Soils. RUDOLF VAN DER LEEDEN and F. SCHNEIDER (*Bied. Zentr.*, 1913, **42**, 145—147; from *Intern. Mitt. Bodenkunde*, 1912, **2**, 81).—Experiments with soils produced by the weathering of gneiss indicated that for the comparison of the hygroscopicity of a soil with that of the silicates dissolved by hydrochloric acid, extraction with aqueous hydrochloric acid is unsuitable, since the solution of colloidal silica, its precipitation with adhering oxides of iron and aluminium and other dissolved substances, introduce errors. The acid may also dissolve colloids which possess only slight hygroscopicity; this could be avoided by employing gaseous hydrogen chloride.

The assumption that the absorption of dyes rises and falls with the amount of colloids is not accepted. Exact experiments on the absorption of dyes and hygroscopicity can only be made when the surfaces of the soils are estimated on the one hand by the employ-

ment of a dye solution, and on the other by using the vapours of organic substances of high molecular weight.

The results of analyses as well as estimations of hygroscopicity indicated that unweathered minerals are dissolved by hot hydrochloric acid. N. H. J. M.

Estimation of Potassium as Platinichloride. GEDEON MEILLÈRE (*J. Pharm. Chim.*, 1913, [vii], **7**, 281—282).—In order to obtain a potassium platinichloride free from the sodium compound, the use of acetone is recommended instead of alcohol generally employed.

If an insufficiency of platinum chloride has been used, the residue may contain a little sodium chloride; this, however, is of no consequence if the platinum is finally weighed as metal. L. DE K.

Detection of Potassium with Tartaric Acid. LUDWIG W. WINKLER (*Zeitsch. angew. Chem.*, 1913, **26**, 208).—The author has observed that tartaric acid in powder is a more delicate reagent for potassium than a solution of the acid. The reaction may be applied as follows: To 10 c.c. of the neutral solution is added 0·5 gram of crystallised sodium acetate, and then 0·5 gram of tartaric acid in fine powder; a precipitate forming rapidly on shaking proves the presence of potassium. Ammonium, rubidium, and cæsium should, of course, be absent. L. DE K.

Estimation of Lithium. LESLIE RUSSELL MILFORD (*J. Ind. Eng. Chem.*, 1912, **4**, 595—597).—The mineral water (200—500 c.c.) is evaporated to dryness with hydrochloric acid, and the silica dehydrated at 120°; the residue, after moistening with hydrochloric acid, is treated with about 25 c.c. of 95% alcohol, and the precipitate collected and washed with the same until free from lithium; the alcoholic solution is evaporated to dryness, and the process repeated with hydrochloric acid and absolute alcohol. The residue, after treating with dilute hydrochloric acid, is rendered alkaline with calcium hydroxide, whereby the magnesium is precipitated as magnesium hydroxide; the calcium is then separated as oxalate, and after twelve hours the filtrate, which practically contains only lithium and ammonium salts, is evaporated and the latter expelled by heating in the usual manner.

The acidified (hydrochloric acid) aqueous solution of the residue is treated with about 30 c.c. of amyl alcohol, the water boiled away, and the filtered solution evaporated to dryness with dilute sulphuric acid; the lithium solution is evaporated down and weighed as lithium sulphate, from which 0·0017 gram must be deducted to correct for the solubility of sodium and potassium chlorides in amyl alcohol. The advantages claimed are: Waters containing many chlorides can be handled with ease without loss of lithium by decrepitation; large volumes of water can be employed; the employment of calcium instead of barium hydroxide does not introduce another metal, and the calcium oxalate precipitate is more insoluble than barium oxalate. F. M. G. M.

Estimation of Calcium as Tungstate. A. SAINT-SERNIN (*Compt. rend.*, 1913, **156**, 1019—1020).—By addition of excess of a 20% solution of normal sodium tungstate to a boiling ammoniacal solution of calcium chloride, the calcium is completely precipitated in a heavy, crystalline form as calcium tungstate, $CaWO_4$. This is filtered, washed and dried at 100°, and weighed as such. Magnesium not being precipitated under these conditions, it furnishes a ready method for the separation of these two elements in analysis.

W. G.

Assay of Barium Sulphate in Radiographic Examinations. GABRIEL GUÉRIN (*J. Pharm. Chim.*, 1913, [vii], **7**, 282—283).—For the above purposes, barium sulphate, in itself perfectly inert, should be quite free from soluble (toxic) barium salts. Fifteen to twenty grams of the commercially pure article are treated with 100 c.c. of 10% hydrochloric acid. After adding a little filter paper pulp and filtering, the clear filtrate is tested for barium by means of sulphuric acid and also with ammonia and potassium dichromate. L. DE K.

Estimation of Zinc by Electroanalysis. ELLWOOD B. SPEAR and SAMUEL S. STRAHAN (*J. Ind. Eng. Chem.*, 1912, **4**, 889—890. Compare A., 1910, ii, 455).—The electrolytic method of estimating zinc described by Kemmerer (A., 1911, ii, 335) is considered the most satisfactory when the following modifications are introduced: (*a*) Cooling the solution for a few minutes before the end of the experiment; (*b*) reducing the amount of potassium hydroxide employed; and (*c*) the employment of a rotating nickel gauze cathode and a stationary platinum plate or spiral anode. The method is shown to entail a compensation of errors, the chief of which are: (1) loss of zinc in the wash-bottle, counterbalanced by the formation of zinc hydroxide on the cathode; (2) the effect of air on an exposed cathode; (3) oxidation of the deposit by anode gases; (4) effect of temperature at the beginning and end of the electrolysis; (5) the effect of ether containing water and oxides on the deposit; (6) a high result from allowing the ether to evaporate off the cathode in a desiccator; (7) the presence of nitrates.

F. M. G. M.

Estimation of Lead in Lead Paints. JULIUS F. SACHER (*Chem. Zentr.*, 1912, ii, 2147; from *Farbenzeit*, 1912, **18**, 295—296).—All new methods for the estimation of lead in paints, including Utz's electrolytic process (this vol., ii, 76) give untrustworthy results. A correct method is that of Schindler and Alexander (Lunge, *Tech. Methods of Chem. Analysis:* compare A., 1893, ii, 599), which is based on a titration with ammonium molybdate. J. C. W.

Separation of Small Quantities of Mercury by Electrolysis. OTTO SCHUMM (*Zeitsch. physiol. Chem.*, 1913, **84**, 239—242. Compare Buchtala, this vol., i, 318; Salkowski, this vol., i, 562).—Polemical. The author's electrolytic method for separating mercury (A., 1905, ii, 286) is upheld in all its details. E. F. A.

Reactions of Mercuric Compounds. MORITZ KOHN and ALFONS OSTERSETZER (*Zeitsch. anorg. Chem.*, 1912, **80**, 218—220).—The estimation of mercuric haloids by means of hydrogen peroxide and alkali (A., 1908, ii, 892) may be improved by using sodium peroxide free from halogen. The salt is boiled with water and a slight excess of sodium peroxide, the precipitated mercury is repeatedly washed, and the halogen is estimated in the filtrate. Mercuric iodide requires a large excess of peroxide, otherwise reduction is incomplete.

The arsenite method (A., 1912, ii, 696) has been applied to mercuric cyanide, but the reaction is very incomplete. C. H. D.

Aluminium Alloys and their Analysis. W. E. VON JOHN (*Chem. Zeit.*, 1913, **37**, 363).—A number of aluminium alloys suffer from the disadvantage that they are attacked by sea-water. It is pointed out that in investigating the effect of sea-water it should be used in the normal condition, since in one case an alloy was hardly attacked by sea-water which had been concentrated to one-fifth of its volume, whereas it was attacked appreciably by the ordinary sea-water.

The analysis of the alloys is best carried out as follows: 1 gram of the alloy is dissolved in hydrochloric acid, the solution evaporated to dryness, and the silica estimated as usual. The lead and tin in the filtrate are estimated in the usual way; to the filtrate from these metals is added bromine water, and then alkali in excess. After heating to boiling and keeping overnight, the precipitate, which contains copper, iron, manganese, and magnesium, is collected, and these metals are estimated as usual. The zinc in the filtrate is precipitated with ammonium sulphide and weighed as sulphide, after which it is dissolved in hydrochloric acid and tested with ammonia for aluminium, which, if present, must be allowed for. The alkaline solution containing the aluminium and zinc may also be poured into acetic acid, and the zinc then precipitated as sulphide with hydrogen sulphide. The zinc sulphide is then dissolved in hydrochloric acid, the aluminium present precipitated as hydroxide, and the zinc again precipitated as phosphate.

If the alloy does not contain silica, lead, or tin, it is dissolved directly in alkali hydroxide. T. S. P.

Alkali-Acidimetric Estimation of Alumina and the Acidimetry of the Free Acid in Aluminium Salts. S. FISCHL (*Chem. Zentr.*, 1913, i, 958—959; from *Abhandl. deut. naturwiss. med. Ver. Böhmen*, 1913, iii, 213—237). — The solution of alumina in hydrochloric or sulphuric acid is roughly titrated with phenolphthalein and diluted to about $0{\cdot}03N$. The total acidity is estimated in one portion by adding a known excess of alkali until a clear solution is obtained in the cold, and then titrating back with hydrochloric acid in presence of barium sulphate in the warm. In another portion, the free acid is titrated with N-alkali in presence of sodium fluoride in a platinum dish. J. C. W.

[Estimation of] Manganese in Ore, Ferromanganese, Spiegeleisen, etc. Volhardt's Method. SIDNEY CROOK (*Chem. News*, 1913, **107**, 157).—Two grams of the sample are treated with suitable acids, finally sulphating with 10 c.c. of concentrated sulphuric acid, and evaporating until fumes appear. The residue is transferred to a litre flask, which should then be half-filled with boiling water. Precipitated zinc oxide emulsion is added until all the iron is thrown down, carefully boiled, filtered, and washed well with hot water. The collected precipitate, which still contains some manganese, is transferred to the original flask, redissolved in 5—10 c.c. of concentrated sulphuric acid, and again precipitated with zinc oxide emulsion. The whole is then added to the main bulk, without filtering, cooled, and made up to a litre. An aliquot portion, equal to 0·25—0·5 gram of the sample, is pipetted into a 1500 c.c. Jena flask, made up to 600 c.c. with water, boiled, and then titrated with potassium permanganate solution (10 grams per litre) until the faint pink colour persists for several hours. In carrying out the titration, continuous and vigorous shaking of the contents of the flask, as well as repeated boiling, is necessary. Towards the end of the titration it is well to filter some of the solution through a hardened filter in order to compare its colour with that of a standard made by adding two drops (0·1 c.c.) of the permanganate solution to one litre of water. The end of the titration can then be told with accuracy.

It may be necessary to make a blank estimation, in order to correct for errors caused by the water, acid, and zinc oxide emulsion used. T. S. P.

Colorimetric Estimation of Small Quantities of Manganese in Water. FRITZ HAAS (*Zeitsch. Nahr. Genussm.*, 1913, **25**, 392—395).—In the method proposed, the manganese is oxidised with potassium persulphate, and the quantity of permanganate produced is ascertained by comparison with standard solutions of the latter. On hundred c.c. of the water under examination are acidified with 5 c.c. of 20% sulphuric acid, 1 gram of potassium persulphate is added, and the solution is heated until a reddish-violet coloration is obtained, or until a brown colour, due to manganese dioxide, develops. The solution is now cooled, a trace of sodium hydrogen sulphite is added, and the oxidation with persulphate is repeated. The coloration obtained is then compared with that exhibited by $N/100$-potassium permanganate solution. The most trustworthy results are obtained when the quantity of manganese lies between 0·05 and 1·0 mg. per litre of water. The presence of iron does not affect the results obtained by the method, and there is no necessity to remove chlorides by previous treatment with silver nitrate and nitric acid. W. P. S.

A Modified Bunsen Valve. LESLIE RUSSELL MILFORD (*J. Ind. Eng. Chem.*, 1912, **4**, 845—846).—A sketch of a modified Bunsen valve attachment used to close the neck of the Erlenmeyer flasks employed for the reduction of iron in the estimation of this metal;

it is made from the bulbous portion of a 10 c.c. pipette, inserted into the one-holed stopper, and fitted on the top with perforated rubber tubing, which is loosely closed with a glass plug.

F. M. G. M.

The Methods of the United States Steel Corporation for the Commercial Sampling and Analysis of Pig Iron. CHEMISTS' COMMITTEE OF THE U. S. STEEL CORPORATION (*J. Ind. Eng. Chem.*, 1912, **4**, 801—812).—A detailed description of the methods adopted as standards by the chemists of the U.S. Steel Corporation for the analysis of pig iron, which is divided into the following sections:

1. Sampling and the character of the sample. Two optional methods are prescribed for taking the sample: (*a*) the plate or pat test, and (*b*) the chilled mould test; the use of the water shot test is considered a violation of the standard methods. The number of samples to be taken, their preparation, with sketches of the moulds to be employed are also given.

2. Methods of analysis. Silicon may be estimated by either Drown's or Ford's hydrochloric acid methods. Sulphur, volumetrically as hydrogen sulphide by titration with iodine, or gravimetrically after oxidation to sulphate.

Phosphorus, volumetrically by either acid-alkali or potassium permanganate titrations; gravimetrically as ammonium phosphomolybdate or magnesium pyrophosphate.

Manganese, by Walter's colour comparison method; by titration with sodium arsenite, or by Ford's gravimetric method.

Total carbon, by direct combustion followed by (*a*) weighing the absorbed carbon dioxide; (*b*) titration with an alkaline hydroxide; (*c*) filtration and ignition of barium carbonate; (*d*) titration of excess of barium hydroxide; or by a solution-combustion method which is described.

Graphitic carbon, by combustion of the graphitic residue, with either absorption of carbon dioxide, or by loss of weight when ignited in a crucible.

Combined carbon, indirectly from the total carbon, or by the colour comparison method.

Titanium, colorimetrically.

Copper, gravimetrically as copper oxide or volumetrically with iodine and sodium thiosulphate. F. M. G. M.

Estimation of Iron and Titanium in Ceramic Materials. REINHOLD RIECKE and RICHARD BETZEL (*Chem. Zentr.*, 1913, i, 656—657; from *Arch. Physikal. Chem. Glas. and Keram. Massen*, 1912, **1**, 45—48).—Since not only the iron, but also the titanium present in the clay, have an influence on the firing-colour, it is advisable to estimate them both. If the iron is to be titrated by permanganate, the solution should be reduced by stannous chloride, hydrogen sulphide, or sulphur dioxide, or if reduced by zinc, the titanium present must be re-oxidised by bismuth oxide. An iodometric estimation is preferable. For the titration of titanium, which is

usually present in less than 1% as dioxide, a colorimetric method requiring a special but simple apparatus is described. J. C. W.

The Colorimetric Estimation of Iron in Lead and its Oxides. JOHN A SCHAEFFER (*J. Ind. Eng. Chem.*, 1912, **4**, 659—660).—A modification of the method previously described by Thomson (T., 1885, **47**, 493), and now adapted for the analysis of lead employed in the manufacture of glass and accumulators.

F. M. G. M.

Estimation of Chromium and Vanadium in Steel. D. J. DEMOREST (*J. Ind. Eng. Chem.*, 1913, **4**, 895).—A modification of the method previously described (A., 1912, ii, 1100), which allows of the estimation of chromium and vanadium in the same sample of steel. The prepared solution is treated with sodium bismuthate, which oxidises the chromium, manganese and vanadium to chromic, permanganic, and vanadic acids respectively; the permanganic acid is destroyed by boiling and manganese dioxide removed by filtration; the chromic and vanadic acids are reduced with ferrous sulphate to tervalent chromium and quadrivalent vanadium, and by subsequent treatment with potassium permanganate the vanadium only reoxidised, so that the amount of ferrous sulphate minus the permanganate employed measures the quantity of chromium.

The vanadium is again reduced with ferrous sulphate (not measured), the excess of ferrous sulphate oxidised with manganese dioxide, and the vanadium titrated.

The manganese dioxide (which must be natural or crystalline) must not be in too finely divided a condition (A., 1912, ii, 1101), but should settle perfectly in a beaker of water within fifteen seconds. F. M. G. M.

A New Volumetric Method for the Estimation of Tin. WILLBUR W. PATRICK and G. C. WILSNACK (*J. Ind. Eng. Chem.*, 1912, **4**, 597—599).—A sample corresponding with 0·5 (or less) of tin is placed in a 500 c.c. Erlenmeyer flask, 1·5 grams of metallic antimony added (if as much or more is not present in the alloy), and the mixture heated with 10 c.c. of concentrated sulphuric acid until solution is complete. The contents of the flask are cooled, treated with 10 c.c. of water and 60 c.c. of concentrated hydrochloric acid, followed by 40 c.c. more water.

The flask is closed with a four-holed rubber stopper fitted with (1) an inlet, (2) an outlet for carbon dioxide, (3) a tube through which the titrating solution is introduced, and (4) a glass rod to the base of which a spiral of Swedish iron is suspended by means of a fused-in platinum hook, which can be raised or lowered to the bottom of the flask as required.

Air is expelled by the passage of carbon dioxide and reduction, completed by the application of heat; the iron spiral is raised, carefully washed, and the tin rapidly titrated with standard iodine solution in the presence of starch.

The modifications necessary if the alloy contains more than 5%

of copper or lead or excess of antimony are also discussed in the original. F. M. G. M.

Estimation of Platinum by Precipitation as Sulphide. RUDOLF GAZE (*Chem. Zentr.*, 1913, i, 464; from *Apoth. Zeit.*, 1912, **27**, 959—960).—The addition of 5—10% of mercuric chloride or oxynitrate expedites the precipitation of platinum as sulphide. The method gives good results in the estimation of platinum in organic double-salts. Barium platinicyanide may be decomposed by concentrated sulphuric acid or by strong ignition, and the residue extracted with aqua regia and precipitated as above. J. C. W.

α-Nitroso-β-naphthol as a Precipitant for Palladium. W. SCHMIDT (*Zeitsch. anorg. Chem.*, 1913, **80**, 335—336).—α-Nitroso-β-naphthol gives a bulky, reddish-brown precipitate with palladium salts, but not with the other platinum metals. This reaction is perceptible with a solution containing 0·001 gram of palladium per litre. The method may be used quantitatively, as the precipitate is readily filtered, and yields the pure metal on ignition. The accuracy of the precipitation is not interfered with by the presence of platinum and rhodium. The precipitate has the composition $(C_{10}H_6O_2N)_2Pd$. C. H. D.

New Method of Purification of Paraffin and Modification by its Aid of Marcusson and Meyerheim's Process for Identifying Different Paraffins by means of the Iodine Value. CONSTANTIN I. ISTRATI and M. A. MIHĂILESCU (*Bull. Acad. Sci. Roumaine*, 1912/13, **1**, 91—94).—The paraffin is dissolved in boiling chloroform, then mixed with an equal bulk of boiling alcohol, and the solution allowed to cool. The solid matter which separates is filtered, and the filtrate distilled with the aid of a fractionating column in such a way that a portion of the chloroform is removed, after which, on cooling the residue in the flask again, it deposits a crystalline crop, which is removed, the filtrate being again subjected to a similar operation. In this manner a sample of white paraffin, m. p. 58°, was resolved into several fractions, the highest m. p. observed for any of them being 78°, whilst the last fraction was liquid at the ordinary temperature.

The modification of Marcusson and Meyerheim's method consists in the replacement of ether by chloroform. The paraffin is dissolved in a boiling mixture of alcohol and chloroform, the solution allowed to cool slowly, and the crystalline precipitate filtered and washed with a mixture of alcohol and chloroform, finally with pure alcohol. The filtrate is evaporated, and the residue again dissolved in alcohol-chloroform. The crop which separates on cooling is removed, and the iodine value determined in the filtrate. The values obtained in this manner are rather higher than those given by the older method, a result which is attributed to the better separation of the paraffins. H. W.

Relations between the Temperatures of the Vapour and of the Boiling Liquid in the Case of Mixtures of Hydrocarbons. DAVID HOLDE (*Chem. Zeit.*, 1913, **37**, 414—415).—The

author has distilled, in an Engler flask, crude Galician petroleum and also a refined (safety) petroleum (flash point 56°, D^{15} 0·800), measuring at the same time the temperatures of the boiling liquid and of the vapour in contact with it. In the case of the crude petroleum the temperature range of the boiling point (thermometer in vapour) was >240°, from 68° to >308°, and the difference in temperature between the vapour and liquid gradually increased from 39° to 59°. In the case of the refined petroleum the temperature range was 68°, from 184° to 252°, and the temperature difference gradually decreased from 8° to 6°. The fact that the temperature difference increases continually in the case of the crude petroleum may be taken as proof that decomposition occurs to some extent, the normal behaviour, as predicted by theoretical considerations, being a gradual decrease in the temperature difference, as in the case of the refined petroleum.

The results of these experiments support the method recommended by the International Petroleum Commission for the investigation of petroleum, namely, the use of an Engler flask, and measurement of the temperature of the vapour and not of the liquid. T. S. P.

Vapour Pressure of Naphthalene and its Estimation in the Purification of Coal Gas. Ernest Schlumberger (*J. Gasbeleuchtung*, 1912, **55**, 1257—1260).—A description of the apparatus employed, and the method of procedure, by means of which the amount of naphthalene present in coal gas is estimated by the determination of vapour pressure. The vapour pressures corresponding with mixtures containing different proportions of coal gas and naphthalene are tabulated at temperatures (taken at intervals of 5 degrees) between 0° and 50°. F. M. G. M.

A New Method for the Estimation of Glycerol. S. H. Bertram (*Chem. Weekblad*, 1913, **10**, 237—239).—The method depends on the formation of a soluble derivative of copper and glycerol on addition of copper sulphate to an alkaline solution of glycerol at ordinary temperature. The copper is estimated by adding excess of potassium iodide to the solution containing acetic acid, and titrating back with $N/10$-thiosulphate. The constitution of the copper compound is unknown, but its copper content corresponds with 1 atom to 2 molecules of glycerol. A. J. W.

Rapid and Accurate Methods for Estimating Phenol. L. V. Redman and E. O. Rhodes (*J. Ind. Eng. Chem.*, 1912, **4**, 655—659).—A discussion of various methods which have been employed for the estimation of phenol with a description of two (the hypobromite method and the bromide-bromate method), in the first of which the phenol is shaken with potassium hypobromite, subsequently treated with iodine, and titrated with sodium thiosulphate; the second method is similar, except that the hypobromite is replaced by a mixture of potassium bromide and bromate

(Koppeschaar's solution). The advantages claimed are, an accuracy of 0·3% with only one minute's continuous shaking.

The phenol should in each case be diluted to approximately $N/100$ concentration, when the resulting precipitate will be white and flocculent, showing no traces of red tetrabromo-*p*-benzoquinone or of yellow tribromophenol bromide. The phenol solution must be acid after the bromine is added; if alkaline, an error (of as much as 67%) is introduced, which increases as the concentration of the phenol in the solution diminishes, and the reaction period increases.

F. M. G. M.

The Estimation of Phenol in Crude Carbolic Acid and Tar Oils. JOHN MORRIS WEISS (*J. Franklin Inst.*, 1912, 683—690).—Eleven different mixtures containing varying proportions of *o*-, *m*-, and *p*-cresols were each treated with 5, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 95% of phenol, and the b. p., density, and solidifying point of each mixture carefully determined. From the data (which is tabulated) it is considered possible to estimate absolute phenol in crude natural mixtures of tar oils within an error of 2·5%.

The synthetic preparation of pure phenol, and the purification of the *o*-, *m*-, and *p*-cresols employed in these tests, are described.

Various anomalies in the physical constants of some of the mixtures are recorded, but as they occur in those containing proportions not found in the crude oil, they are not considered likely to lead to inaccuracies if intelligently considered. F. M. G. M.

The Estimation of Eucalyptol (Cineole) in Essential Oils. FRANCIS D. DODGE (*J. Ind. Eng. Chem*, 1912, **4**, 592).—Eucalyptol is stable in the presence of cold potassium permanganate, whereas the terpenes and unsaturated compounds also present in essential oils are oxidised thereby to soluble products; the unattacked eucalyptol can be measured, and its purity confirmed by physical tests. About 10 c.c. of the oil are shaken at 0° with the addition of a 5—6% solution of potassium permanganate until reduction is complete; after allowing it to remain at 0° during twelve to eighteen hours, the precipitated manganese dioxide is dissolved with sulphurous acid (or sodium hydrogen sulphite and hydrochloric acid), water added, and the unoxidised oil separated. F. M. G. M.

Estimation of Formic Acid in Foods HEINRICH FINCKE (*Zeitsch. Nahr. Genussm.*, 1913, **25**, 386—391).—Results of estimations of formic acid by the mercuric chloride method are recorded, and the advantage of adding sodium chloride and sodium acetate to the solution before reduction are pointed out (compare A., 1911, ii, 232). Attention is drawn to the effect of the alteration of the atomic weight of mercury on the factor for calculating the quantity of formic acid from the weight of mercurous chloride. For the detection of formic acid, reduction of the acid with magnesium in the presence of hydrochloric acid is recommended, the resulting formaldehyde being detected by means of milk and hydrochloric acid containing a trace of iron. W. P. S.

Analysis of Mixtures of the Lower Fatty Acids. KURT LANGHELD and ARTUR ZEILEIS (*Ber.*, 1913, **46**, 1171—1177).—Many physiologico-chemical investigations lead to mixtures of the lower members of different aliphatic series. As most of these substances can be easily converted into the fatty acids, an attempt has been made to solve the problem of estimating the latter in mixtures, and, in the first place, in mixtures of those acids which correspond with the most commonly occurring amino-acids, namely, acetic, *iso*butyric, *iso*valeric and α-methylbutyric acids. Formic acid is omitted because it can be estimated separately. The method depends on the oxidative degradation of these acids by chromic acid. This process is well-nigh independent of concentration, but is influenced by temperature to a remarkable extent, for by regulating this, the oxidation can be stopped at different stages in exact concordance with the theoretical views represented by the equations:

$$
\begin{aligned}
&CH_3{\cdot}CO_2H \longrightarrow 2CO_2\\
&CHMe_2{\cdot}CO_2H \longrightarrow C(OH)Me_2{\cdot}CO_2H \longrightarrow CH_3{\cdot}CO{\cdot}CH_3(+CO_2)\\
&\qquad \longrightarrow CH_3{\cdot}CO_2H(+CO_2) \longrightarrow 2CO_2\\
&CHMe_2{\cdot}CH_2{\cdot}CO_2H \longrightarrow C(OH)Me_2{\cdot}CH_2{\cdot}CO_2H \longrightarrow CH_3{\cdot}CO{\cdot}CH_3(+2CO_2)\\
&\qquad \longrightarrow CH_3{\cdot}CO_2H(+CO_2) \longrightarrow 2CO_2\\
&C_2H_5{\cdot}CHMe{\cdot}CO_2H \longrightarrow C_2H_5{\cdot}C(OH)Me{\cdot}CO_2H \longrightarrow CH_3{\cdot}CO{\cdot}C_2H_5(+CO_2)\\
&\qquad \longrightarrow C_2H_5{\cdot}CO_2H(+CO_2) \longrightarrow 3CO_2.
\end{aligned}
$$

At 65°, the first phase, the oxidation of secondary chains, is completed; at 100°, the oxidation of the ketones into the acids; and at 170°, the complete oxidation. Knowing the total acidity in terms of $0{\cdot}1N$-alkali, it is possible, by measuring the carbon dioxide evolved in these three stages, and with the aid of appropriate formulæ, to estimate mixtures of these acids. The results are only approximate, but since very little substance is required, the method may be worthy of application to physiological problems. J. C. W.

The Purine Content of Blood and Its Estimation. ROBERT BASS and WILHELM WIECHOWSKI (*Chem. Zentr.*, 1913, i, 331; from *Wien. klin. Woch.*, 1912, **25**, 1863—1864).—Uric acid and purine bases are not precipitated from very dilute solutions by phosphotungstic acid. Such liquids as urine or blood filtrates, which contain substances which are precipitated by this reagent, may therefore be freed from those materials without loss of uric acid or purine bases, especially when precautions are taken not to add an excess of precipitant. After removing the phosphoric acid from the concentrated filtrate, silver nitrate is added, and the precipitate is decomposed by hydrogen sulphide and filtered. Uric acid crystallises out on concentrating the filtrate with hydrochloric acid, and is weighed.

Uric acid is found to be a constant constituent of human or bovine blood, but not of horse blood, whereas purine bases are common to all, but are found in largest quantity in human blood.

J. C. W.

Detection of Uric Acid in Blood. FRITZ OBERMAYER, HUGO POPPER, and E. ZAK (*Chem. Zentr.*, 1913, i, 658—659; from *Wien. klin. Woch.*, 1912, **25**, 1967—1968. Compare preceding abstract).—The serum is freed from traces of albumin and allied substances by centrifugation with crystallised phosphotungstic acid (Merck), which does not precipitate uric acid, and then the filtrate is rendered alkaline and treated with a special phosphotungstic acid from Schuchardt, which gives a blue coloration with uric acid even in the dilution 0·01 mg. to 5 c.c. water. Other purine substances which are found in blood do not react. J. C. W.

Behaviour of Uric Acid to Zinc Salts. M. KASCHIWABARA (*Zeitsch. physiol. Chem.*, 1913, **84**, 223—233).—On mixing solutions of zinc salts with uric acid, precipitates are obtained rich in zinc and containing small quantities of uric acid. Compounds of the two in definite proportions were not obtained.

In the quantitative estimation of uric acid in urine, slightly higher values are found using the zinc method than with the silver method. The uric acid obtained by the former method is of satisfactory purity. E. F. A.

Colorimetric Estimation of Uric Acid in Urine. OTTO FOLIN and WILLEY DENIS (*J. Biol. Chem.*, 1913, **14**, 95—100).—Full details are given of the technique in the colorimetric method introduced by Folin and Macallum (A., 1912, ii, 495; this vol., ii, 80). It is possible to carry out the process in fifteen minutes. W. D. H.

A Simple All-Glass Extraction Apparatus. CLAYTON BEADLE and HENRY P. STEVENS (*Analyst*, 1913, **38**, 143—144).—The apparatus consists essentially of an Erlenmeyer flask about three inches in diameter and 4½ inches in height to the bottom of the neck. The latter is made wide and long, 1⅜ to 1½ inches internal diameter, and 4½ inches long The condenser consists of a glass vessel of test-tube shape, fitted at the top with a water inlet and outlet and of about 1¼ to 1⅜ inches external diameter, which is slipped into the neck of the flask and supported by a flange resting on the rim. The actual extraction tube consists of a glass thimble with siphon tube attached about 3 inches long, and 1 to 1¼ inches external diameter. The thimble hangs by means of a flange on three or four projections at the bottom of the neck of the flask, made by softening the same and forcing a sharp-pointed instrument in to the depth of about ¼ inch. The apparatus has the advantage that the substance to be extracted is immersed in the solvent or its vapour at the boiling point of the liquid. L. DE K.

Glycerides of Fats and Oils. VI. The Theoretical Basis of Polenske's "Difference" Number. ALOIS BÖMER and R. LIMPRICH (*Zeitsch. Nahr. Genussm.*, 1913, **25**, 367—386).—A method proposed by Polenske (*Arbeit. Kaiserl. Gesundh.*, 1907, **26**, 444) for the detection of certain fats in other animal fats, which is based on the differences between the melting and solidifying points

of the fats, was found to be useful for the detection of tallow in lard, provided that the proportion of the former was not less than 15%. The method depends on the presence of different palmityldistearins in the fats; lard contains α-palmityldistearin and has a "difference" number of 18·4, whilst tallow contains β-palmityldistearin and shows a "difference" number of 11·8. Previous crystallisation of the fats from ether does not increase the sensitiveness of the method. W. P. S.

Analysis of Altered Milks. L. VUAFLART (*Ann. Falsif.*, 1913, **6**, 148—149).—In using the method described by Kling and Roy (A., 1909, ii, 525) it is advisable to divide the sample of milk into two equal portions, one portion being reserved for analysis in case of accident to the first, or it may be employed for a duplicate estimation. The total weight of the sample is ascertained, and one-half of it is acidified with acetic acid, heated, and the coagulum separated by filtration; after being washed, the coagulum is dried at 95°, extracted successively with acetone and ether, and then mixed with the residue obtained by evaporating the serum and washings to dryness. The nitrogen is estimated in the residue by Kjeldahl's method. The author considers that milk should contain at least 29 grams of protein (nitrogen × 6·39) per litre, a slightly lower standard than the one suggested by Kling and Roy; the quantity of fat present should be not less than 30 grams per litre. W. P. S.

Estimation of Proteins in Milk (by Formaldehyde Titration). WILLEM C. DE GRAAFF and (Mlle.) A. SCHAAP (*Ann Falsif.*, 1913, **6**, 149—157).—In the estimation of proteins by the formaldehyde process described by Steinegger (A., 1906, ii, 130) the authors prefer to use sodium hydroxide solution for the titration as they find that the acidity of formaldehyde solutions does not increase with dilution when this alkali is used unless the dilution is excessive; Richmond (A., 1911, ii, 236) has recommended the use of strontium hydroxide solution in order to avoid this increase of acidity. From the results obtained, the factor 0·0777 is deduced for converting the aldehyde figure into nitrogen, or 0·495 for converting it into protein; these agree with the factors given by Steinegger, but are slightly different from those found by Richmond. In the case of heated milk, the results obtained are not as concordant as those given by unheated milk. With human milk the nitrogen factor was found to be 0·0693, and the protein factor 0·443. Buttermilk yielded an aldehyde figure varying from 10·41 to 11·29. W. P. S.

Estimation of Sugar. II. IVAR BANG (*Biochem. Zeitsch.*, 1913, **49**, 1—18).—A modification of the author's titrimetric method for estimating sugar is described, for which at least an equal accuracy is claimed, and which has the advantage in that the standard solutions are more readily prepared and the materials required are less costly. The copper solution is made in the following way:

160 grams of potassium hydrogen carbonate, 100 grams of potassium carbonate, and 66 grams of potassium chloride are dissolved in 700 c.c. of water, the first-named substance being dissolved before the addition of the others with the aid of gentle heat (30°); 100 c.c. of a 4% solution of hydrated copper sulphate are then added, and the solution is diluted to 1 litre. This serves as the stock solution, of which, for sugar estimations, 300 c.c. are diluted to 1 litre with saturated potassium chloride solution. The sugar reduces the copper salt to cuprous chloride, which is kept in solution by the large excess of potassium chloride. The reduced cuprous salt present is then estimated by titration with iodine, which reacts according to the equation $CuCl + I + K_2CO_3 = CuCO_3 + KCl + KI$. The iodine solution required for this purpose is made by mixing 1 c.c. of 2% potassium iodate solution with 2—2·5 grams of potassium iodide and 10 c.c. *N*/10-hydrochloric acid, and diluting to 1 litre. A *N*/100-iodine solution is thus obtained. Starch solution (1% in saturated potassium chloride solution) is used as indicator. For ordinary estimations 55 c.c. of the diluted copper solution are heated for three minutes with the sugar solution, which must not contain more than 10 mg. sugar, and the mixture is then allowed to cool. Special arrangements are described for preventing oxidation during this process. The reduced copper salt is then estimated by the iodine solution; 2·70 c.c. *N*/100-iodine solution are equivalent to 1 mg. of dextrose. The sugar solution should be free from proteins and substances which are acted on by iodine; hence certain precautions are necessary in applying the method to the estimation of sugar in urines. S. B. S.

A Method of Microchemical Estimation of Certain Constituents of the Blood. IVAR BANG (*Biochem. Zeitsch.*, 1913, **49**, 19—39).—The blood, which need not weigh more than 0·1 gram, is taken up on a weighed strip of filter paper, and then rapidly weighed on a torsion balance designed by Hartmann and Braun. The weighing can be so rapidly performed that no appreciable loss due to evaporation of moisture takes place. To estimate the sugar in this, the paper is transferred to a test-tube, to which is added 7 c.c. of a hot saturated potassium chloride solution, previously acidified by the addition of 2 or 3 drops of 40% acetic acid. The liquid is then transferred to a 50 c.c. flask, the paper is washed with 4 c.c. potassium chloride solution, and then 3 c.c. of the undiluted stock solution containing copper sulphate, potassium carbonates, and potassium chloride (preceding abstract) are then added, and with the precautions described (*loc. cit.*) the reduction is carried out. As only fractions of a mg. of sugar are present, the iodine solution (*N*/100) necessary to titrate the reduced copper is less than 1 c.c., hence a special microburette is employed. Exact details are given by the author, together with illustrations of the method of application.

A method is also given for the microchemical estimation of sodium chloride. To about 100 mg. of blood (weighed on the filter paper by the torsion balance) are added 10 c.c. of a hot

solution of magnesium sulphate containing nitric acid. After cooling, 2 c.c. of $N/100$-silver nitrate solution are added, and then a definite quantity of kieselguhr, without which a clear filtrate is not obtainable. The mixture is shaken and then filtered, and the precipitate is washed with water. To the filtrate is then added 2 c.c. of a solution made by dissolving 0·015 gram of potassium iodate and 1·7 gram of potassium iodide in a litre. The excess of iodide (not precipitated by the silver) is then estimated by titration from a microburette with $N/100$-silver nitrate solution. The silver does not react with the iodine until it has reacted with all the iodide. The titration is carried out in the presence of a few drops of starch solution indicator made by dissolving 1 gram of soluble starch in 100 c.c. of 20% potassium nitrate solution. The number of c.c. of silver solution multiplied by 0·585 gives the number of mg. of sodium chloride. A correction must be made by blank experiment for the adsorption of silver salt by the kieselguhr. Examples of the application of the method are given, and also suggestions for the micro-estimation of water, hæmoglobin, total nitrogen, nitrogen of extractives, albumin, and globulin.

S. B. S.

Estimation of Sugars by the Kjeldahl Bertrand Method. PAUL BEYERSDORFER (*Zeitsch. ges. Brauwesen*, 1912, **35**, 556—559, 569—572, 582—584).—A detailed account of numerous experiments on the estimation of sugars (especially in beer and worts), from which the author deduces a method combining that of Kjeldahl with that of Bertrand (A., 1907, ii, 136), in which the cuprous oxide obtained by the first process is treated with ferric sulphate, and the ferrous salt so obtained titrated with potassium permanganate.

F. M. G. M.

Chemical Estimation of Lactose in Milk. RICCIARDO SANFELICI (*Chem. Zentr.*, 1913, i, 566—567; from *Staz. sperim. agrar. ital.*, 1912, **45**, 908—916).—The following solutions are recommended for the titration of lactose: i, 4·158 grams of copper sulphate to 1 litre of water; ii, 20·4 grams of Rochelle salt, 20·4 grams of potassium hydroxide, 300 c.c. of ammonia (D 0·91), water to 1 litre. Twenty c.c. of milk are diluted with 30 c.c. of water, boiled, and treated with 5 drops of acetic acid, when the casein and fat are precipitated and the albumin coagulated. The liquid is cooled, made up to 100 c.c., filtered into a burette, and run into a boiling mixture of 10 c.c. of solutions i and ii, 20 c.c. water, and 10 c.c. concentrated ammonia. The results are usually about 0·2% higher than with Fehling's solution.

J. C. W.

Estimation of Sugars in Foods (Honey, Confectionery, Jams, etc.). C. F. MUTTELET (*Ann. Falsif.*, 1913, **6**, 138—143).—Sucrose, dextrose, and lævulose may be estimated in a solution by determining the cupric reducing power and the optical rotation; in calculating the quantities of the different sugars present the following constants are taken into account: sucrose has

$[\alpha]_D^{20}$ +66·50°; dextrose, $[\alpha]_D^{20}$ +53·00°; lævulose, $[\alpha]_D^{20}$ −93·50°; invert sugar, $[\alpha]_D^{20}$ −20·25°. The sugars in from 5 to 10 grams of the material under examination are obtained in 100 c.c. of solution, after the removal of other reducing and optically active substances, and the reducing power of this solution is determined both before and after inversion, the results being expressed as grams of invert sugar per 100 c.c. of solution; let these quantities be p and q respectively. The rotation of the solution is also determined at 20° in a 200 mm. tube. The amounts of the different sugars per 100 c.c. are then calculated from the equations: Sucrose $= 0·95 (q-p)$; dextrose $= p - L$ (L = grams of lævulose); lævulose $= \dfrac{(1·06 \times p) - d}{2·93}$. In the last equation, $d = D - c$, where D is the rotation observed and c the rotation due to the amount of sucrose present (c = sucrose × 1·33). The quantities of sugars found are, finally, calculated into percentages of the original substance.

W. P. S.

Inversion of Raw Sugar Solutions with Ammonium Chloride. FRIEDRICH STROHMER and OTTOKAR FALLADA (*Österr-ung. Zeitsch. f. Zucker-Ind. u. Landw.*, 1912, **41**, 932—938).—A further account of the method (*Proc. 8th Internat. Cong. Appl. Chem.*, 1912) in which the author employs ammonium chloride for inversion when estimating sugar in unpurified solutions. F. M. G. M.

Estimation of Starch and Dextrin in Sugar Products, Confectionery, etc. A. AUGUET (*Ann. Falsif.*, 1913, **6**, 143—147).—In the method proposed, 0·5 gram of the substance is inverted by heating at 70° with 1% hydrochloric acid, and the reducing sugars are then estimated by titration with Fehling's solution in the usual way. Another portion of 0·5 gram of the sample is inverted by heating it with 2% hydrochloric acid for one hour at 110°, and the reducing sugars now present are estimated. The difference between the two estimations, expressed in terms of invert sugar, is multiplied by 0·9 to give the quantity of starch or dextrin. A preliminary examination of the substance under the microscope, and a test with iodine solution, will show whether starch or dextrin is present, or which of these preponderates. W. P. S.

Difficulties in the Colorimetric Estimation of Vanillin. W. S. HUBBARD (*J. Ind. Eng. Chem.*, 1912, **4**, 669—670).—The American official method (Bureau of Chemistry) of estimating vanillin colorimetrically with bromine water and ferrous sulphate is considered to have the following disadvantages:

(1) A difficulty in getting the maximum coloration; the original method of adding the ferrous sulphate first gives a deeper colour than the present one, where the bromine is added first.

(2) It is difficult to add only enough lead cream to decolorise the solution, and when different quantities are added, the depth of colour subsequently obtained varies.

(3) Dilution of the sample influences the colour.

(4) Much larger amounts of ferrous sulphate are necessary in comparison with bromine water to produce a maximum colour.

(5) Lead cream forms a yellow, crystalline lead vanillin derivative, $(C_8H_7O_3)_2Pb$, which renders a quantitative estimation impossible in the presence of lead.

(6) It seems possible that vanillin is oxidised to pyrocatechuic acid. F. M. G. M.

A New Colorimetric Method for the Determination of Vanillin in Flavouring Extracts. OTTO FOLIN and WILLEY DENIS (*J. Ind. Eng. Chem.*, 1912, **4**, 670—672).—The Winton method (A., 1905, ii, 620) for estimating vanillin, although accurate, is somewhat lengthy, and the following colorimetric method has now been employed. The recently described phosphotungstic-phosphomolybdic acid reagent (A., 1912, ii, 1011), when added to an acid solution of vanillin, gives, on addition of sodium carbonate a rich blue colour. The vanillin extract (5 c.c.) is treated with 75 c.c. cold water and 4 c.c. of a solution of lead acetate; the volume made up to 100 c.c., the solution filtered, and a measured quantity of the filtrate shaken with 5 c.c. of the reagent, and after five minutes made up to a known volume with a saturated solution of sodium carbonate. After filtration, the resulting dark blue liquid is compared in a Duboscq colorimeter with a similarly treated standard vanillin solution. F. M. G. M.

Estimation of Acetone in Urine. O. SAMMET (*Zeitsch. physiol. Chem.*, 1913, **83**, 212—225).—Various methods for the estimation of acetone have been submitted to critical examination, particular attention being paid to the application of the methods to the estimation of acetone in urine. Graaf's *p*-nitrophenylhydrazone method (A., 1907, ii, 588) was found to yield from 95·5 to 96·2% of the quantity of acetone actually present when the amount of acetone varied from 0·1 to 0·2 gram per 100 c.c. of urine. Messinger's method (compare A., 1908, ii, 234) also yielded trustworthy results. When this method is used for the estimation of acetone in urine, the latter should be treated with tartaric acid and distilled; calcium carbonate is then added to the distillate, and the mixture again distilled. The second distillate is rendered alkaline with potassium hydroxide solution, an excess of $N/10$-iodine solution is added, and, after shaking, the mixture is acidified with hydrochloric acid, and the excess of iodine is titrated with thiosulphate solution. Each c.c. of $N/10$-iodine solution is equivalent to 0·000967 gram of acetone. The yield obtained by the method was about 96% of the quantity of acetone present. Oppenheimer has employed a method proposed originally by Denigès (A., 1899, i, 475), but the author finds that the results obtained are about 10% too high when Oppenheimer's factor (0·055) is used for converting the weight of the precipitate into acetone; better results are obtained when the factor 0·0495 is employed. The volumetric method of estimating the mercury in the precipitate is untrustworthy. The author has also attempted to estimate the amount of

acetone from the volume of the precipitate obtained in Denigès' method; the precipitate was subjected to centrifugal action until it ceased to decrease in volume, and it was found that the volume of the precipitate multiplied by 0·0912 gave the weight of acetone. This is only the case when the volume of the precipitate does not exceed 0·4 c.c., and even then the results obtained are not strictly concordant. W. P. S.

Estimation of Acetone Substances in Blood and Tissues by Micro-methods. W. McKim Marriott (*Proc. Amer. Soc. Biol. Chem.*, 1912–13, xxvii; *J. Biol. Chem.*, **14**).—Acetone, acetoacetic acid, and β-hydroxybutyric acid may be estimated in 2 to 5 c.c. of blood. Acetone is distilled off and estimated by the turbidity it occasions in an alkaline mercury silver cyanide solution by the nephelometer; β-hydroxybutyric acid is estimated by oxidation to acetone after removal of proteins and sugar. W. D. H.

Applied Plant Microchemistry. VII. Microchemistry and Microsublimation of Some Methane Derivatives. Otto Tunmann (*Chem. Zentr.*, 1913, i, 192; from *Apoth. Zeit.*, 1912, **27**, 971—974, 983—985).—Diagrams are given showing the different sublimation forms of hydroxymethylanthraquinone from rhubarb root, mannitol from manna, *Olea europaea* and *Fraxinus ornus*, maleic acid and its anhydride from *Sorbus aucuparia* and *Euphorbium*, citraconic acid and its anhydride from the citric acid of *Citrus*, sorbic acid from *Sorbus aucuparia*, and fatty acid crystals with their myelin forms from *Areca catechu*, *Illicium religiosum*, and *Elaeis guinensis*. J. C. W.

The Detection and Estimation of Cyanogen and Hydrogen Cyanide. F. H. Rhodes (*J. Ind. Eng. Chem.*, 1912, **4**, 652—655).—Two absorption tubes, the first containing 10 c.c. of a 10% solution of silver nitrate and one drop of $N/6$-nitric acid, and the second, 10 c.c. of $N/2$-potassium hydroxide, are connected, and the gaseous mixture of cyanogen and hydrogen cyanide passed through them, followed by a slow current of air for about ten minutes. The tube containing potassium hydroxide is then disconnected, treated with 5 c.c. of a solution of ferrous sulphate and one drop of a solution of ferric chloride; after about fifteen minutes the precipitated ferrous-ferric hydroxides are dissolved with dilute sulphuric acid, when the appearance of a distinct green colour, or of a blue precipitate, proves the presence of cyanogen in the original gas. The hydrogen cyanide is quantitatively absorbed by the silver nitrate, whilst the cyanogen is converted by the potassium hydroxide into potassium cyanide and potassium cyanate, which can be quantitatively estimated if required:

$$(CN)_2 + 2KOH = KCN + KCNO + H_2O.$$ F. M. G. M.

Estimation of Creatine and Creatinine in Diabetic Urines. Isidor Greenwald (*J. Biol. Chem.*, 1913, **14**, 87—94).—In urines containing acetoacetic acid or acetone, creatinine may be estimated

accurately by Folin's method only after these substances are removed. Dextrose in concentrations up to 5% has no appreciable effect on the estimation of creatine by the Folin method.

W. D. H.

The Colour Reactions of Certain Indole Derivatives and their Significance with Regard to the Glyoxylic Reaction. (Miss) ANNIE HOMER (*Biochem. J.*, 1913, **7**, 116—126).—The formation of coloured condensation products from indole derivatives and certain aldehydes necessitates the use of condensing agents. The reaction takes place between the ·NH group of the indole nucleus and the ·CHO group of the aldehyde. The evidence adduced confirms the view originally advanced by Rosenheim that the Adamkiewicz reaction is primarily a formaldehyde reaction. In Hopkins and Cole's modification of the test, glyoxylic acid reacts by virtue of its decomposition into formaldehyde; the latter is in a nascent state, and therefore more reactive. W. D. H.

Some Colorimetric Estimations; Rowntree and Geraghty's Method for Diagnosing the Kidneys; the Estimation of Thiocyanates in Saliva and of Iodine in Urine. WILHELM AUTENRIETH and ALBERT FUNK (*Chem. Zentr.*, 1913, i, 661; from *München. med. Woch.*, 1912, **59**, 2657—2660, 2736—2739).—Rowntree and Geraghty's method for observing the functions of the kidneys (*J. Pharm. exper. Ther.*, 1910, **1**, 519) depends on the injection of phenolsulphonephthalein and its detection in the urine by means of the red colour produced by alkalis. For quantitative purposes, Autenrieth and Koenigsberger's colorimeter is recommended. A normal kidney excretes 45—60% of the reagent during the first hour after intramuscular injection, and 70—90% by the end of two hours; a kidney which excretes less than 45% is unhealthy.

The same apparatus may be applied to the estimation of thiocyanates in saliva; 0·1 to 1·0 mg. KCNS in 10 c.c. of solution may be estimated.

The colorimetric estimation of iodine in urine is very exact, since iodine may be completely extracted by chloroform, and the solution is easily standardised. If the iodine is present in ionic combination, it is liberated by sodium nitrite, but if not, the urine must be evaporated and the iodine set free from the ash. J. C. W.

Estimation of Pepsin. STEFAN VON BOGDANDY (*Zeitsch. physiol. Chem.*, 1913, **84**, 18—28).—The principle involved consists in precipitating the unchanged casein after digestion with pepsin for a stated time and the determination of the optical rotatory power of the filtrate. The precipitating reagent contains 150 grams of sodium sulphate, 50 grams of magnesium sulphate, and 100 c.c. of 96% alcohol in 1000 c.c.; 60 c.c. of a $3\frac{1}{2}$% casein solution containing 5·5 c.c. of normal hydrochloric acid per 100 c.c. are digested with pepsin at 40°, 30 c.c. of the precipitating reagent are added, and the volume made up to 100 c.c.; the contents of the vessel are well

shaken and filtered, and the clear liquid examined in the polarimeter.

The method is applied to determining the influence of varying the time, amount of enzyme or substrate, and the amount of acid on the velocity constants of the reaction calculated from the expressions of Schütz and of Arrhenius. The results confirm those obtained by the alternative methods, to which the new method is to be preferred on account of its simplicity and accuracy. E. F. A.

New Reagent for Detecting Blood. ROBERT F. RUTTAN and R. H. M. HARDISTY (*The Canadian Med. Assoc. J.*, Nov., 1912. Reprint. 4 pp.).—A 4% solution of tolidine in glacial acetic acid is recommended for the detection of small quantities of blood. One c.c. of the liquid to be tested for blood is treated with 1 c.c. of 3% hydrogen peroxide and 1 c.c. of the reagent; if blood is present a green to bluish-black coloration develops gradually and persists for several hours. The reagent was found to be capable of detecting 1 part of blood in 7,000,000 parts of aqueous solution, 1 in 24,000 parts of urine, 1 in 100,000 parts of fæces, or 1 in 30,000 parts of stomach-contents; it is more sensitive than the similar benzidine reagent (A., 1911, ii, 348). W. P. S.

Application of the Ammonium Carbonate Method for the Estimation of Humus in Hawaiian Soils. J. B. RATHER (*J. Ind Eng. Chem.*, 1913, **5**, 222—223).—The ammonium carbonate method (compare *ibid.*, 1911, **3**, 660) for the estimation of humus in soils has given uniformly good results on a number of the soil types of the United States, but on exceptional soils, such as those of Hawaii, it must be modified, as follows, in order to remove the clay. The solution is prepared according to the official method, except that it is decanted instead of being filtered; 100 c.c. are placed in a graduated flask, 2 grams of ammonium carbonate added, and the whole heated for an hour on the steam-bath. After keeping overnight, 50 c.c. of the supernatant solution are pipetted off, and evaporated to dryness in a tared dish; dried for three hours at 100°, weighed, ignited, and weighed again. The loss in weight represents the humus. T. S. P.

Estimation of Colloids in Effluents containing Sugar. PAUL ROHLAND and V. MEYSAHN (*Zeitsch. Ver. deut. Zuckerind.*, 1913, 167—168).—One hundred c.c. of the neutral effluent free from suspended matters are treated with 1 c.c. of a 1% aniline-blue solution, and then evaporated to a syrupy consistence. This is mixed with hot water, and the insoluble, coloured residue is collected on a weighed filter, washed with hot water, dried, and weighed. The excess of aniline-blue is estimated colorimetrically in the filtrate, thus giving the weight of the dye contained in combination with the colloids in the insoluble residue; on subtracting the weight of the dye from that of the total precipitate, the weight of colloid is found. W. P. S.

General and Physical Chemistry.

Determination of the Refractive Indices of Gases under High Pressures. II. The Dispersion of Air and Carbon Dioxide. LODEWYK H. SIERTSEMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 925—931. Compare A., 1912, ii, 213).—The author has measured the refractive index of air at pressures varying from 30 to 100 atmospheres, and of carbon dioxide at pressures between 20 and 47 atmospheres. The observations were made with light of wave-length ranging from $\lambda = 405$ to $\lambda = 644\mu\mu$. The results show that in both cases the dispersion constants are independent of the pressure within the limits of experimental error. The values of the constants are compared with those obtained by previous observers.

H. M. D.

Further Remarks on a Formula for the Index of Refraction of Binary Mixtures. FRÉDÉRIC SCHWERS (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 447—452).—A reply to the criticism of Mazzucchelli (this vol., ii, 165).

R. V. S.

Iridescent Layers of Gelatin and their Employment in the Manufacture of Artificial Pearls. RAPHAEL E. LIESEGANG (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 181—188).—The author has made experiments on the nature of the iridescent films which are obtained when a solidified gelatin solution of a calcium salt is allowed to interact with a solution of an alkali phosphate. To obtain these films, a drop of calcium nitrate solution is added to 5 c.c. of a 10% solution of gelatin, which is spread on a glass plate and allowed to solidify; a solution of trisodium phosphate is then brought into contact with the layer of gelatin, and the plates are left undisturbed for some hours. The iridescence appears to be due to the precipitation of calcium phosphate in the form of a more or less regular succession of layers of precipitate, which give rise to a grating-like structure.

The conditions under which this diffusion effect may be utilised for the production of "artificial pearls" are discussed. The iridescent gelatin films may be hardened by the action of formaldehyde vapour.

H. M. D.

Dispersion of Metals. LYNDE P. WHEELER (*Phil. Mag.*, 1913, [vi], **25**, 661—679; *Amer. J. Sci.*, 1913, [iv], **35**, 491—508).—From an examination of the available data for the dispersion of silver, copper, gold, nickel, and cobalt, it is found that the results obtained by different observers differ in general by an amount which is considerably greater than the errors inherent in the methods of measurement employed.

From a comparison of the data with the dispersion formulæ derived from the electron theory, it appears that the number of

free electrons is not constant, but increases with the frequency of the currents set up by the incident radiation. The rate of increase is relatively small in the infra-red, but is much greater in the regions where the metals are more transparent.

It is also shown that the dispersion of the dielectric constant can be calculated from the optical constants for the above metals. The value of the dielectric constant at any wave-length is resolvable into two parts, which may be distinguished as the "dielectric" and "conductor" parts. The latter, which depends on the presence of free electrons, is more important than the pure dielectric term, especially at the shorter wave-lengths. In general, the form of the dispersion curves is not inconsistent with that indicated by theory, but the experimental data are scarcely accurate enough to test the point satisfactorily. H. M. D.

Absorption of Light by Inorganic Salts. VII. Aqueous Solutions of Iron Salts. JOHN S. ANDERSON (*Proc. Roy. Soc. Edin.*, 1913, **33**, 35—43. Compare A., 1911, ii, 785, 786; 1912, ii, 597).—The apparatus employed for the measurements was the same as that described in previous papers. The salts examined were ferric chloride, bromide, nitrate, and sulphate, and ferrous chloride and sulphate. Observations were made over the region extending from $\lambda=434\mu\mu$ to $\lambda=1300\mu\mu$, and curves are plotted from the results which show the variation of the molecular extinction coefficient with the wave-length of the absorbed rays, and also the influence of the concentration of the dissolved salt on the absorption.

For the chloride, nitrate, and sulphate, the infra-red band increases in height, and the maximum point of the band shifts towards the visible region on dilution, whereas with ferric bromide the height of the band decreases with dilution, although the shift is in the same direction as for the other ferric salts. The infra-red band of ferrous chloride shows but little alteration when the concentration of the solution is varied.

The absorption in the visible spectrum increases with dilution in the case of ferric nitrate and sulphate, but decreases with dilution for the bromide. For the chloride the absorption decreases at first with dilution, and then increases to a slight extent. This is supposed to be due to the formation of colloidal hydroxide. The absorption of freshly prepared solutions of the ferric salts differs quite appreciably from that of solutions which have been prepared for some time. H. M. D.

Absorption of Light by Inorganic Salts. VIII. Alcoholic Solutions of Copper, Cobalt, and Nickel Salts in the Ultra-violet. ALEXANDER R. BROWN (*Proc. Roy. Soc. Edin.*, 1913, **33**, 44—48. Compare preceding abstract).—The salts examined were the chlorides and bromides, and in the case of copper, the sulphate, observations being made over the region $\lambda=265\mu\mu$ to $\lambda=450\mu\mu$. The calculated molecular extinction coefficients are plotted against the wave-lengths, and the resulting curves are compared. The

nickel salts afford evidence of a new absorption band with its maximum at about $\lambda = 410\mu\mu$. H. M. D.

Absorption of the Ultra-violet Rays by Ketones, Diketones, and Ketonic Acids. JEAN BIELECKI and VICTOR HENRI (*Compt. rend.*, 1913, **156**, 1322—1324. Compare this vol., ii, 263).—The authors have determined the molecular coefficients of absorption and the positions of maximum and minimum absorption of a number of aliphatic ketones and diketones and ketonic acids, and from their results have drawn the following conclusions. All substances having the general formula, $C_nH_{2n+1}\cdot CO\cdot C_mH_{2m+1}$, have an absorption band between $\lambda = 2700$ and 2800, the position and height of the band varying but little with m and n. For the homologues above methyl ethyl ketone, a minimum absorption is often noticeable at λ 2400. The method of linking in the alkyl radicles and the position of the ketonic group have a marked effect on the value of the coefficient of absorption. The introduction of a second ketone group into the molecule increases the absorption, without altering the position of the maximum. The introduction of the carboxyl group into a ketone has a double effect in that the absorption due to the carboxyl group is increased, whilst that of the ketone group is diminished. Where a substance can exist in both the enolic and the ketonic form, the absorption varies considerably with the proportion of each form present. Methyl and ethyl acetoacetate exhibit a somewhat unusual absorption band in the region $\lambda = 2400$. W. G.

A Fluorescence Spectrum of Iodine Vapour. JOHN C. MCLENNAN (*Proc. Roy. Soc.*, 1913, *A*, **88**, 289—296).—An apparatus is described by means of which it has been possible to subject iodine vapour to intense illumination by light of wave-length extending from beyond $\lambda = 700\mu\mu$ down to $\lambda = 185\mu\mu$. The apparatus consists of an outer glass illuminating tube of the ordinary Cooper-Hewitt type, and an inner tube of clear fused quartz, which is sealed into the former by wax joints. The outer tube is furnished with mercury electrodes, and carries the mercury arc, whilst the inner tube, after the introduction of crystals of iodine, is exhausted and sealed off.

The fluorescence spectrum, which is exhibited by the iodine vapour under these conditions, is characterised by the presence of a large number of narrow bands extending from about $\lambda = 460$ to about $\lambda = 210\mu\mu$. More than eighty such bands have been recognised on the photographic records, and the mean wave-lengths of these are recorded.

When the inner quartz tube is replaced by a similar tube of glass, the band spectrum disappears. From this it is inferred that the emission of the banded spectrum is not due to the elevated temperature of the iodine vapour in the tube, but is a true resonance or fluorescence effect. The fact that the glass tube inhibits the banded spectrum indicates further that the exciting light consists of short-waved rays, which are absorbed by the walls of the glass tube.

The spectrum investigated by the author shows none of the lines

belonging to the fluorescence spectrum of iodine vapour examined by Wood (compare A., 1911, ii, 82, 170, 950; A., 1912, ii, 1018). The absence of these lines is probably due to the existence of a very considerable temperature gradient in the iodine vapour. In these circumstances, the light which constitutes the spectrum excited by the green and yellow mercury lines has to pass through a considerable column of cool iodine vapour, which causes the absorption of the fluorescence lines. H. M. D.

The Relationship between Fluorescence and Chemical Constitution. JOHANNES STARK (*Zeitsch. Elektrochem.*, 1913, **19**, 397—401).—Polemical. An answer to Liebig's criticism (this vol., ii, 170) of Stark's theory of fluorescence (this vol., ii, 2). Stark briefly reiterates the main points of his theory, and points out reasons why fluorescence has not been observed in so large a number of organic compounds. He points out that Liebig's view, that the fluorescence of acetone, diacetyl, etc., is due to their decomposition by the light employed in the experiments, is not in accordance with experimental facts. These substances show the fluorescence instantaneously and at its maximum intensity as soon as the light is brought to bear on them, and do not slowly grow in intensity as would be required if Liebig's view were correct. J. F. S.

Photoelectric Investigation of Fluorescent Substances. WILHELM E. PAULI (*Ann. Physik*, 1913, [iv], **40**, 677—700).—A number of fluorescent substances have been examined with respect to their photoelectric activity in order to ascertain whether there is any connexion between the two effects. The substances chiefly examined were anthracene, 2 : 5-dimethoxybenzylideneindandione, *m*-aminocyanostilbene, and 2 : 5-dimethoxycyanostilbene, all of which are excited to maximum fluorescent activity by light in the visible region. In regard to their photoelectric properties, it was found that none of these substances is excited to measurable photoelectric activity by light of wave-length greater than $\lambda = 420\mu\mu$, although they all become active when subjected to the influence of ultra-violet rays. If the distribution curves showing the influence of the wave-length of the exciting light on the fluorescent and photoelectric effects are compared, it is evident that the two phenomena are not genetically related. The results are discussed with reference to the explanation of the fluorescence and photoelectric emission effects in terms of the electron theory. H. M. D.

The Various Photoelectric Effects shown by Anthracene, their Relations to One Another and to the Fluorescence and the Formation of Dianthracene. MAX VOLMER (*Ann. Physik*, 1913, [iv], **40**, 775—796).—From an investigation of the photoelectric properties of solutions of anthracene in carefully purified hexane, it has been found that the Hallwachs effect is not produced by light of that range of wave-lengths which gives rise to fluorescence and to polymerisation of the anthracene, that is, by light extending from $\lambda = 400$ to $\lambda = 225\mu\mu$. With shorter-waved rays, the Hallwachs effect can, however, be readily detected.

The longer-waved rays referred to give rise to a different type of photoelectric effect, which consists in the decomposition of the solid anthracene with the formation of ions, which are sent off by the layer of anthracene on the illuminated electrode under the influence of the applied electric field. According to whether the electrode is positively or negatively charged, the emitted ions are positive or negative. A similar effect is found in the case of solutions of sulphur in hexane, except that in this case the effect is unipolar, and the photoelectric ionic emission appears to be confined to positively charged ions.

It has been further shown that hexane solutions of anthracene increase in electrical conducting power to a large extent when subjected to the influence of ultra-violet rays of wave-length less than $\lambda = 225\mu\mu$. This alteration in the conductivity appears to be due to ionisation in the solution, and is attributed to the emission of electrons by the dissolved molecules under the influence of the short-waved rays.

The observations are discussed in reference to Stark's theory of fluorescence and to the nature of the process which yields dianthracene. In particular it is shown that Byk's theory of the polymerisation process, in so far as this assumes that the primary stage consists in the emission of electrons, is inconsistent with the author's observations. H. M. D.

An Electrically Heated Contrivance Attached to the Polarimeter for Determining Rotatory Powers at a Constant Temperature. EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1913, **84**, 300—304).—An apparatus is described and figured to take six polarimeter tubes 2·5 cm. in length, of 2 c.c. capacity, in which the tubes are placed and heated electrically to a constant temperature. By rotating a screw, the tubes are brought one after the other into the field of vision and observed. E. F. A.

Optical Observation Tubes (Polarimeter Tubes). SIGMUND NEUMANN (*Chem. Zeit.*, 1913, **37**, 520—521).—When a glass polarimeter tube gets broken there is often a difficulty in fitting the metal end pieces and caps to a new tube, owing to the want of an exact fit. This difficulty is obviated if each end of the tube is made conical in shape, or perhaps it is better to say, funnel-shaped. A metal ring, made in two halves, and screwed on the outside, is made to fit the cone, and is kept in position by a narrow ring screwing on to it. The end piece, containing the cover glass, then screws on to the metal ring. Owing to the conical shape, it is not necessary for the tube and ring to fit exactly, the desired tight joint being made by means of, for example, a wrapping with the insulation ribbon used by the electrician. The fittings need not necessarily be of metal; ebonite, or a combination of ebonite and metal, may be used. The conical end pieces have the further advantage that small air bubbles may be collected in them without interfering with the line of vision through the tube. T. S. P.

Measurements on the Ultra-violet Magnetic Rotation in Gases. J. F. Sirks (*Physikal. Zeitsch.*, 1913, **14**, 336—343).—The magnetic rotation of the plane of polarisation of ultra-violet rays of different wave-lengths has been examined in experiments with oxygen, hydrogen, and carbon dioxide. In the case of oxygen the measurements of the rotation extend to $\lambda = 265{\cdot}4$, of hydrogen to $\lambda = 237{\cdot}8$, and of carbon dioxide to $\lambda = 248{\cdot}2\mu\mu$. The rotation increases rapidly as the wave-length of the ultra-violet light diminishes, and the values for the different gases appear to fit in satisfactorily with the data obtained by Siertsema for the rotation of rays in the visible spectrum. By combining the two series of results, and plotting the rotation (relative to the rotation for the yellow mercury line) as ordinate against wave-length as abscissa, it is shown that continuous curves are obtained in the case of each of the three gases. The curve for oxygen is much lower than the curves for the two other gases, and of these the hydrogen curve is the higher.

The observed magnetic rotation of ultra-violet rays in hydrogen is shown to be at variance with the assumption that the action of the molecules on the ultra-violet light can be referred to a single type of electron, for which e/m is constant. H. M. D.

The Dissociation of Gaseous Compounds by Light. Gaseous Hydrogen Compounds of the Nitrogen and Carbon Groups. Different Gases. Daniel Berthelot and Henry Gaudechon (*Compt. rend.*, 1913, **156**, 1243—1245. Compare this vol., ii, 369).—The rule that, for the hydrogen compounds of elements of the same group, the stability with respect to light diminishes as the atomic weight increases, holds good in the case of the nitrogen and carbon groups. Zinc ethyl is rapidly decomposed by the light from a mercury-quartz lamp. Carbonyl chloride is slowly decomposed by the extreme ultra-violet rays, whilst sulphur hexafluoride is unaffected by the light from a mercury lamp. W. G.

A Simple Method for the Absolute Measurement [of the Energy] of Ultra-violet and Visible Light Rays. Christian Winther (*Zeitsch. Elektrochem.*, 1913, **19**, 389—397).—An instrument is described, termed a fluorometer, by means of which the energy of a ray of given wave-length can be measured irrespective of the presence of ultra-red rays. The principle involved consists in allowing a beam of light from a normal lamp, after passing through light filters, to enter a rectangular quartz vessel, which is filled with a fluorescent material. In this way a narrow, fluorescent beam is produced in the quartz vessel. A second beam is produced, parallel with and a few millimetres removed from the first beam, by the light under investigation. This second beam enters at the opposite side of the vessel. By means of a lens and cross wire moving over a graduated scale, the position of equal brightness is measured. From this value, by means of the expression $\log i_0/I_0 = (m + m_n)(d_2 - d_1)$, where i_0 and I_0 represent the light quantities in the two cases, m and m_n the extinction coefficients of

the two rays, and d_2 and d_1 the lengths of the two fluorescent beams at which equal brightness is obtained. The method of determining the energy quantity from these results is fully explained, together with possible errors and precautions necessary in using the method. The fluorescent solutions employed by the author are: (1) Rhodamine-*B*, made up of 0·004 gram per litre, useful for wave-lengths 600 to 460$\mu\mu$, and can also be used for the ultra-violet from 340$\mu\mu$ and downwards. (2) Sodium fluorescein, made up of 0·01 gram per litre + 2·50 c.c. of *N*-sodium hydroxide, useful for wave-lengths from 520$\mu\mu$ down to 254$\mu\mu$. (3) Quinine sulphate, made up of 0·1 gram per litre + 4 c.c. *N*-sulphuric acid, useful down to 260$\mu\mu$. In addition to its uses for the measurement of energy values, this instrument is shown to be serviceable in measuring absorption curves, and also the reaction velocities of light-sensitive and non-sensitive systems. A number of light filters for various regions are described, and a criticism of many of the older light filters is given.

J. F. S.

A Quantitative Study of Some Photochemical Effects Produced by Ultra-violet Light. J. Howard Mathews and Leon H. Dewey (*J. Physical Chem.*, 1913, **17**, 211—218).—Various solutions of 0·1*N* strength were exposed at 25° in a quartz flask to a Cooper-Hewitt quartz mercury vapour lamp at 10 cm. distance. Under these conditions oxalic acid is very slightly affected, but in presence of uranium nitrate, sulphate or acetate is rapidly oxidised at a linear rate proportional to the uranium concentration. It is deduced that the decomposing action of ultra-violet light is dependent on the amount of light photochemically absorbed.

Potassium permanganate and dichromate solutions are very stable towards ultra-violet light, but the oxidation of sodium sulphite in contact with air is accelerated thereby. R. J. C.

The Photosensitiveness of Fehling's Solution. Alan Leighton (*J. Physical Chem.*, 1913, **17**, 205—210).—According to Byk (A., 1905, ii, 70), Fehling's solution is decomposed by light of wave-lengths less than 400$\mu\mu$, corresponding with an absorption band in the ultra-violet, whereas the red and yellow waves of the visible absorption bands have no action. This is contrary to the rule that radiations which are absorbed by a substance tend to destroy it.

It is suggested that the red light absorbed by Fehling's solution is not active enough to produce decomposition unaided, whereas in presence of a suitable reducing agent its activity might be sufficiently reinforced for it to do so. In accordance with this suggestion, the author finds that in presence of quinol within certain very narrow limits of concentration, Fehling's solution is reduced by red light, but is stable in the dark. R. J. C.

Phototropic Phenomena with Stilbene Derivatives. Hans Stobbe and Heinrich Mallison (*Ber.*, 1913, **46**, 1226—1238).—It has been discovered that a small class of compounds, of which

p-diacetyldiaminostilbene-*o*-disulphonic acid is typical, exhibits phototropy; the substance mentioned, when exposed to direct sunlight for a few minutes, changes from bright yellow to reddish-brown, and reassumes its original colour when kept in the dark; the salts of the substance behave in a similar manner, the only variation being in the colours. The most effective light rays are included between λ 490 and 271$\mu\mu$, and, indeed, this group of rays exerts a much more marked effect than the beam of light from which it is selected, because yellow and red rays accelerate the reverse change, thus favouring the restoration of the substance to the original form. Experiments with the sodium salt of diacetyldiaminostilbenedisulphonic acid show that rise in temperature has much less effect on the direct change than on the reverse, so that with an increase in temperature the illumination to produce a constant effect must be greater. It is also discovered that the presence of oxygen is necessary to the effect of light on the substance and its salts, and the application of paper soaked with an alcoholic solution of tetramethyldiaminodiphenylmethane (Arnold and Mentzel, A., 1902, ii, 352) proves the simultaneous formation of a little ozone. A photographic plate failed to detect any luminescence during the reversion of the "excited" substance to its original condition.

An examination of a number of derivatives shows that, although many give an irreversible colour change, phototropy occurs only with those which, in addition to the ethylenic linking, contain the sulphonic acid group, together with the formyl or acetyl radicle.

It remains undecided whether the oxygen exerts a mere contact effect, or acts by addition and elimination, but assuming the latter view, explanations are tentatively proposed as to the possible mechanism of the change. D. F. T.

Quantitative Relation between the Range of the α-Particles and the Number of Changes Emitted During Disintegration. A. VAN DER BROEK (*Phil. Mag*, 1913, [vi], **25**, 740—742).—Only the charges carried by the α-particles are considered, those carried by the β-particles being apparently neglected. The following relations seem to exist: $\log V_{\alpha} = A + nB$, and $\log \lambda = C + nD$, where V_{α} is the velocity of the α-ray, n the number of charges expelled from the commencement of the disintegration series, B and D general constants, and A and C special constants for each series. F. S.

Magnetic Spectrum of the β-Rays of Radioactinium and its Disintegration Products. OTTO VON BAEYER, OTTO HAHN, and LISE MEITNER (*Physikal. Zeitsch.*, 1913, **14**, 321—323).—The radioactinium, which had accumulated in an actinium solution after keeping for some weeks, was precipitated by ammonium thiosulphate after the addition of a small quantity of zirconium nitrate. This was purified by a second precipitation, dissolved in dilute hydrochloric acid with the addition of a drop of dilute nitric acid, and the boiling solution electrolysed with a silver wire as cathode. In this way a thin layer of radioactinium was obtained, which was employed in

the photographic investigation of the magnetic spectrum. The photograph obtained by exposure of the plate for nine hours to the action of the freshly prepared substance affords evidence of the emission of β-rays with velocities equal to 0·73, 0·67, 0·60, 0 53, 0·49, 0·43, and 0·38 of the velocity of light. At the end of ten days a further photograph was taken of the magnetic spectrum, which showed the emission of β-rays with the velocities 0·91, 0·74, 0·66, 0·60, 0·42, and 0·38. The intensities of the lines on the two photographs indicate that the rays 0·91, 0·74, 0·66, and 0·60 are due to actinium-*X* and the active deposit, whilst the rays 0·53, 0·49, 0·43, and 0·38 are due to radio-actinium.

The highly penetrating rays which have been previously referred to (A., 1908, ii, 1007) are now shown to be γ-rays. H. M. D.

Analysis of the γ-Rays from Radium-*B* and -*C*. ERNEST RUTHERFORD and H. RICHARDSON (*Phil. Mag.*, 1913, [vi], **25**, 722—734). —An analysis of the γ-rays of radium, now known to be complex, and due in part to radium-*B* as well as radium-*C*, has been made by absorption methods. An α-ray tube, filled with radium emanation, was placed in a magnetic field to deflect primary β-rays, and the ionisation in the electroscope measured both in air and in a mixture obtained by passing hydrogen through methyl iodide, in order to exaggerate the relative effect of the very easily absorbed radiation. After passage through 6 cm. of aluminium, the absorption is exponential with the value $\mu=0·115$ or $\mu/D=0·0424$, as found by Russell and Soddy. Between 0·05 and 6 cm. of aluminium, a curve was obtained which, when the effect of the hard γ-rays was subtracted, was exponential with the value $\mu=0·51$ in aluminium. This is due to radium-*B*. Similarly, between 0 and 0·08 cm. of aluminium, a radiation, exponentially absorbed with $\mu=40$, was obtained. Evidence of a still softer radiation ($\mu=230$) was also obtained, but it is inconclusive.

From pure radium-*C*, deposited on nickel by von Lerch's method, the radiation is exponentially absorbed ($\mu=0·115$) after 0·2 cm. of aluminium. A soft radiation was present, but it was probably due to a secondary characteristic radiation from nickel, and was not observed when silver was used. When lead was used as the absorbent, the soft radiations from radium-*B* were not exponentially absorbed, and the value of μ varied from 11 to 2·8.

Thus, radium-*B* emits certainly two, and perhaps three, types of γ-rays, whilst radium-*C* emits only one. The radiation, $\mu=40$, corresponds with the characteristic *X*-radiation in the L series to be expected from an element of atomic weight 214. The second type, $\mu=0·51$, probably corresponds with another series not so far observed for the *X*-rays. The energy of the softer type of γ-rays from radium-*B* ($\mu=40$) is very small compared with that of the more penetrating types from radium-*B* and -*C*. F. S.

Production of Photochemically Active Rays in Ordinary Chemical Reactions. J. HOWARD MATHEWS and LEON H. DEWEY (*J. Physical Chem.*, 1913, **17**, 230—234. Compare A., 1912, ii, 116). —When zinc is dissolved in acid, or calcium carbide is acted on

by water in proximity to a photographic plate, and the gases evolved are led away, the plate remains unaffected. When, however, as in Matuschek and Nenning's experiments (A., 1912, ii, 116), the gaseous products are allowed to come into contact with the plate, reduction occurs, and images are formed of pieces of tinfoil, etc., laid upon the plate in such a way as to protect it from the gases. Writing may be produced on a photographic plate, using a jet of hydrogen as a pen and afterwards developing.

No photographic effect could be detected in the case of reactions, such as the slaking of lime, which give no gaseous products. The conclusion is drawn that Matuschek and Nenning's chemically active rays do not exist. R. J. C.

The Rontgen Ray Luminescence of Mercury Vapour. ST. LANDAU and H. PIWNIKIEWICZ (*Physikal. Zeitsch.*, 1913, **14**, 381—386).—It is shown that the action of *X*-rays on mercury vapour causes the emission of a bluish-green light. The intensity of the luminous emission increases with rise of temperature, but this is entirely due to the increase in the density of the saturated vapour. From observations with unsaturated mercury vapour, it appears that the temperature of itself has no influence on the intensity of the luminosity.

The luminosity becomes less intense when foreign gases are admixed with the mercury vapour. The comparative observations made with nitrogen, carbon dioxide, and hydrogen show that the first two gases have approximately the same influence, whilst hydrogen is appreciably more active in reducing the luminosity. The spectrum of the *X*-ray luminescence appears to be continuous with a maximum intensity at about $\lambda = 410\mu\mu$. H. M. D.

Relationship between the Fluorescent Röntgen Rays. W. KAUFMANN (*Physikal. Zeitsch.*, 1913, **14**, 386—387).—It has been pointed out by Owen (A., 1912, ii, 516) that the absorption by various gases of the characteristic fluorescent rays which are emitted by the elements between iron and molybdenum is proportional to the fifth power of the atomic weight of the radiator. This relationship would appear to hold whatever the nature of the absorbing substance, and, furthermore, to be applicable to fluorescent rays of either the *L* or the *K* group. If the logarithms of the atomic weights of the radiators are taken as abscissæ, and the logarithms of the specific absorption of the characteristic rays in aluminium as ordinates, points are obtained which lie on a straight line, the tangent of the slope of which is very nearly equal to 5. For the two groups of rays, the lines are practically parallel. The *L*-rays emitted by a metal have the same properties as the *K*-rays emitted by another metal, the atomic weight of which is 1/2·7 of that of the first metal. H. M. D.

Demonstration of Fluorescent Röntgen Radiation. W. KAUFMANN (*Physikal. Zeitsch.*, 1913, **14**, 387—388).—An apparatus has been designed which affords a convenient means of demon-

strating the emission of fluorescent secondary rays by different metals when these are subjected to the action of Röntgen rays. In this apparatus, arrangements are made for moving disks of various metals into such a position that they are exposed to the rays from the anti-cathode of an X-ray bulb, which is placed so that the rays pass through an aperture in a lead plate into a wooden box, which on its lower side is provided with a narrow observation tube. Attached to the lower side of the lead plate which covers the top of the wooden box is a fluorescent screen, which is so arranged that it can only be acted on by the secondary rays emitted by the metal in front of the aperture, and not by the primary rays. By the movement of a rod to which the metal disks are attached, these can be brought into position at will and examined in respect of their behaviour towards the primary rays. By varying the pressure in the discharge tube, the character of the primary rays is readily varied, and the different metals can be compared at various stages of exhaustion. H. M. D.

Carriers of the Negative Thermionic Current in a Vacuum. GWILYM OWEN and ROBERT HALSALL (*Phil. Mag.*, 1913, [vi], **25**, 735—739).—The authors have made further experiments to determine the nature of the ions which are emitted at high temperatures by palladium, pure and commercial platinum, and iridium. From the influence which a magnetic field exerts on the negative thermionic current, it appears that the carriers consist almost entirely of electrons, and that if heavy ions are present at all, the proportion of the current carried by them is less than one two-thousandth, and probably less than one ten-thousandth, even at the highest temperatures. H. M. D.

The Actinium Products of Long Life. OTTO HAHN and MARTIN ROTHENBACH (*Physikal. Zeitsch.*, 1913, **14**, 409—410).—Actinium, radioactinium, and actinium-X have been obtained in as pure state, in the radioactive sense, as possible in order to determine the periods of the changes, and whether actinium itself gives a detectable radiation.

Actinium-X was prepared from radium-free actinium by precipitating the actinium and radioactinium with ammonia, adding iron to the acidified filtrate, and again precipitating with ammonia, and removing the actinium-X from the filtrate by a barium sulphate precipitation. The half-period, determined as the mean of a large number of closely agreeing decay curves of the β-rays, was 11·6 ($\pm$0·1) days ($1/\lambda(\text{day})^{-1}=16·8$). The usually accepted values are 10·2 and 15 days respectively.

Radioactinium was prepared by precipitating zirconium in a feebly acid solution of actinium by sodium thiosulphate and purifying the precipitate from actinium by repetition of the process. The β-ray decay curve agreed with the theoretical, for the half-periods of 19·5 days and 11·6 days for radioactinium and actinium-X respectively, and was exponential from the 115th to the 174th day from preparation, when the β-rays became too small for measure-

ment. After 450 days no α-radiation could be detected, showing that there is no appreciable residual activity. The value of $1/\lambda(\text{day})^{-1}$ for radioactinium is thus 28·2, in agreement with previous values.

Actinium was purified repeatedly from its products, as rapidly as possible to minimise their regeneration, and initially gave no detectable β-rays and only a very small trace (0·2 to 0·3% of the maximum) of α-rays. The possibility is not excluded that actinium may give a very strongly absorbed β-radiation, which, like that of radium-*D*, could be shown only by photographing the magnetic spectrum of the β-rays. F. S.

The Existence of Uranium-*Y*. ALEXANDER FLECK (*Phil. Mag.*, 1913, [vi], **25**, 710—712).—All attempts to repeat the work of Antonoff (A., 1911, ii, 844), who obtained evidence of a product, uranium-*Y*, with period 1·5 days, giving soft β-rays and some α-rays, and present in the uranium series in minute quantity, have been unsuccessful. Various methods of removing thorium in minute amount from large amounts of uranium proved incomplete, and with such uranium, the presence of thorium-*B* gave effects similar to those observed by Antonoff. With uranium, free from thorium, no trace of any other product except uranium-*X* was obtained.
F. S.

Growth of Radiothorium from Mesothorium-2. JOHN A. CRANSTON (*Phil. Mag.*, 1913, [vi], **25**, 712—715).—The object was to ascertain whether the production of radiothorium from mesothorium-2 was direct or occurred through an intermediate product, the parent of ionium, the analogue of radiothorium in the uranium series, being experimentally still unknown. By adding a trace of thorium to the mesothorium-barium solution, and precipitating with ammonia, mesothorium-2, radiothorium, and thorium-*B* and -*C* are obtained with the thorium. The precipitate, dissolved in the smallest quantity of acid, is treated with hydrogen peroxide, and the thorium and radiothorium removed, the final traces of thorium-*B* and -*C* being removed by adding a lead and bismuth solution and precipitating with hydrogen sulphide several times. The pure mesothorium-2 preparation was examined in a magnetic field to deflect β-rays from the electroscope, and the growth of α-rays with time observed. The curves agreed with the theoretical curves, calculated on the assumption that the production of radiothorium occurs directly, except over the initial few hours, when a rapid decay of an initial α-radiation rather than a rise from zero occurred. The difference curve is approximately exponential with the period of mesothorium-2, and suggests the possibility that some of the mesothorium-2 atoms disintegrate, with expulsion of an α-ray instead of a β-ray. The proportion, however, cannot be greater than 3 in 100,000, and owing to the similarity of period between mesothorium-2 and thorium-*B*, the point is left open for further examination. F. S.

The Preparation of Radioactive Substances from Thorium. Fritz Glaser (*Chem. Zeit.*, 1913, **37**, 477—478).—A substance, with activity corresponding with that of thorium-*X*, has been separated by means of the insolubility of its sulphate from the sulphuric acid solution of monazite sand. This substance, which is termed provisionally thorium-*Y*, as its manner of preparation is different from that of thorium-*X*, is left undissolved when thorium phosphate, precipitated by neutralising or diluting the monazite solution, is treated with sulphuric acid. F. S.

Radioactivity of Typical Soils in the United States. Richard B. Moore (*Bied. Zentr.*, 1913, **42**, 213; *Internat. Cong. Appl. Chem.*, 1912).—The radioactivity of twelve soils was investigated by Strutt's method. The radioactivity seems to be connected with the mineral composition rather than with the chemical composition. No definite conclusions could, however, be drawn. N. H. J. M.

Anomalous Dispersion in the Region of Short Electric Waves. F. Eckert (*Ber. Deut. Physikal. Ges.*, 1913, **15**, 307—329). —Experiments have been made to determine the behaviour of metals, water, and alcohols towards electric waves of short wavelength. The wave-lengths examined ranged from 17·5 to 88 mm. In contrast with certain previous statements, it has been found that the reflexion capacity of the metals amounts to 100% in agreement with theoretical requirements. This result is independent of the position of the plane of the electric vector.

Absorption measurements were made for water, methyl, ethyl, propyl, and *iso*butyl alcohols, and for glycerol, and in all cases anomalous dispersion was found in the region of wave-lengths submitted to examination. It is suggested that the absorption of these substances is not due to the presence of the hydroxyl group, but to the complex molecules which are formed as a consequence of association. The variation of the absorption with temperature is in agreement with this view. H. M. D.

Influence of the Valency of the Metal on the Photo-electrical Effect of Metallic Compounds. G. A. Dima (*Compt. rend.*, 1913, **156**, 1366—1368).—The author has compared the photo-electrical effects produced by salts of metals, capable of yielding two or more classes of compounds with varying valency of the metal, such as mercury, tin, iron, copper, etc., and in all cases finds that the compound in which the valency of the metal is least appears to have the greatest photo-electrical power. W. G.

Cathodic Sputtering. George W. C. Kaye (*Proc. Physical Soc. London*, 1913, **25**, 198—201).—An account is given of the volatilisation of an aluminium cathode in a discharge tube containing helium. The cylindrical electrodes were made by bending thin sheets of aluminium so that two opposite edges were nearly in contact. The sputtered deposit which appeared on the glass walls when the discharge tube was run at a moderate potential indicates that the

disintegration of the aluminium was practically restricted to the edges of the cathode. This would seem to show that the particles are shot off exclusively from those regions where the potential gradient has a maximum value. H. M. D.

Calculation of Equivalent Conductivity at Infinite Dilution. STUART J. BATES (*J. Amer. Chem. Soc.*, 1913, **35**, 519—535).—In interpreting the results of an investigation of the properties of solutions of electrolytes, the concentrations both of the ions and of the non-dissociated molecules must be known with considerable accuracy, and this involves an exact knowledge of Λ_0. The methods employed by Kohlrausch and Noyes for calculating Λ_0 values are discussed, and it is shown that these demand the assumption that the expression $(C\gamma)^2/C(1-\gamma)$ for the ionisation constant becomes zero at zero concentration. Graphic and algebraic methods for determining the value of n in Storch's equation (A., 1896, ii, 288) are developed. The variations of n with the concentration are compared for weak, medium, and strong electrolytes, and it is shown that, in all cases, as the concentration decreases, the value approaches more closely to that required by the law of mass action.

Methods are given for calculating the upper and lower limits between which the value of Λ_0 must lie. In the case of the uni-univalent salts for which Kohlrausch obtained data for solutions as dilute as 0·0001N, the difference between the limits is about 0·2%. An empirical graphic method is described for determining an upper limit and a "probable" value of Λ_0. The limiting values and "probable" values have been calculated for several salts, and show good agreement. The "probable" values have been adjusted by Kohlrausch's law of the independent migration of ions, and the resulting Λ_0 values are smaller than those generally employed. E. G.

Conductivity Maxima in Glycerol. STEWART J. LLOYD (*J. Physical Chem.*, 1913, **17**, 264—267).—Zinc chloride appears to be indefinitely soluble in glycerol at 150°. The solutions exhibit a maximum conductivity at 50° with 0·188 gram of zinc chloride per c.c., and at 100° with 0·271 gram. The maximum had not been attained at 150° with the strongest solution measured, namely, 0·6131 gram per c.c.

The falling off in the conductivity in concentrated solutions is held to be closely connected with the increased viscosity. The temperature-coefficient is very large, corresponding with a rapid fall in viscosity as the temperature is raised. Concentrated solutions solidify to a jelly-like paste on cooling from 150°. R. J. C.

Electric Conductivity of Mixtures of Selenious Acid and Ammonia. EUGÈNE CORNEC (*Ann. Chim. Phys.*, 1913, [viii], **28**, 697—701).—Measurements have been made of the electric conductivity of solutions obtained by mixing aqueous solutions of ammonia and selenious acid in different proportions. Five series of experiments were made, in which the concentrations of the

alkaline and acid solutions were respectively 1/8, 1/16, 1/32, 1/64, and 1/128 molar. The results are shown by a series of curves obtained by plotting the molecular conductivity as a function of the ratio of the proportions of the constituent solutions. The conductivity curves for the three most dilute solutions exhibit a minimum at the point corresponding with the acid selenite, NH_4HSeO_3, and in all cases the curves show a maximum at the point corresponding with $(NH_4)_2SeO_3$. There is no evidence of the formation of any other compound, as was suggested by the results obtained by Miolati and Mascetti (A., 1901, ii, 381). H. M. D.

Citrophosphate Solutions. III. The System Citric Acid–Phosphoric Acid–Sodium Hydroxide–Water. UGO PRATOLONGO (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 387—391. Compare this vol., ii, 282).—The author has investigated at 20° that part of the diagram of this system in which the production of citrophosphate compounds is most probable, and from the results (which are exhibited in curves) no evidence of the existence of citrophosphate can be obtained. The only solid phases observed were citric acid, monosodium citrate and disodium phosphate. R. V. S.

Aqua Regia. II. Effect of Chloride Ion on the Potential of the Nitric Acid Electrode. WILLIAM C. MOORE (*J. Amer. Chem. Soc.*, 1913, **35**, 333—340).—In an earlier paper (A., 1911, ii, 719) it has been shown that the chloride ion decreases the efficiency of dilute nitric acid in the oxidation of ferrous salts. In order to find an explanation, a study has been made of the effect of chloride ions on the oxidation potential of nitric acid. An attempt was made to obtain a value for the oxidation potential of a $N/10$-nitric acid electrode, saturated with nitric oxide, but constant results could not be obtained on account of the increase in the concentration of nitrous acid due to the reduction of the nitric acid by the nitric oxide and by the reduction of nitrate to nitrite ions. The experiments showed, however, that the potential of the nitric acid electrode was reduced in presence of the chloride ion, this being due probably to a decrease in the tendency towards nitrite ion formation.

The oxidation potential of $N/10$-nitric acid in equilibrium with nitrous acid and nitric oxide at atmospheric pressure is quite definite, and the chloride ion has no effect on it. The mean value of this potential is 0·4723 volt, measured against a $N/10$-calomel electrode at $25·17 \pm 0·02°$. E. G.

Potential of the Lithium Electrode. GILBERT N. LEWIS and FREDERICK G. KEYES (*J. Amer. Chem. Soc.*, 1913, **35**, 340—344).—The potential of the lithium electrode has been determined by a modification of the method employed in the case of the sodium and potassium electrodes (A., 1910, ii, 1027; 1912, ii, 225). The results show that the potential of lithium in a N-solution of lithium ions at 25° is 3·3044 volts against the normal calomel electrode taken as zero. This value is the sum of (1) 2·3542 volts, the potential of lithium amalgam (containing 0·0350% Li) against an aqueous

solution containing lithium ions in N-concentration, and (2) 0 9502 volt, the difference of potential between lithium and 0·0350% lithium amalgam in a solution of lithium iodide in propylamine.

The temperature-coefficient of the latter *E.M.F.* is 0·000322 volt per degree, and hence the heat of solution of 1 gram-atom of lithium in 0·0350% lithium amalgam is −19,605 cal. E. G.

An Apparatus and a Method for the Determination of the Velocity of the Chemical Reactions which take place on Electrodes during the Passage of a Current. DAVID REICHINSTEIN (*Zeitsch. Elektrochem.*, 1913, **19**, 384—389).—The apparatus used in the investigation consists of a multiple rotating commutator, by means of which the primary and secondary currents can be made and broken at definitely known intervals of time. The author deduces expressions which give the velocity constants for reactions of the first and second order. They have the forms: $k_0=(m_0-m)/mt$ and $k_0/V=(m_0-m)^2/m_0tm^2$ respectively, where k_0 is the constant of the velocity of decomposition (for example, in the decomposition of the platinum hydrogen alloy with the formation of molecular hydrogen), m_0 is proportional to the quantity of copper deposited in a copper coulombmeter in the secondary circuit, m to a similar value in the primary circuit, t represents the time from the commencement of the experiment at which the values m_0 and m were obtained, and V is the volume occupied by the reacting substance on the electrode. The method is used for determining the velocity of evolution of oxygen from a platinum electrode. The results are regarded as orienting only. J. F. S.

Electromotive Force Produced by the Flow of Solutions of Electrolytes through Capillary Tubes. LOUIS RIÉTY (*Compt. rend.*, 1913, **156**, 1368—1370)—An extension of the measurements of the *E.M.F.* produced by the flow of electrolytic solutions through capillary tubes (compare A., 1912, ii, 622) to solutions of potassium chloride, nitrate, sulphate, and hydroxide, and hydrochloric and sulphuric acids of varying concentrations. By determining the viscosity and conductivity of the solutions, the author has also calculated the potential difference at the point of contact of the glass and the electrolyte. The values of this potential difference in the case of potassium nitrate steadily decrease as the concentration increases, showing no minimum up to a concentration of 1 gram-molecule per litre. For dilute solutions, the potential difference at the point of contact is much less for potassium salts than for copper salts (*loc. cit.*). W. G.

New Processes for the Production of Electricity which Explain Some Bioelectrical Phenomena. REINHARD BEUTNER (*Zeitsch. Elektrochem.*, 1913, **19**, 319—330).—The various theories which have been propounded to explain the origin of the potential difference occurring at membranes are discussed (compare Ostwald, A., 1890, ii, 1354; Walden, A., 1893, ii, 203). Experiments are described which imitate the processes on living membranes. Loeb

(A., 1912, ii, 663) has shown that the biological potential differences are reversible for cations of different kinds, and the author shows that this can be imitated by means of substances which are insoluble in water, but which possess acidic properties, for example, salicylaldehyde saturated with salicylic acid. The physical character of the phenomenon can be explained by the Nernst hypothesis for the potential difference between two immiscible phases, and from the experimental data furnished by such mixtures, for example, the potential difference of dimethylaniline and salicylaldehyde mixtures, which show reversibility for ions of similar charge. In this particular case the explanation is as follows: It is assumed that in the regions, on both sides of the dividing layer, a double decomposition occurs between the various electrolytes, and from differences of solubility of the two changed products in the different layers, a diffusion occurs which causes an increase in the concentration of the ions, and it is in respect of these that the reversibility occurs. From the Nernst theory the division layer behaves as an electrode. In accordance with the foregoing a formula is deduced for the salicylaldehyde potential differences which agrees well with the experimental data. J. F. S.

A New Kind of Electromotive Force and Some Possible Applications to Physico-chemical Problems. REINHARD BEUTNER (*J. Amer. Chem. Soc.*, 1913, **35**, 344—352).—An account is given of certain galvanic cells composed of insoluble organic liquids and aqueous solutions, such as:

$$-N/10\text{-KCl} \mid \text{salicylaldehyde} \mid N/1250\text{-KCl}+,$$

which has an *E.M.F.* 0·083 volt. The potassium chloride can be replaced by almost any other soluble salt. These phenomena can be explained by assuming that the $K^{\cdot}$ concentration of the salicylaldehyde is due to the presence of salicylic acid, which reacts with the potassium chloride with formation of potassium salicylate and hydrochloric acid. It is probable that owing to a difference in the solubility of these products in salicylaldehyde they are not equally distributed between the two phases (salicylaldehyde and water), and the effect of this unequal distribution is that the concentrations of $K^{\cdot}$ in water and in salicylaldehyde are not proportional. A theory has been evolved according to which the change of the potential difference with the concentration must become more like that at a metal electrode the smaller the concentration. These considerations have shown that, besides salicylaldehyde, other insoluble organic substances show a similar change in the potential difference with the concentration of the aqueous solution provided that (1) the substance contains a strong acid, capable of reacting with the salt of the aqueous solution; and (2) the concentration of the salt produced by the reaction in the insoluble organic substance is far greater than the potassium chloride concentration. In the case of benzaldehyde, the effect of the concentration on the potential difference is less marked, since benzoic acid is a weaker acid than salicylic. If benzyl alcohol is used, no *E.M.F.* is observed, and with phenol only a very small *E.M.F.* is found.

If, in place of the salicylaldehyde, aniline or toluidine is employed, a change of potential is observed in the opposite direction. As water is slightly soluble in aniline, the compound $Ph{\cdot}NH_3{\cdot}OH$ may be supposed to be formed, which would react with potassium chloride, thus: $Ph{\cdot}NH_3{\cdot}OH + KCl = Ph{\cdot}NH_3{\cdot}Cl + KOH$, the aniline behaving like a reversible Cl' electrode. In the case of the cell $+N/10\text{-}KCl$ | toluidine | $N/1000\text{-}KCl-$, an *E.M.F.* $-0{\cdot}105$ volt was observed, and similar *E.M.F.*'s were found with xylidine and methylaniline.

All these cells are mere concentration cells, the *E.M.F.* being due to the difference in concentration of two solutions of the same salt. In the case of cells composed of solutions of two different salts of equivalent concentration, the *E.M.F.*'s produced are nearly as large as those of cells with metal electrodes.

Several applications of these phenomena are discussed. E. G.

New Electric Properties of a Semipermeable Membrane of Copper Ferrocyanide. Reinhard Beutner (*J. Physical Chem.*, 1913, **17**, 344—360. Compare Loeb and Beutner, A., 1912, ii, 663).—A precipitation membrane of copper ferrocyanide behaves as an electrode, reversible for various univalent positive ions, but, unlike the vegetable membranes previously investigated, indifferent to bivalent cations.

The experiments described were made with an open tube of gelatin jelly, containing potassium ferrocyanide, bathed at one end in copper sulphate solution, so that a membrane was formed at the surface of the jelly. On connecting the copper sulphate solution and the top of the jelly to calomel electrodes by potassium chloride solution, the potential was from 0·10 to 0·13 volt, whereas the liquid potentials in the circuit could hardly exceed 0·01 volt. The contact *E.M.F.* of the ferrocyanide membrane appears to be due to the difference in potassium concentration on either side of it. On the one side is the potassium ferrocyanide, and on the other, in the copper sulphate solution, is the potassium sulphate generated by the formation and steady increase in thickness of the membrane. When the diffusion away of potassium sulphate is accelerated by stirring the copper sulphate solution, the *E.M.F.* rises temporarily.

Univalent positive ions must be able to diffuse into the membrane, which, it is suggested, consists of a complex compound of copper and potassium ferrocyanides. The *E.M.F.* observed is opposite in sign to that given by metallic electrodes in concentration cells, since these are only sensitive to anions.

The effects of varying the composition and concentration of the electrolytes bathing a ferrocyanide membrane are in accordance with the author's views. R. J. C.

Constitution of Certain Liquid Amalgams. Joel H. Hildebrand (*J. Amer. Chem. Soc.*, 1913, **35**, 501—519).—The formula given by the author for the *E.M.F.* of liquid amalgam concentration cells (*Trans. Amer. Electrochem. Soc.*, 1913, **22**, 319) has now been integrated exactly by the aid of the vapour pressure law, and

applied to the amalgams of zinc, lead, tin, thallium, indium, and cadmium.

In the case of zinc amalgams, the results of *E.M.F.* and vapour pressure determinations are in good agreement, and indicate that the zinc is not combined with the mercury, but is associated in accordance with the equation $2Zn = Zn_2 + 2400$ joules. The equilibrium constant of this reaction and the degree of dissociation at different dilutions are given and are shown to accord well with the measurements of *E.M.F.* and its temperature-coefficient. The same formula applies to the lead and tin amalgams, but with a different constant, corresponding with a much greater degree of association. The thallium amalgams give results corresponding with the formula for cases in which combination occurs. Indications have been obtained of the compound $TlHg_6$, which in the more concentrated amalgams seems to break up into a simpler compound, probably $TlHg_2$. Indium amalgams appear to contain $InHg_4$, which is converted into a simpler compound in the more concentrated amalgams. Cadmium amalgams seem to contain both free cadmium and the compound CdHg, in proportions depending on the law of mass action; in the most dilute amalgams, two-thirds of the cadmium is present in the combined state.

The validity of the fundamental formula is discussed, and it is shown to be of considerable value for determining the constitution of metallic solutions and for investigating the unknown factors which influence the vapour pressure of solutions. E. G.

The Spontaneous Charging of Photo-electric Cells in the Dark and the Nature of the Active Rays of Potassium. HANS THIRRING (*Physikal. Zeitsch.*, 1913, **14**, 406—408).—Experiments are described which show that the acquirement of a negative charge by the potassium of a photo-electric cell when this is kept in the dark is not due to the emission of positively charged particles, but is simply a Volta effect. The potassium cell behaves like a galvanic element with an *E.M.F.* of about 2·8 volts, and with an internal resistance of the order of 10^{12} ohms. The magnitude of this resistance affords a measure of the ionisation which results from the potassium radiation. H. M. D.

A Special Type of Polarisation in Connexion with Self-induction in Concentration Cells. JOHANNES J. VAN LAAR (*Chem. Weekblad*, 1913, **10**, 305—313. Compare van Deventer, this vol., ii, 14).—A theoretical paper, in which the author discusses the cause of a special type of polarisation only observed with zinc and allied metals. The name "polarisation due to impotence" is proposed for the phenomenon. A. J. W.

Polarisation Through Impotence. CHARLES M. VAN DEVENTER (*Chem. Weekblad*, 1913, **10**, 369—370. Compare preceding abstract).—A criticism of van Laar's paper, and a suggestion of the title, "Potential anomaly through impotence," as better describing the phenomenon than that given by van Laar. A. J. W.

Hydrolysis of Salts of Strong Acids. JOHANNES J. VAN LAAR (*Chem. Weekblad*, 1913, **10**, 334—345).—A theoretical paper investigating the influence of possible hydrolysis in very dilute salt solutions on the *E.M.F.* of a concentration cell. The author considers that even for great dilution with salts of strong acids the influence of hydrolysis is a negligible factor. A. J. W.

Electrolysis of Crystalline Compounds. I. Silver Iodide. GIUSEPPE BRUNI and G. SCARPA (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 438—443).—The authors immersed two silver electrodes in fused silver iodide, and after solidification passed a current between them. The anode dissolved, and silver was deposited on the cathode. The deposited silver tended to form threads pointing towards the anode, and unless weak currents (0·1 ampere) were passed, it was difficult to avoid their becoming connected. In quantitative experiments at 160°, 200°, 250°, 300°, and 400°, Faraday's laws were verified. If silver iodide possesses a metallic as well as an electrolytic conductivity (as has been suggested), it must constitute only a very minute fraction of the total conductivity. R. V. S.

The Electrolytic Regeneration of Chromic Acid from Solutions of Chromium Sulphate. PAUL ASKENASY and A. RÉVAI (*Zeitsch. Elektrochem.*, 1913, **19**, 344—362).—The paper deals with the regeneration of chromic acid from chromium sulphate by anodic oxidation in cells without diaphragms. The oxidation occurs readily on lead anodes with excellent current efficiency; the object of the investigation is to define the cathode conditions, so that only a minimum of reduction shall occur there, and so make it possible to work without a diaphragm. The experiments were made with a solution containing 81 grams of chromic acid in 500 c.c. of solution and so much sulphuric acid as corresponds with an excess of 10% when all the chromic acid has been converted into chromic sulphate. This corresponds to the solution which is technically employed for the regeneration of chromic acid. It is shown that at the commencement of the regeneration, that is, when the concentration of chromic acid is small, it is better to use low current densities at the cathode, and to increase the current density as the concentration of chromic acid increases. Temperature has little influence on the process. The addition of magnesium sulphate prevents reduction at the cathode when dilute solutions and low current densities are employed, but if there is only a small percentage of chromic acid present it has the opposite effect, and if high current densities are used it has no effect. The influence of chromium sulphate is to prevent reduction with both high and low current densities except in solutions which contain very little chromic acid. The addition of sodium and potassium sulphates is without influence on the reaction. Dilution is favourable to the oxidation under all circumstances, but more especially with high current densities and in the presence of magnesium sulphate when low current densities are employed. A high concentration of sulphuric acid has a slightly favourable action. The following conditions are found to be most successful for the technical regeneration of chromic acid. The con-

centration of chromic acid must not exceed 100 grams per litre, the cathode current density should be above 200 amperes per sq. decimetre, under which conditions the addition of other salts becomes unnecessary. Should other conditions be chosen, the addition of other salts must be made cautiously, as, although they allow a high concentration of chromic acid to be obtained with good current efficiency, the current efficiency is very poor when only a small concentration of chromic acid is present. A complete list of the literature on the electrolytic deposition of chromium metal is appended to the paper. J. F. S.

Coefficient of Magnetisation of Water and Oxygen. AUGUSTE PICCARD (*Arch. Sci. phys. nat.*, 1913, [iv], **35**, 209—231).—Details are given of the methods adopted for the determination of the strength of the field employed in the magnetisation experiments which were made according to Quincke's meniscus method. No results are communicated in the present paper. H. M. D.

Magnetic Induction in Ferric Oxide at Various Temperatures and in Different States and the Possible Chemical Changes Indicated by the Observations. GEORGE E. ALLAN and JOHN BROWN (*Proc. Roy. Soc. Edin.*, 1913, **33**, 69—84).—The magnetic properties of artificial and natural ferric oxide have been examined with special reference to the influence of temperature. It was found that both pure artificial ferric oxide and impure hæmatite become magnetic when heated in air in a magnetic field. On cooling from about 1000° both substances were found to have become more or less permanently magnetised. The effect is attributed to the formation of ferroso-ferric oxide.

When the pure oxide was heated in hydrogen, the temperature at which the substance acquired magnetic properties was higher (300°), but this temperature was much more sharply defined than when the oxide was heated in air. The curves which show the dependence of the magnetic effect on the temperature in the case of the oxide heated in hydrogen have maxima at 425°, 575°, and 750°, and these are supposed to indicate the optimum temperatures for the various stages in the reduction of the ferric oxide.

H. M. D.

Magnetic Researches. VII. Paramagnetism at Low Temperatures. H. KAMERLINGH ONNES and E. OOSTERHUIS (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 965—971. Compare A., 1912, ii, 228, 425, 1133).—The variation of the magnetic susceptibility of crystallised manganous sulphate ($MnSO_4,4H_2O$) with temperature is found to be in accordance with Curie's law between 0° and about −200°. At liquid hydrogen temperatures deviations occur. The anhydrous salt behaves differently, in that the value of $\chi(T+\Delta)$ remains constant down to −210° if $\Delta=24$. As in the case of ferrous sulphate, the presence of water of crystallisation causes Δ to become equal to zero. For both manganous and ferrous sulphates, the number of magnetons in the crystalline and anhydrous salts

is the same, and in both cases the number is one less than that which appears to be characteristic of the dissolved salt.

Some observations have also been made on the susceptibility of platinum and liquid oxygen. In the case of platinum the susceptibility changes very little between the ordinary temperature and $-260°$. Between 64·9° abs. and 90·1° abs. the relationship between the susceptibility of liquid oxygen and the absolute temperature can be expressed by $\chi(T+71)=$constant. Since gaseous oxygen obeys Curie's law at temperatures above that of the room, it would appear that there is a change in its behaviour at some point between $-180°$ and 0°. H. M. D.

Thermometry. JOHN H. COSTE (*J. Soc. Chem. Ind.*, 1913, **32**, 341—345).—A discussion of the errors affecting the mercury thermometer. T. S. P.

Isotherms of Monatomic Substances and of their Binary Mixtures. XIV. Calculation of Some Thermal Quantities for Argon. H. KAMERLINGH ONNES and C. A. CROMMELIN (*Proc. K. Akad. Wetensch. Amsterdam.* 1913, **15**, 952—960. Compare A., 1912, ii, 900).—From the coefficients of the empirical equation of state for argon, the authors have calculated the values of a number of thermodynamic quantities. These are utilised for a comparison of the behaviour of argon with that of *iso*pentane, and it is shown that in several respects there is a close similarity in the behaviour. H. M. D.

Thermal Conductivity, Specific Heat, and Viscosity of Gases. ARNOLD EUCKEN (*Physikal. Zeitsch.*, 1913, **14**, 324—332).—The question of the partition of energy in the collision of gas molecules is discussed with reference to the variation of the phenomenon of partition according to whether the energy is translational, rotatory, or vibrational. In this connexion, a comparison is made between the values of K, given by the equation $K=k/c_v\eta$, where k is the thermal conductivity, C_v the specific heat at constant volume, and η the viscosity, and the corresponding values calculated on the basis of the kinetic theory. The comparison is made for a considerable number of gases of varying degrees of molecular complexity, and it is found that in several cases the observed and calculated values are in good agreement, indicating that the energy exchange is practically complete. In other cases the observed values are smaller than the theoretical numbers. This behaviour is not confined to the polyatomic gases, but is also shown by helium, especially at low temperatures.

Reference may be made to the tabulated data for the thermal conductivities, which have been measured at 0°, and in some cases at $-252°$. H. M. D.

Expansion of Vapours and their Specific Heats. Application to Vapour Engines. ANTON LEDUC (*Ann. Chim. Phys.*, 1913, [viii], **28**, 577—613).—A method of calculating the ratio of the specific heats of vapours at constant pressure and volume is described. The

formula involves a knowledge of (*a*) the compressibility of the vapour at the temperatures under consideration; (*b*) the pressure of the saturated vapour and its variation with temperature; and (*c*) the latent heat of vaporisation and the specific heat of the liquid, and the variation of these with the temperature.

From the available experimental observations, the requisite data have been deduced for water, ethyl ether, and benzene, and these are applied in the calculation of the specific heats and the specific heat ratio for the saturated vapours. For water, results are recorded for temperatures between 80° and 160°; for benzene, between 40° and 120°; and for ethyl ether, between 0° and 60°. In the case of benzene and ether, the ratio of the specific heats increases with the temperature according to a linear formula, but for water vapour, the relationship is more complex, and may be represented by the equation: $\gamma = 1{\cdot}373 + 0{\cdot}0^3 4\theta - 0{\cdot}0^5 8\theta^2 - 0{\cdot}0^7 3\theta^3$, where $\theta = t^{\circ} - 100^{\circ}$.

Similar calculations have been made for the unsaturated vapours, and the variation of the specific heat ratio with the pressure of the vapour has also been examined.

In the final section, the calculated numbers are considered with reference to the efficiency of steam and ether vapour engines, and also to the influence of superheating on the efficiency. H. M. D.

Concentrated Solutions. II. ÉMILE BAUD (*Ann. Chim. Phys.*, 1913, [viii], **29**, 124—143. Compare A., 1912, ii, 1147).—The relation between the composition and freezing point of concentrated solutions has been further examined, and formulæ deduced which are applicable to binary mixtures which absorb or evolve heat when the components are mixed together. To test the formulæ, experiments have been made with mixtures of *cyclo*hexane and ethylene bromide, *cyclo*hexane and acetic acid, and benzene and carbon tetrachloride. For each of these pairs, the freezing-point curves and the heat changes which occur when the components are mixed in varying proportions have been determined, and it is found that the derived formulæ are in fair agreement with the observed freezing points for the different mixtures.

From the freezing-point diagrams, it is seen that *cyclo*hexane and ethylene bromide show a eutectic at −25°, corresponding with about 85 mols. % of *cyclo*hexane. The behaviour of *cyclo*hexane and acetic acid is similar, a eutectic being obtained at −2·5° and about 95 mols. % of *cyclo*hexane. The *cyclo*hexane curve is in this case characterised by a very strongly marked inflexion. The diagram for benzene and carbon tetrachloride shows that the curves for the pure substances are intercepted by a curve corresponding with the compound C_6H_6,CCl_4, which melts at about −34°.

H. M. D.

Latent Heat of Evaporation of Aqueous Salt Solutions. ROBERT G. LUNNON (*Proc. Physical Soc. London*, 1913, **25**, 180—191).—The heat absorbed in the vaporisation of steam has been measured

for a number of saturated aqueous solutions of salts, and also for a number of unsaturated solutions of varying concentration. A measured quantity of heat was supplied to the boiling solution contained in a calorimeter by means of a small electric lamp. The calorimeter was placed inside a double-walled vessel surrounded by a solution boiling at the same temperature as the solution under examination. The steam from the inner vessel escaped through a tube into a detachable condenser, the weight of which could be determined at suitable intervals.

The latent heats thus obtained for various saturated solutions were as follows, the numbers in brackets representing the respective boiling points of the solutions: Sodium nitrate (121·0°), 459; potassium nitrate (116·8°), 421; sodium chloride (110·0°), 508; potassium chloride (109·0°), 493; potassium chromate (106·8°), 505; potassium dichromate (104·8°), 489. The differences between these numbers and the corresponding latent heat values for pure water represent the heats of solution of the various salts. For the sodium and potassium salts of the same acid it appears that the heat of solution is proportional to the concentration of the saturated solution when this is expressed as grams of salt per gram of water.

From the experiments with unsaturated solutions of sodium nitrate and potassium nitrate, it is found that the latent heat is approximately constant for all concentrations until saturation is attained. H. M. D.

The Vapour Pressures of Liquid Tin Amalgams of Low Mercury Content. ADOLF SIEVERTS and HERMANN OEHME (*Ber.*, 1913, **46**, 1238—1246).—In previous investigations (compare A., 1910, ii, 851) Sieverts and his co-workers have found that diatomic gases dissolve in solid and liquid metals in a quantity which is directly proportional to the square root of the gas pressure, which behaviour can be explained on the assumption that each gas molecule, when dissolved, dissociates into the two atoms. For monatomic gases such a behaviour is improbable; the amount dissolved should be directly proportional to the pressure and in accordance with Henry's law. Attempts to show that this is the case were unsuccessful in the case of helium and argon (A., 1912, ii, 1052), owing to their insolubility, consequently the authors have determined the solubility of mercury vapour, which is known to be monatomic, in liquid tin. The method consisted in the determination of the vapour pressure of dilute amalgams, a special apparatus being designed for the purpose, in which the vapour pressure of the amalgam was balanced against the hydrostatic pressure of a column of molten tin.

The amalgams used contained 0·8—8% of mercury, and the vapour pressures for temperatures between 300° and 360° varied between 2 and 70 mm. of mercury. For this range the vapour pressure was found to be approximately proportional to the concentration, in accordance with Henry's law. The same was found to hold between the temperatures of 515° and 528° for 2 and 10% amalgams, the pressures varying from 173 to 886 mm. of mercury. T. S. P.

Thermal Investigations in a Vacuum. W. HEIKE (*Intern. Zeitsch. Metallographie*, 1913, **4**, 143—154).—A new form of porcelain vessel is described for melting metals, sulphides, or arsenides out of contact with air. The vessel consists of a narrow cylinder with elongated neck. The closed end is so shaped as to form a tube, projecting into the interior of the vessel, and serving as a protecting sheath for the thermo-couple. After filling with metal, the vessel is exhausted and sealed by heating the slightly constricted neck in an oxygen blowpipe and twisting while soft. The porcelain tube is heated in a vertical electric tube furnace. Good cooling curves are readily obtained, even with sulphides and other mixtures which undergo more or less decomposition when melted in an open vessel. C. H. D.

Simple Inexpensive Calorimeter for Determining the Heat of Solution and of Neutralisation. ERNEST ANDERSON and H. A. NOYES (*J. Physical Chem.*, 1913, **17**, 249—251).—The apparatus consists of a wide-mouthed Dewar bulb of about 450 c.c. capacity, closed by a rubber stopper, carrying a Beckmann thermometer, and a glass tube bearing for a rotatory glass stirrer. The rise in temperature in 400 c.c. of water due to the stirring was less than 0·001° per minute, and the fall in temperature due to heat leakage 0·01° per minute for 9° difference between internal and external temperatures. The calorimeter was designed for students' use only. R. J. C.

Thermodynamic Investigations on Copper Sulphate. A. SIGGEL (*Zeitsch. Elektrochem.*, 1913, **19**, 340—344).—The paper deals with the equilibrium of the dissociation of monohydrated copper sulphate, $CuSO_4,H_2O \rightleftharpoons CuSO_4 + H_2O$. The various quantities necessary for the calculations are redetermined in the course of the work. The heat of hydration is found to be 6592 cals. (mean) at 22°, which agrees better with the Schottky (A., 1908, ii, 1016) value of 6600 than with Thomsen's value 6460. The dissociation tension was also determined at temperatures from 99° to 147·4°, and the following values found: 99°, 6·0 mm.; 110·2°, 12·0 mm.; 130·9°, 38·2 mm.; 137·2°, 53·5 mm.; and 147·4°, 90·4 mm. Using these data, the affinity is calculated, and the various factors controlled by calculations based on the Nernst thermodynamic theory. Agreement is found to be good, and to confirm the Nernst theory fully. J. F. S.

Thermochemical Study of Uranyl Nitrate and its Hydrates. ROBERT DE FORCRAND (*Compt. rend.*, 1913, **156**, 1207—1210).—The author has measured the heat of solution of the four hydrates of uranyl nitrate previously described (this vol., ii, 413), and from his values has calculated the boiling point of each of them. His results differ somewhat from those of Marketos (A., 1912, ii, 848). The thermochemical values obtained are in accord with the phenomena of successive dehydration exhibited by the hydrates. W. G.

Ignition Temperatures, Especially of Combustibles. H. HOLM (*Zeitsch. angew. Chem.*, 1913, **26**, 273—279).—The ignition temperature determined by the author is that at which the substance takes fire spontaneously in air at ordinary pressure. The apparatus used consisted of a vertical Heræus furnace; a porcelain crucible lid was inverted over the end of the porcelain tube in the centre of the furnace, and on the lid was one junction of a thermocouple. Gases were introduced through a narrow porcelain tube opening 1—2 mm. above the crucible lid; liquids were allowed to fall drop by drop on to the lid, whilst solids, finely powdered, were dropped on to the lid from time to time in quantities sufficient to cover the point of a knife. The experiments were made at intervals of 10° rise in temperature.

The greater majority of substances investigated were liquids; for example, petroleum, paraffin oil, ether, alcohol, benzene, etc.; the gases were ammonia, coal gas, and hydrogen, and the solids, cellulose, peat, and various coals. The solids ignite at the lowest temperatures, and the gases at the highest.

The results are fully discussed, both from the practical (industrial) and theoretical point of view. T. S. P.

Rectilinear Diameter for Argon. ÉMILE MATHIAS, H. KAMERLINGH ONNES, and C. A. CROMMELIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 960—965).—For temperatures between $-175{\cdot}39°$ and $-131{\cdot}54°$, the relation between the mean density of the liquid and its saturated vapour is expressed by $D = 0{\cdot}20956 - 0{\cdot}0026235t$. The slope of the rectilinear diameter is greater than that for any other substance yet investigated with the exception of xenon. On the assumption that the diameter remains rectilinear up to the critical, the above equation yields $\rho_k = 0{\cdot}53078$ for the critical density. The value previously obtained for the critical density from the argon isotherms was 0·509, and it would therefore appear that the above equation does not hold in the neighbourhood of the critical point. In this region the diameter becomes convex towards the axis of temperature.

From a comparison of the reduced density curves and diameters for ethyl ether, *iso*pentane, oxygen, xenon, argon, and helium, it appears that the equations of state for different substances deviate to an extent which appears to be related to the divergence of their critical temperatures. H. M. D.

Method of Determining Vapour Densities at High Temperatures and a New Form of Quartz Manometer. GEORGE E. GIBSON (*Proc. Roy. Soc. Edin.*, 1913, **33**, 1—8).—The highest temperature attainable in vapour density measurements in which quartz or glass manometers are used is about 750°, but it is shown that determinations may be made at much higher temperatures if the main bulk of the vapour is heated in a quartz tube to the desired temperature and the manometer is heated separately to a temperature which is less than 750°. The manometer consists of a bulb, about 1 c.c. in capacity, which is blown on the end of a

quartz tube 3 mm. in diameter and is flattened at one end so as to form a flexible quartz membrane, about 0·1 mm. in thickness. The deformation of the membrane is recorded by an optical arrangement, and by adjustment of the pressure in an outer tube, into which the manometer tube is fitted, the deformation is reduced to zero. When suitable precautions are taken, this null method of measuring pressures is found to give accurate results. From a series of pressure readings at temperatures ranging from 437° to 912°, with a weighed quantity of mercury in the apparatus, values were obtained for the vapour density of mercury varying from 99·5 to 101·2. H. M. D.

The Density of Double Salts. Case of the Copper Ammonium Chlorides. EDOUARD CHAUVENET and GEORGES URBAIN (*Compt. rend.*, 1913, **156**, 1320—1322).—A study of the molecular volumes of copper chloride and cupric ammonium chloride, in the hydrated and anhydrous states, leads to the conclusion that the molecular volume, like the other physical properties, obeys the law of additivity, and therefore that the molecular volume of a double salt is usually equal to the sum of the molecular volumes of its constituents. The authors consider that this double chloride can exist as a compound in the anhydrous form, although its heat of formation, as calculated for this state, is practically zero. W. G.

The Atomic Constants and the Properties of Substances. RICHARD D. KLEEMAN (*Proc. Camb. Phil. Soc.*, 1913, **17**, 175—179).—It is shown by reference to the data for about twenty organic substances that the molecular volume at the critical point can be satisfactorily represented by means of the expression $14{\cdot}04\Sigma C_v$, in which C_v denotes the apparent volume of an atom relative to that of a hydrogen atom.

It has been shown in a previous paper that the attraction constant C_a of an atom is approximately proportional to the square root of the atomic weight (m). A comparison is now made of the values of C_a and C_v, with $\sqrt{m}$ for eight different elements. Considerable divergences are found in both cases, hydrogen exhibiting the largest deviations.

The formula $T = 17{\cdot}69(\Sigma C_a)^2/(\Sigma C_v)^{7/3}$ is employed in the calculation of the critical temperatures of a number of substances, and the values compared with experiment. Association of liquid molecules tends to raise the critical temperature, and to cause deviations from the calculated value. H. M. D.

The Elastic Limit of Alloys. A. PORTEVIN (*Compt. rend.*, 1913, **156**, 1237—1240).—The author has studied the elastic limit of alloys of three types, using Fremont's method, determining the deformation in pyramidal specimens on compression. In the case of alloys formed from a single, chemically homogeneous, solid solution, the limit of elasticity, which is a vectorial quantity for a grain, becomes scalar for the mass, since the large number of grains present all the possible orientations. The same holds good for alloys formed from a single chemically heterogeneous solid solution with an

additional complication, namely, that the elastic limit is not reached at the same time in all points of the grain. In the case of a complex of two phases presenting two constituents, one constituent is deformed first alone, and it is impossible to define by any single number the elastic limit, since it extends between limits which depend both on the mechanical anisotropy of the grains and the chemical heterogeneity of the alloy. W. G.

The Influence of Chemical Constitution on Interfacial Tension. WILLIAM B. HARDY (*Proc. Roy. Soc.*, 1913, *A*, **88**, 303—313).—By means of a method involving the determination of the weight of the drops which are delivered by capillary tubes of known diameter, the author has measured the work which is expended in the formation of unit area of interface by the molecular forces which operate between two immiscible liquids. From experiments in which a large number of liquids were examined in combination with water, it has been found that the work done by the molecular forces varies very considerably with the chemical nature of the second liquid at which the interface is formed.

For a number of saturated substances, the value of the interfacial tension was found to vary from 20·8 to 24·5. The introduction of an ethylene linking raises the value to a considerable extent, the numbers for octane and octylene being 20·8 and 36·2 respectively. For benzene the value is 32·2. The introduction of a hydroxyl group into a ring compound increases the value by about 20 units, but the increase is only about half as large in the case of a paraffin hydrocarbon. The presence of the carbonyl group has a similar influence on the value of the interfacial tension.

In general, the interfacial tension increases with the chemical reactivity of the second liquid, the greatest values being obtained in the case of acids, alcohols, and esters. This would seem to show that the chief modifying factor in all interfaces is the development of a contact difference of potential due to polarisation of the molecules. H. M. D.

The Tension of Composite Fluid Surfaces. II. WILLIAM B. HARDY (*Proc. Roy. Soc.*, 1913, *A*, **88**, 313—333. Compare A., 1912, ii, 838).—The problem of the spreading of one fluid over the surface of another is further considered with special reference to the changes of tension which are produced by the spreading of various liquids on water. The curves which are obtained by plotting the surface tension as a function of the thickness of the spreading layer of liquid consist in certain cases of a series of straight lines, and these are interpreted in terms of the author's theory. H. M. D.

Law of Hydrodiffusion of Mixtures of Potassium and Sodium Chlorides and the Dependency of the Coefficient of Diffusion of these Mixtures on the Relative Initial Concentrations of the Components. V. S. TITOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, *Phys. Part*, 61—86).—The author has investigated the applicability to the diffusion of a mixture of two electrolytes with

a common ion of Fick's law (*Ann. Phys. Chem.*, 1855, **4**, 59), analogous to Ohm's law and to Fourier's law of thermal conductivity.

The diffusion of aqueous mixtures of potassium and sodium chlorides is in good agreement with Fick's law, especially when the diffused salts are measured in gram-equivalents. From this law it follows that, when an aqueous solution diffuses into water and the whole column of liquid is divided at any moment into eight equally deep horizontal layers, each pair of layers equidistant from the middle will contain together one-fourth of the total solute. This result is in very close accord with the results of experiments on mixtures of the two above chlorides. T. H. P.

Effect of Interionic Forces on the Osmotic Pressure of Electrolytes. SAMUEL R. MILNER (*Phil. Mag.*, 1913, [vi], **25**, 742—751).—In a previous paper (*ibid.*, 1912, [vi], **23**, 551) it has been shown that a completely dissociated mixture of ions possesses a finite virial. In applying this result to solutions, it follows that the osmotic pressure of the ions of an electrolyte differs from that of the undissociated molecules. By reference to the freezing-point data for dilute solutions of a number of binary electrolytes, it is shown that the observed lowering of the freezing point can be satisfactorily accounted for on the assumption that the electrolytes are completely ionised, and that the interionic forces have the effect of reducing the osmotic pressure below the value which would correspond with the simple gas law. H. M. D.

Miscibility of Liquids at Pressures up to 3000 Atmospheres. PHILIPP KOHNSTAMM and JEAN TIMMERMANS (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 1021—1037).—An apparatus is described which has been employed in experiments on the influence of pressure on the critical solution temperature of binary mixtures up to pressures of about 3000 atmospheres. The arrangement is such as to enable the phenomenon to be investigated by direct visual observation of the change which occurs in the nature of the system at the temperature in question.

The results obtained with the following pairs of liquids are recorded in tables, in which the values of dt/dp are indicated for the different pressure intervals—hexane and nitrobenzene, di*iso*amyl and nitrobenzene, American petroleum and nitrobenzene, *cyclo*hexane and aniline, water and triethylamine, water and methyl ethyl ketone. The behaviour of these systems is quite in accordance with theoretical predictions, and the last-mentioned pair is of particular interest in that it represents a system in which the transition from a partly miscible to a completely miscible condition can be actually effected at constant temperature by a change in the pressure. H. M. D.

Binary Mixtures and Concentrated Solutions. III. FRIEDRICH DOLEZALEK (*Zeitsch. physikal. Chem.*, 1913, **83**, 40—44).—Polemical. An answer to Patterson (A., 1910, ii, 107) and van Laar's (A., 1910,

ii, 583) criticism of the author's paper (A., 1909, ii, 22). It is shown that Patterson's objections rest mainly on a printer's error, and that the densities of the mixtures were calculated in the usual manner, and not as is suggested in Patterson's paper. The theory put forward by van Laar is shown to be opposed both to experimental facts and thermodynamical considerations (see also Dolezalek, A., 1910, ii, 184). J. F. S.

Binary Mixtures and Concentrated Solutions. IV. The Mixture Ethyl Ether-Chloroform. FRIEDRICH DOLEZALEK and A. SCHULZE (*Zeitsch. physikal. Chem.*, 1913, **83**, 45—78. Compare A., 1909, ii, 22; 1910, ii, 184, and preceding abstract; also Dolezalek and Schulze, A., 1913, ii, 108).—The authors have studied the system ethyl ether–chloroform from the point of view of the Dolezalek theory of mixtures. It is shown that a complex compound is formed by ether and chloroform, which is made up of one molecule of ether and one molecule of chloroform. The conditions are such that the equilibrium $C_4H_{10}O + CHCl_3 \rightleftarrows C_4H_{10}O,CHCl_3$ is set up and obeys the law of mass action. Naturally, the physical constants of such a mixture could not be calculated from the usual mixture laws. The molecular condition of the mixture is determined by the authors at temperatures 20—100°, and it is shown that with increasing temperature the dissociation of the molecular compound increases rapidly. By cautious cooling of an equimolecular mixture, it was possible to isolate the compound in the solid state, and to show that it melted at $-80°$, or 30° above the melting point of ether. It is also shown that on mixing unsaturated ether and chloroform vapours, a contraction occurs which at 80° and 1 kilo. per sq. cm. pressure points to the presence of 0·64 mol. % of the compound in the vapour. The vapour-pressure curves of the ether–chloroform mixtures are convex to the concentration axis, nevertheless the values can be calculated over the whole concentration range by means of the law that "The partial pressure of each component of a mixture is equal to the saturation pressure of the pure component multiplied by the molecular fraction of this component in the liquid mixture." The vapour-pressure curve approaches the ideal straight line curve with increasing temperature, as it must do according to the theory, for with increasing temperature the compound dissociates, and it becomes potentially a mixture of two substances without action on one another. The heat developed on mixing chloroform and ether was measured, and from the values it was calculated that the heat of formation is about 3000 cal. The heat capacity of the compound is considerably greater than that of its components, since on heating, a considerable portion of the heat is used in dissociating the compound. It is shown that if the formation of the compound is considered, the specific heat of the mixtures for all concentrations can be calculated. On mixing ether and chloroform, a considerable contraction occurs, so that the density of the mixtures differs widely from the values calculated by the volume mixture law. But if the constitution of the mixture is calculated from the mass action constant and the

concentration of the three substances considered, the density can be calculated, which agrees well with the observed values. The coefficient of refraction for long wave-lengths is determined, and the divergence of the values from those calculated by the Lorentz formula is shown to be due to the presence of the compound, and not, as has often been stated, to molecular attraction as represented by the van der Waal theory. The viscosity of mixtures is also considered, and it is shown from the values of Thorpe and Roger (T., 1897, **71**, 373) that, although they in no sense agree with values calculated from a mixture formula, yet if the presence and amount of the compound is brought into the calculation, values are obtained with which they agree in the highest degree. In conclusion, the authors state that to portray the whole physicochemical behaviour of an ether–chloroform mixture, it is sufficient to determine the vapour pressure for one single concentration, and to calculate the mass action constant from this. By means of this constant all the properties of the mixture over all concentrations can be calculated by the method given in the paper. J. F. S.

Precipitation of Salts by the Corresponding Acids. IRVINE MASSON (*Proc. Roy. Soc. Edin.*, 1913, **33**, 64—68).—The extent to which the solubility of salts in water is affected by the presence of the corresponding acids may be determined by solubility measurements or precipitation experiments. The relationship between the two methods is discussed, and it is shown that the "critical" concentration of acid (A), which just fails to precipitate salt when a small quantity of the acid solution is added to a neutral saturated solution of the salt, is equal to the product of the solubility of the salt in pure water (B), and the initial slope of the solubility-acidity curve (k_0), that is, $A = k_0 B$. The data obtained for sodium and barium chlorides are in satisfactory agreement with this deduction, but there is an appreciable divergence between theory and experiment in the case of barium nitrate.

According to Engel's data for the solubility of the chlorides of the alkali and alkaline earth metals in water and hydrochloric acid solutions, it appears that k_0 is approximately equal to unity in all cases. H. M. D.

Chemical Significance of Crystalline Form. THEODORE W. RICHARDS (*J. Amer. Chem. Soc.*, 1913, **35**, 381—396).—In this paper, the author's theory of the compressibility of atoms (T., 1911, **99**, 1207) is considered in its relation to the structure of crystals. Barlow and Pope's valency-volume hypothesis is discussed, and it is held that it does not afford the most reasonable explanation for the actual molecular volumes of solids. Some of the arguments advanced in favour of the approximate equality of the valency-volumes are just as valid in support of any other theory involving close-packing of molecules, and there are certain facts which seem quite beyond the reach of this hypothesis.

The present theory accords with all the crystallographic facts hitherto recorded. It assumes, like Barlow and Pope's hypothesis,

that the atoms in solids are closely-packed, and thus maintain the form and rigidity of the structure. It proposes, however, that the atoms are compressible, and that their volumes are not arbitrary, but depend on the pressure to which they are subjected. This theory affords a better explanation of the usual forms of elements and binary compounds than Barlow and Pope's, and also accounts for the fact that elements forming isomorphous compounds need not have exactly the same atomic volume. It also furnishes a conception as to the manner in which potassium and ammonium can replace one another isomorphously, a problem which seems inexplicable on the constant valency-volume hypothesis. E. G.

Linear Velocity of Crystallisation of Isomorphous Mixtures. MEINHARD HASSELBLATT (*Zeitsch. physikal. Chem.*, 1913, **83**, 1—39. Compare Tammann (A., 1897, ii, 444; 1899, ii, 272, 548), Friedländer and Tammann (A., 1898, ii, 17), Bogojavlenski (A., 1899, ii, 206), Pickardt (A., 1903, ii, 66), Dreyer (A., 1904, ii, 611). The fusion curves of binary isomorphous mixtures, which give mixed crystals continuously over the whole range of concentrations, were determined for the following pairs: Cadmium nitrate tetrahydrate–calcium nitrate tetrahydrate; *m*-chloronitrobenzene–*m*-bromonitrobenzene; *m*-chloronitrobenzene–*m*-iodonitrobenzene; *m*-bromonitrobenzene–*m*-iodonitrobenzene; *m*-bromonitrobenzene–*m*-fluoronitrobenzene; and *m*-chloronitrobenzene–*m*-fluoronitrobenzene. For the mixture, cadmium nitrate–calcium nitrate, it is shown that mixed crystals are formed only with the unstable variety of calcium nitrate; the melting points of the mixtures lie between those of the two components without showing either maximum or minimum melting points. In the mixtures of the halogen nitrobenzenes, the pair *m*-bromonitrobenzene–*m*-chloronitrobenzene show no minimum melting point, whilst all the other pairs do. The velocity of crystallisation of the above-mentioned pairs of substances is determined, and this quantity is generally between that of the pure substances, except more especially in the case of the mixtures containing the fluorine derivatives, where a minimum is observed. The velocity of the transition of the unstable variety of calcium nitrate into the stable variety is measured. It is shown that in the case of each of the halogen derivatives of nitrobenzene an unstable variety exists; the melting points of these are determined, and have the following values:

	$C_6H_4F{\cdot}NO_2$.	$C_6N_4Cl{\cdot}NO_2$.	$C_6H_4Br{\cdot}NO_2$.	$C_6H_4I{\cdot}NO_2$.
Stable.........	3·1°	44·6°	54·0°	34·6°
Unstable ...	4·1	24·0	17·5	9·9

It is thought to be likely that other unstable modifications are also capable of existence.

The systems azobenzene–benzylideneaniline; benzylideneaniline–benzylaniline were examined, and shown not continuously to produce mixed crystals, but to give eutectic mixtures. This fact is in opposition to the various results in the literature. In agreement with Bogojavlenski and Sacharov, it is shown that the velocity

of crystallisation changes with the concentration, and that in the heterogeneous region it is very small. The maximum velocity of crystallisation is shown to occur at 25—30° supercooling in the same way as for pure substances. The relationship between the velocity of crystallisation and the cooling bath temperature is of the same nature as that for pure substances. If one component of an isomorphous binary mixture is abnormal, the mixture takes up a mean position between the two substances. In some cases the temperature at the crystallisation surface exerted considerable influence on the maximum crystallisation velocity, whilst in other cases it is without influence. In the latter case the velocity of crystallisation is additive, and the curves are thereby caused to lie below the straight line. With mixtures which do not form mixed crystals in all proportions it is shown that the velocity of crystallisation decreases very much, although in these cases the decrease is less than in the case of substances which do not form mixed crystals at all. The velocity of crystallisation in cases of substances which only form mixed crystals over certain concentrations is very variable, owing to the concentration differences in the still liquid mixture. J. F. S.

Colloidal Sulphur. SVEN ODÉN (*Nova Acta Regiæ Soc. Sci. Upsala*, 1913, [iv], **3**, 1—193).—A detailed account is given of the author's work on the preparation, purification, and physical properties of colloidal solutions of sulphur, and on the phenomena associated with the coagulating action of electrolytes. Many of the observations have been published previously (A., 1911, ii, 388, 971; 1912, ii, 240, 1143).

In regard to the conditions which are favourable to the formation of colloidal sulphur, the observations indicate that the most important factor is a high concentration of the substances, by the interaction of which sulphur is set free. Although low temperatures have been stated to be favourable to the production of colloids, this is contrary to the author's experience, for experiments on the interaction of 3*N*-sodium thiosulphate solution with concentrated sulphuric acid, at temperatures between −5° and +35°, gave a maximum yield of colloidal sulphur at 25°.

The physical properties examined were the density, thermal expansion, viscosity, surface tension, diffusibility, refractivity, osmotic pressure, and colour.

From the behaviour of colloidal sulphur towards electrolytes, it would appear that the phenomena of coagulation can in general be more satisfactorily interpreted in terms of Freundlich's theory as compared with the various other theories which have been put forward up to the present. H. M. D.

Validity of the Boyle-Gay-Lussac Laws for Colloidal Solutions. III. ARNE WESTGREN (*Zeitsch. physikal. Chem.*, 1913, **83**, 151—195. Compare A., 1910, ii, 772; 1911, ii, 703).—The present paper is a continuation of the work of Svedberg, and deals chiefly with the relationships between the compressibility, concentration, and size of the particles. The measurements are made by

a method differing but slightly from that described by Svedberg (*loc. cit.*). The substances employed in the present experiments were sols of mercury, sulphur, and selenium, and emulsions of castor oil and wool fat. Four different mercury sols were employed, prepared as follows: (1) By precipitation of a 0·25 mol. solution of mercuric chloride in 0·9% gelatin by a drop of sodium hydroxide solution, and then reduction with a few drops of hydrazine hydrate solution, the diameter of the particles was $53\mu\mu$; (2) electric formation by means of an arc between mercury and iron, the diameter of the particles was $69\mu\mu$; (3) as (2), except that a gelatin solution was used instead of water, the diameter of the particles was $137\mu\mu$; (4) by precipitation of a 5% mercuric chloride solution by sodium hydroxide, and reduction of the mercuric oxide by hydrazine, the diameter of the particles was $190\mu\mu$. Four sulphur sols were employed, the particles of which had diameters $140\mu\mu$, $164\mu\mu$, $278\mu\mu$, and $358\mu\mu$. Four selenium sols were used, the particles of which had diameters $107\mu\mu$, $132\mu\mu$, $181\mu\mu$, and $242\mu\mu$. The castor oil emulsion particle had diameters $316\mu\mu$, and the wool fat emulsion $212\mu\mu$. From a very large number of observations it is shown that the curve representing the relation between β/β_0 and the number of particles for mercury sols is very like that for gold sols. In the case of sulphur sols and the emulsions the compressibility relationship (β/β_0) is a linear function of the concentration. The selenium sols take up a position intermediate between that of gold and gamboge. From the curves for sols of gold, mercury, and sulphur, it is shown that the product of the diameter of the particles (d) and the concentration of the sol (c) is constant, and that $\beta/\beta_0 = 1 - \text{const.}d^2c$. The relationship between the compressibility ratio and the specific gravity (s) of the dispersed substance is given by $\beta/\beta_0 = 1 - \text{const.}s^{\frac{1}{3}}$. From the two equations, the relationship between the compressibility ratio, diameter of the particles, concentration, and specific gravity is given by the expression $\beta/\beta_0 = 1 - \text{const.}d^2s^{\frac{1}{3}}c$. J. F. S.

The Theory of Intra vitam Staining. RUDOLF HÖBER and OTTO NAST (*Biochem. Zeitsch.*, 1913, **50**, 418—436).—The theory of Ruhland (A., 1909, ii, 257), according to which the staining capacity of a dye is a function of its dispersion grade in solution, is criticised. The authors draw the conclusion that this theory cannot be substantiated, either for acid or basic dyes. It does not explain, for example, why certain highly dispersed acid dyes are not taken up by numerous animal and vegetable cells, although it is possible that dyes cannot be taken up when their dispersion grade is below a certain limit, and they are readily precipitated by small dilutions of salts. The permeability cannot therefore be explained simply as a filtration process where the plasma membrane acts as an ultrafilter. S. B. S.

The Relationship between Colloid Coagulation and Adsorption and the Velocity of Coagulation. N. ISHIZAKA [and, in part, HERBERT FREUNDLICH] (*Zeitsch. physikal. Chem.*, 1913, **83**, 97—128).—The object of the present paper is to show that the relationship

between coagulation by electrolytes and adsorption, which was found to hold by Freundlich (A., 1910, ii, 692) for As_2S_3 sols, also hold for aluminium hydroxide sols. The $Al(OH)_3$ sol was prepared according to the method of Crum (*Annalen*, 1854, **89**, 156), and the alumina used for the adsorption experiments was "grown alumina," that is, such prepared by rubbing aluminium foil with mercury. The adsorption of the salts, sodium chloride, potassium chloride, ammonium chloride, potassium thiocyanate, potassium nitrate, potassium sulphate, potassium chromate, potassium dichromate, potassium ferrocyanide, potassium salicylate, potassium oxalate, potassium sulphanilate, and potassium succinate was determined with alumina, and the change in the concentration of the anion determined. The adsorption isothermal $a = ac^{1/n}$ held in every case. The coagulation value of $Al(OH)_3$ sol was determined for the same salts. The method adopted for obtaining this value was to determine the electrolyte concentration which produced a given change in the viscosity of the sol in a given time. In accord with the Freundlich theory, it is shown that those anions which have a strong coagulating action are also strongly adsorbed, and those which are weakly coagulating, for example, the univalent inorganic anions, are also only slightly adsorbed. The inorganic anions are not equally adsorbed from equivalent solutions, as is the case for inorganic cations, but the bi- and ter-valent anions were more strongly adsorbed. The coagulations values of the uni- and multi-valent ions show an even greater difference. The adsorption of the $Al(OH)_3$ particles on coagulation were measured in several instances, and here also the adsorption isothermal held. The course of the coagulation with time was followed by measuring the viscosity of the sol, to which the electrolyte had been added, from time to time. The results agree with those obtained by Paine (A., 1911, ii, 337) for the copper sol. It is shown that the results and also those of Paine, as expressed in the coagulation-time curve, can be obtained by means of the formula:

$$k = 1/z^2(1+b)\{b/(1-b)[\log_{nat}(1+bx) - \log_{nat}(1-x)] + x/1-x\},$$

in which x is the amount coagulated, the total quantity being taken as unity, z the time, b and k constants, of which k is a function of the electrolyte concentration and b a function of the inflexion point of the curve. The coagulation constant k is related to the electrolyte concentration by the expression $k = \lambda c^q$, and between this expression and that of Paine, $V = Lc^p$, the following relationships exist: $k = hV^2$; $\lambda = hL^2$; and $q = 2p$, where h is a proportionality constant. It is further shown that the maximum viscosity of a coagulated sol increases with its content of colloidal particles, but in the case of large content the increase is somewhat larger. The maximum viscosity depends in a degree on the nature of the coagulating electrolyte. The lyotropic colloids are noticeable by the fact that the viscosity is smaller on coagulation by nitrate and thiocyanate anions than by sulphate and succinate anions. Shaking and other mechanical influences change the viscosity of concentrated sols. The adsorption of potassium dichromate by alumina, just as by carbon, causes a portion of the electrolyte to

change into chromate. A method for the quantitative estimation of small amounts of sulphanilic acid is worked out, and depends on the formation of an azo-dye. J. F. S.

General Principles of Equilibria in Divided Systems. RICHARD C. TOLMAN (*J. Amer. Chem. Soc.*, 1913, **35**, 307—316).—The general conditions for heterogeneous equilibria, summarised in the ordinary phase rule, are only applicable to systems in which the different phases are not sub-divided. In the present paper, consideration is given to the principles of isothermal equilibrium in a divided system, that is, a heterogeneous system in which at least one of the phases is present in more than one region, regions being divided from the rest of the system by boundary surfaces at which an abrupt change of properties takes place. The number of degrees of freedom in a divided system is given by the equation $f = c - r + v$, where c is the number of components, r the number of regions, and v the least number of variables, of which the specification, together with the compositions, is necessary for the thermodynamical description of each region. For systems containing thermodynamically identical regions, r may be taken as the number of non-duplicated regions, and v the number of variables necessary for the thermodynamic description of these non-duplicated regions. For the case that the only division is into thermodynamically identical regions, the equilibrium rule assumes the form $f = c - p + v$, where p is the number of phases.

A special analysis of the equilibrium in systems containing non-identical regions of the same phase has shown that such regions must differ from each other in the value of at least two variables besides concentrations, that each new such region, put into an equilibrium system, introduces at least one new degree of freedom, and that the degrees of freedom thus introduced are not identical with those which the system already possessed.

Discussions are given of the conditions under which variables may be neglected, of the conditions in permanent systems which are not in equilibrium, and of metastable, stable, and indifferent equilibria. E. G.

Equilibria in Dispersed Systems and the Thermodynamic Theory of Colloids. RICHARD C. TOLMAN (*J. Amer. Chem. Soc.*, 1913, **35**, 317—333).—Dispersed systems may be regarded as a special case of divided systems (preceding abstract) in which the degree of division of at least one of the phases, the dispersoid, has become so high that the properties of the system depend appreciably on the size or number of the dispersoid particles present. A study has been made of the conditions for thermodynamic equilibrium in such systems. The different variables are considered on which the free energy of a dispersoid and dispersing medium depend, and it is shown that for equilibrium all the particles of dispersoid must be of the same size, and that with either a positive or negative value of surface tension between the phases the equilibrium is metastable.

Several dispersed systems with positive or negative surface tension are discussed, and the equilibrium rule for divided systems (*loc. cit.*)

applied. It is suggested that a zero value of surface tension between the phases is necessary for the permanent stability of dispersed systems, and therefore for the permanent colloidal state. On this basis, colloidal solutions have the same number of degrees of freedom as "true" solutions. Many of the properties of lyophobic and lyophyllic colloids can be explained on the assumption that the surface tension between a lyophobic dispersoid and its dispersing medium is positive unless the dispersoïd particles are electrically charged, and that for lyophyllic colloids the surface tension between undispersed dispersoid and dispersing medium is negative. E. G.

Equilibria in Ternary Systems. II. FRANS A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 853—867).—A theoretical paper in which the conditions regulating the equilibrium of ternary systems at constant pressure and varying temperature are examined. H. M. D.

Equilibria in Ternary Systems. III. FRANS A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 867—879. Compare preceding abstract).—The nature of the equilibrium in a ternary system, which is characterised by the existence of a point with a minimum vapour pressure, is discussed in detail. H. M. D.

Chemical Reactions and Radius of Curvature. G. REBOUL (*Compt. rend.*, 1913, **156**, 1376—1378. Compare this vol., ii, 303).—If two cylinders of copper of different radius are placed side by side in an atmosphere of some corroding gas at low pressure, the cylinder having the smaller radius of curvature is attacked first, and protects the other from attack until it is itself completely coated with a film of compound. Similarly raised points on a plate are attacked first, and at very low pressures may protect the surface of the plate for several centimetres round each point. W. G.

Velocity of Decomposition of Ozone in Aqueous Solution. VICTOR ROTHMUND and A. BURGSTALLER (*Monatsh.*, 1913, **34**, 665—692).—The ozoniser used was constructed according to the Siemens-Berthelot principle, the six ozonising tubes being arranged, however, in series and not in parallel. By cooling the tubes with a mixture of solid carbon dioxide and acetone, the percentage of ozone in the oxygen used could be made as great as 25—30%.

The velocity experiments were all carried out at 0°, the authors having first proved that the only decomposition product of ozone is oxygen; no trace of hydrogen peroxide is formed in pure aqueous solutions, or of persulphuric acid in sulphuric acid solutions. The estimation of the amount of ozone present in the various solutions was made by adding the aqueous solution to a solution of potassium iodide containng excess of sodium carbonate, then acidifying with dilute sulphuric acid, and titrating the liberated iodine; special experiments showed that this method gave exact results.

The stability of ozone solutions decreases as the concentration of hydrion decreases, but there is no proportionality between this

concentration and the velocity of decomposition; in alkaline solutions ozone is very unstable. In acid solutions the velocity of decomposition, under apparently the same conditions, was found to be very variable; the cause of this variability could not be traced to the presence of a catalyst; in fact, such substances as copper sulphate, colloidal platinum, stannous sulphate, etc., did not act as catalysts. In alkaline solution the irregularities above-mentioned were not noticeable.

In the most strongly acid solutions investigated ($0.01N$), the reaction is approximately of the second order; in the weakly acid, and in the alkaline solutions, the order of reaction lies between the first and second. If the assumption is made that a mono- and a bi-molecular reaction are superposed on each other, the differential equation $dx/dt = A(a-x)^2 + B(a-x)$ is obtained, where A and B are constants; this satisfies the experimental results, but still requires explanation. In acid solutions, the first term is the most important, whilst in weakly acid and alkaline solutions, the second term plays the greater part. T. S. P.

Hygroscopy of Salts. JOSEF HABERMANN (*Zeitsch. anal. Chem.*, 1913, **58**, 303—304).—The publication of Schuyten's paper on this subject (A., 1912, ii, 746) leads the author to state that he has been for some time engaged in the study of hygroscopic salts and will shortly publish the first part of his results.

Air of any constant degree of humidity is most readily obtained by the use of aqueous salt solutions (sodium chloride, sodium nitrate, and others). L. DE K.

Rate of Reduction of Mercuric Chloride by Phosphorous Acid. GEORGE A. LINHART (*Amer. J. Sci.*, 1913, [iv], **35**, 353—368. Compare Montemartini and Edigi, A., 1903, ii, 65).—Owing to the unsatisfactory nature of the results which have hitherto been obtained for the kinetics of the reaction between mercuric chloride and phosphorous acid, the author has carried out fresh experiments. By Ostwald's isolation method, it is shown that the reaction is of the first order with respect to mercuric chloride; the total reaction is of the second order (compare Montemartini and Edigi, *loc. cit.*; also Garner, Foglesong, and Wilson, A., 1911, ii, 972), taking place in two stages, probably the following: (1) $HgCl_2 + H_3PO_3 = HCl + HgCl + H_2PO_3$; (2) $2H_2PO_3 + H_2O = H_3PO_3 + H_3PO_4$, reaction (2) being very rapid as compared with (1), so that the concentration of the phosphorous acid at any time t may be denoted approximately by $(b - x/2)$, instead of $(b - x)$, b being the initial concentration, since for every two molecules decomposed one molecule is regenerated.

The reaction is accelerated by hydrion. If no hydrogen chloride is present at the outset, the velocity constant of the second order goes through a minimum, which is shown to be due chiefly to the formation of complexes between the mercuric chloride and hydrogen chloride liberated during the reaction. When hydrogen chloride

is present at the outset, the velocity constant of the second order increases continuously, which increase can be explained by the breaking down of the complexes with decreasing concentration, assuming that only the single molecules $HHgCl_3$ react with the phosphorous acid. Making this assumption, the author deduces the velocity equation: $dx/dt = k(a - x/2)(b - x/2)(C + x)$, where a, b, and C are the respective concentrations of the mercuric chloride, phosphorous acid, and hydrogen chloride at the commencement of the reaction. With this equation concordant velocity constants are obtained. T. S. P.

Oxidation of Ferrous Salts. F. R. ENNOS (*Proc. Camb. Phil. Soc.*, 1913, **17**, 182).—The rate of oxidation of ferrous salts in aqueous solution and in absence of free acid has been investigated by bubbling air or oxygen through the solutions at a constant rate of about one litre in three hours. At 60°, the rate of oxidation of the chloride, sulphate, and acetate is represented approximately by the ratio 1 : 10 : 100. In the case of the sulphate, the reaction velocity is proportional to the partial pressure of the oxygen, and the reaction appears to be of the second order so far as the ferrous salt is concerned. From the experiments on the influence of temperature, dilution, and nature of the acid radicle, it is found that the oxidation depends on the non-ionised part of the ferrous salt. H. M. D.

Velocity of the Reaction between Sodium Thiosulphate and Sodium Bromoacetate. ARTHUR SLATOR (*Zeitsch. physikal. Chem.*, 1913, **83**, 256).—The author draws attention to the results of Krapivin (this vol., ii, 310), which agree with his own (T., 1904, **85**, 1287; 1905, **87**, 481); also Slator and Twiss (T., 1909, **95**, 93). It is pointed out that the reaction between sodium thiosulphate and ethyl monobromoacetate takes place rapidly, and is suitable for use by students. J. F. S.

Hydrolysis of Esters of Substituted Aliphatic Acids. WILLIAM A. DRUSHEL and E. W. DEAN (*Amer. J. Sci.*, 1913, [iv], **35**, 486—490. Compare A., 1912, ii, 927).—The rates of hydrolysis of the ethyl esters of lactic, glyceric, and α- and β-ethoxypropionic acids have been compared at 25°, 35°, and 45°, the experiments being made in dilute solution with $0{\cdot}1N$-hydrochloric acid as catalyst. The calculated velocity coefficients for 25° are as follows: Propionate, 71·6; lactate, 73·2; glycerate, 18·5; α-ethoxypropionate, 19·7; and β-ethoxypropionate, $14{\cdot}3 \times 10^{-5}$. The temperature-coefficient for the interval 25—35° varies from 2·43 to 2·51.

From a comparison of the data for the propionate, lactate, and glycerate, it is evident that the substitution of the second hydroxyl group has a very much greater influence on the rate of hydrolysis as compared with the effect produced by the first. Although the lactate is hydrolysed somewhat more quickly than the propionate at 25°, the reverse holds at 45°. H. M. D.

Hydrolysis of Ethyl Acetate by Neutral Salt Solutions. WILLIAM E. HENDERSON and DAVID R. KELLOGG (*J. Amer. Chem. Soc.*, 1913, **35**, 396—418).—It has been shown by Kellogg (A., 1909, i, 203, 627) that the rate of hydrolysis of ethyl acetate by water is greatly accelerated by potassium chloride, bromide, or iodide. In continuation of this investigation, the catalytic action of the chlorides of sodium, lithium, calcium, strontium, barium, and cadmium, and of cadmium iodide, has been studied at 100°. Conductivity and viscosity data have been obtained for these salts at concentrations and temperature employed in the hydrolysis experiments, and from them the degree of ionisation has been calculated.

The results show that the accelerating effect of lithium chloride is greater than that of sodium chloride, whilst the degree of ionisation is less, and that the chlorides of calcium, barium, and strontium have a greater effect than either sodium or potassium chloride, although they are less ionised. Cadmium chloride, the least ionised of any of the chlorides studied, produces the greatest effect, whilst cadmium iodide, which is less ionised than any of the other salts, produces the greatest effect of all.

It is evident that the effect produced by a neutral salt on the hydrolysis of ethyl acetate is due to a specific influence of the non-ionised portion of the salt rather than to any function of the ions.

E. G.

Rate of Conversion of Cinchonine into Cinchotoxine. HENRY C. BIDDLE and LUDWIG ROSENSTEIN (*J. Amer. Chem. Soc.*, 1913, **35**, 418—426. Compare A., 1912, i, 296).—This investigation was undertaken with the object of devising a quantitative method for studying the transformation of alkaloids into their toxic isomerides, which should be more accurate than the ether extraction method employed previously. Two methods are described, one gravimetric, and the other polarimetric, and these have been applied to the determination of the specific reaction velocity of the conversion of cinchonine into cinchotoxine by the catalytic action of acetic acid.

The reaction has been found to be unimolecular with respect to the alkaloid, and the catalysis unimolecular with respect to non-dissociated acetic acid. The acetate ion has little or no influence on the rate of reaction, and the retarding effect of hydrogen ions at low concentrations is very small. E. G.

The Rate of Extraction of a Protein (Salmine) from Desiccated Tissue by an Aqueous Solvent. T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1913, **14**, 237—240).—The rate of extraction of salmine from dried fish spermatozoa by dilute acid is expressed by the formula $x = Kt^m$, where x is the amount extracted, t the time, and m and K are constants. The rate is determined by capillary forces. The accompanying chemical phenomena (decomposition of compounds of salmine within the tissue, formation of salmine chloride, etc.) occur at a relatively great velocity, and hence do not affect the rate of extraction. W. D. H.

Atomic Weight Estimation from Special Groupings of the Hydrides. FREDERICK H. LORING (*Chem. News*, 1913, **107**, 193).—The fact that the molecular weights of the hydrides vary in a linear manner with the position of the contained elements in the periodic table is suggested as affording a means of fixing approximately the values of the atomic weights of certain elements. H. M. D.

General Characters of the Actions between Atoms. MARCEL BRILLOUIN (*Ann. Chim. Phys.*, 1913, [viii], **28**, 567—577. Compare A., 1913, ii, 193).—The discussion commenced in the first paper (*loc. cit.*) is continued and extended to the consideration of valency, the mechanical explanation of which is shown to be difficult. Organic radicles are then dealt with, and it is suggested that radicles of the same valency are characterised by the existence of an external field of force, determined solely by the valency, and independent of the chemical constitution of the radicle. An attempt is then made to define precisely the field of force acting on an atom, the action between two or more atoms, and, finally, the conditions of saturation. From these investigations the conclusion is drawn that a univalent atom cannot be isotropic, and cannot be regarded as a point. T. A. H.

The General Theory of Valency. HUGO KAUFFMANN (*Zeitsch. anorg. Chem.*, 1913, **81**, 83—96).—Certain conclusions from the theory of subsidiary valencies have been tested by optical means. Methoxyl increases the basic character of distyryl ketone, and deepens the colour of its salts. The dimethylamino-group is a stronger auxochrome than methoxyl, and the basicity of tetramethylaminodistyryl ketone is actually much greater, but the colour of its salts is lessened, and in an excess of dilute acids even colourless salts are obtained. This apparently anomalous result is due to the formation of internal salts. Weak auxochromes have a greater effect on halochromy in concentrated sulphuric acid than strong auxochromes. The halochromy is governed by the capacity of the auxochrome to gather to itself valencies of hydrogen. Acetylation deepens the colour observed in the halochromy of amino-derivatives. This effect has been studied in a number of cases. C. H. D.

Radioactive Changes and the Valency Question from the Point of View of Atomic Structure. KASIMIR FAJANS (*Ber. Deut. physikal. Ges.*, 1913, **15**, 240—259).—The simple relation between the radioactive changes and the chemical character of the resulting elements appears to be conclusive in favour of the view that radioactive change is concerned with the same region of the atom as chemical phenomena. The periodic system is supposed to indicate genetic relations between all the elements, and the most natural supposition is that they are produced by the continuation of the three known radioactive series, and that each element consists of at least three non-separable elements ("Pleiad"). In attempting to continue these series the question arises whether the two end products of the thorium series, for example, can be identical, for the

energy content of the atoms must be different. The relative poverty of thorium minerals in lead as compared with those of uranium is explained by the smaller life-period of "thorium lead" than that of "uranium lead." It is necessary to suppose that, in addition to helium, at least a second atomic constituent exists, and this is taken to be hydrogen. Helium and hydrogen atoms are supposed to exist in the outer regions of heavy atoms, and the valency of the atom is conditioned by the power of these helium and hydrogen atoms to lose two or one electron respectively. In the group of rare earth elements, the evolution is regarded as being conditioned by the expulsion of singly charged hydrogen atoms rather than of helium atoms, producing an oscillation of the resulting elements between the third and fourth groups of the periodic table. A connexion between the age of minerals, their content of rare-earth elements and the amount of hydrogen contained is indicated, and also the possibility that the rare-earth elements may be found to generate hydrogen in detectable quantities. Further, it is supposed that the change in the rare-earth group, $A \xrightarrow{H} B \xrightarrow{\beta} A'$, may produce two similar but still separable elements A and A', whereas in the radio-elements in which helium is expelled instead of hydrogen, the elements are non-separable. In the VIII group something of the same sort may occur.

In explanation of β-ray changes, with increase of maximum valency by one unit, it is supposed that a helium atom arrives at the surface of the atom from its interior, and exchanges places with a hydrogen atom. The relation of these views to other structural theories is discovered. F. S.

Relation of the Value of "a" of van der Waals' Equation to the Molecular Weight and the Number of Valencies of the Molecule. ALBERT P. MATHEWS (*J. Physical. Chem.*, 1913, **17**, 183—204 Compare this vol., ii, 300).—The author has already deduced that $a = N^2M^2K$, where N is the number of molecules in one c.c. of gas under standard conditions, M the "mass of cohesion" of a molecule, and K a constant, and that M^2K is related to the surface tension. The function M^2K is also related to the molecular weight W and the sum of the valencies in the molecule Z by the empirical equation, $M^2K = 2{\cdot}98 \times 10^{-37}(WZ)^{2/3}$, so that $a = 2{\cdot}256 \times 10^{-4}(WZ)^{2/3}$. The value of the constant, 2·98, is the mean of the values given by 26 non-associating substances of which the critical data were determined by Young, the extreme values being 2·73 and 3·09. A similar value was obtained from forty-one other substances, the critical data of which are not so well established.

Associating substances, including hydrogen chloride, give a higher value than 2·98, but a number of simple gases, such as nitrous oxide, chlorine, etc., behave normally when suitable valency numbers are chosen. Thus chlorine in Cl_2 is supposed to be tervalent, oxygen in O_2 univalent, and carbon in CO_2 bivalent. Substances of low molecular weight and great simplicity, such as hydrogen and methane and substances of high molecular weight, such as

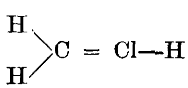
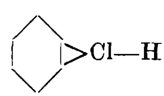
diphenyl, also give abnormal values of the constant. This is possibly because the accepted values of a are incorrect.

The close approximation of the constant to the figure representing the gravitational attraction of two average molecules, namely, $3{\cdot}11 \times 10^{-37}$, is regarded as a coincidence. R. J. C.

Valency of Chlorine as Determined from the Molecular Cohesion of Chlorine Compounds. Albert P. Mathews (*J. Physical Chem.*, 1913, **17**, 252—263. Compare preceding abstract).—The sums of the valencies in twenty-one compounds containing chlorine have been calculated from the critical data by means of the author's formula connecting a of van der Waals' equation and molecular cohesion with valency. The conclusion is drawn that chlorine is seldom or never univalent, but is certainly tervalent in most of the cases dealt with. This result finds support in Pascal's measurements of diamagnetism (1911) and Drude's theory connecting valency with absorption of light (1904).

Valencies are classified as "acting," "active but not acting," and "resting." Molecular cohesion is unaffected by resting or self-polarised valencies, but is affected equally by active and acting valencies. Active valencies are recognised by a tendency towards molecular association as in hydrogen chloride, but in non-associating substances all the valencies must be acting valencies.

The author gives structural formulæ with "acting" tervalent chlorine for a number of well-known compounds. Some of these formulæ are very unusual. Thus methyl chloride and chlorobenzene are represented as:


and


respectively. These formulæ are claimed to have advantages over the usually accepted ones in explaining some of the properties of the substances represented.

The valency of bromine and iodine cannot be decided owing to the uncertainty of most of the critical data, but fluorine appears to be univalent in fluorobenzene. R. J. C.

Valency of Oxygen, Sulphur, Nitrogen, and Phosphorus Determined from the Molecular Cohesion. Albert P. Mathews (*J. Physical Chem.*, 1913, **17**, 331—336. Compare this vol., ii, 494).—The total valency in a number of esters, calculated from the critical data, indicates that one of the oxygen atoms is quadrivalent, as suggested by Stieglitz. The oxygen in several ketones, nitrobenzene, acetic anhydride, and ethyl acetoacetate also appears to be quadrivalent, whereas in ether, sulphur dioxide, and carbon dioxide it is bivalent, and in carbon monoxide and gaseous oxygen univalent.

Sulphur is said to be quadrivalent in sulphur dioxide and sulphuryl chloride, and sexavalent in hydrogen sulphide and a number of other compounds, but in no case is it bivalent.

Nitrogen appears to be univalent in gaseous nitrogen as well as

in nitric oxide, whilst nitrous oxide, with a total valency of six, must be written N·O·N or N·N⁚O. In other compounds nitrogen is ter- or quinque-valent, according to the usual view.

In phosphine the valency of phosphorus is certainly greater than three, and possibly, in a few molecules, greater than five.

R. J. C.

Valency of the Argon Group as Determined from the Molecular Cohesion. Albert P. Mathews (*J. Physical. Chem.*, 1913, **17**, 337—343. Compare this vol., ii, 494).—The elements of the argon group, being liquefiable, must have some molecular cohesion. It follows that they must have some valency, it having been shown that there is a close connexion between the two attributes. The valencies as computed from the critical data are as follows: Helium, 0·1; neon, 0·32; argon, 1·12; krypton, 1·23; xenon, 1·80. Using the values of *a* calculated from the surface tension, a similar set of valency numbers is obtained.

The author holds that valencies are necessarily integral, so that fractional values represent some kind of equilibrium. The following hypothesis is suggested in explanation of the fractional values. The elements of the argon group have no principal valency, but a pair of secondary valencies, one of which is positive and one negative. At any given moment only a certain proportion of the atoms have their secondary valencies unlocked. The proportions are: Xenon, 90%; krypton, 65%; argon, 60%; neon, 16%; helium, 5%. This decrease in the proportion of open valencies corresponds with a progressive decrease in the solubility of these gases in water.

R. J. C.

The Nature of Auxiliary Valencies. IV. Metal Ammonias. III. Fritz Ephraim (*Zeitsch. physikal. Chem.*, 1913, **83**, 196—220. Compare A., 1912, ii, 546; this vol., ii, 129, 130).—A continuation of the work on metallic ammines of bivalent metals. The sulphates of the metals nickel, cobalt, iron, copper, manganese, zinc, mercury, tin, lead, calcium, strontium, and barium are examined as to their ammine derivatives. The temperatures are determined at which the hexammine or pentammine of the above-mentioned metals exhibit a pressure of ammonia of 500 mm., and it is found, except in the case of cadmium, that the larger the atomic volume of the metal the smaller the temperature. The metals mercury, tin, lead, calcium, strontium, and barium are not included in the above generalisation, since they do not form comparable ammines. It is shown that the value $\sqrt[3]{Tv}$ is constant when hexammines or pentammines of the sulphates of bivalent metals are considered; it has a mean value of 13·8. The value $\sqrt[3]{v}\,.\,\sqrt{T}$ is also constant, and has a mean value of 36·5. Cadmium sulphate ammines are exceptional to this, and have values 16·1 and 42·3 respectively. The physical meaning of the value $\sqrt[3]{Tv}$ is critically considered. It is shown that those sulphates of bivalent metals which form hexammines do not form pentammines, and vice versâ. The metals nickel, cobalt, iron, manganese, and cadmium form derivatives with

6, 4, and 2 molecules of ammonia, those of copper with 5, 4, and 2, and those of zinc with 5, 4, and 3 molecules of ammonia. The heat of dissociation of the various ammines is calculated by means of the formula $\log p = -Q/4{\cdot}571T + 1{\cdot}75T + 3{\cdot}3$. The modulus of the ratio between the dissociation pressure of the iodide and corresponding sulphate at a series of temperatures is calculated for the metals nickel, cobalt, iron, manganese, cadmium, and zinc. This value is very constant, and for the first four metals has a value about 1·22, whilst for the two latter the value is about 1·05—1·13. Measurements of pressures are also given for lead iodide, bromide, and chloride, and for cupric chloride. Finally, measurements are given for an isomorphous mixture of nickel and cobalt chlorides in equal proportions by weight. The values are considerably changed from those of the pure substances. J. F. S.

The Nature of Auxiliary Valencies. FRITZ FRIEDRICHS (*Zeitsch. physikal. Chem.*, 1913, **83**, 242—244).—Polemical against Ephraim (this vol., ii, 130). It is shown that in the case of insoluble solutes no transition point is to be expected; that the differences stated by Ephraim to exist between hydrates and ammines are due to the fact that he compared insoluble ammines with soluble hydrates without considering the influence of solubility on the dissociation curve; and finally it is shown that hydrates and ammines are analogous in every possible way. J. F. S.

The Importance of Symmetry in the Systematics of Chemical Compounds. A. SCHLEICHER (*Zeitsch. anorg. Chem.*, 1913, **81**, 97—101).—Theoretical. C. H. D.

New Supports for Burettes and Funnels. A. BOUCHONNET (*Bull. Soc. chim.*, 1913, [iv], **13**, 460—464).—To the base of these supports a copper rod is fixed, which fits inside a copper tube bearing a disc of opal glass and an adjustable casting, to which four simple clamps for burettes, or four bevelled rings for funnels or two of each are attached. The vessels may therefore be rotated with the receivers which are placed beneath them on the glass disk, or, by loosening the screws which fix the clamps to the stem, the disk may be moved independently. J. C. W.

An Apparatus for Extraction of Solids and Liquids. HANS ARON (*Biochem. Zeitsch.*, 1913, **50**, 386—387).—Two forms of apparatus for extraction respectively of solids and liquids are figured. A wide glass mantle is ground into a wide-mouthed flask, which contains the liquid used for extraction. The upper part of the mantle is narrowed, and connected with the inner tube of a condenser. Into the wide end of the mantle, the syphon apparatus is introduced and suspended from hooks in the upper part of the mantle. The latter differs in form according to whether the apparatus is employed for extraction of solids or liquids. The advantage claimed is that the substance extracted is continually surrounded by the boiling vapours of the liquid used for extraction. S. B. S.

Apparatus for the Recovery of Solvents in the Evaporation of Solutions. WALTHER FRIESE (*Pharm. Zentr-h.*, 1913, **54**, 419—420).—The apparatus consists essentially of two parts: a double-walled, inverted funnel-shaped vessel, through which cold water can be circulated; and a glass or metal annular trough, in which the above vessel rests on three supports. This trough is also provided with a tube for removal of condensed solvent.

In use, the trough is laid on the rim of the crystallising or evaporating dish, which is heated on the water-bath. The vapours of the solvent, mixed with some water vapour, are condensed on the sides of the funnel, from which they flow into the trough, and thence into a suitable receiver. A quantitative recovery of the solvent is not claimed. H. W.

Inorganic Chemistry.

Simple Apparatus for Catalytic Reductions with Hydrogen. HUGO VOSWINCKEL (*Chem. Zeit.*, 1913, **37**, 489).—The apparatus consists of two glass bottles of 1000—1500 c.c. capacity, each of which is provided with a side tubulure at the bottom. They are connected with each other by means of a piece of glass tubing passing through the tubulures, and the neck of each bottle is fitted with a rubber bung, glass and rubber tubing, and screw-clip. About 1000—1500 c.c. of water is placed in the bottles, and then pressure applied to the one bottle (*A*) until the other (*B*) is full of water. *B* is then connected to the hydrogen cylinder and filled with hydrogen, *A* at the same time becoming filled with water. *B* is then connected to the apparatus where the catalytic reduction is to take place, and *A* to the hydrogen cylinder, the valve of which is regulated to give the necessary pressure. When all the hydrogen in *B* has been used up, *A* has become full of hydrogen, and *B* of water; it is only necessary then to reverse the apparatus, and so on. T. S. P.

Action of Some Organic Acids on the Decomposition of Hydrogen Peroxide. C. PORLEZZA and G. NORZI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 238—245).—The decomposition of hydrogen peroxide is considerably accelerated by the presence of small quantities of manganous sulphate in neutral solution. The decomposition of hydrogen peroxide is retarded by uric acid, and even more by oxalic acid, hippuric acid, and benzoic acid. R. V. S.

Studies in Oxidation. HENRY E. ARMSTRONG and REGINALD T. COLGATE (*J. Soc. Chem. Ind.*, 1913, **32**, 391—397).—The paper is divided into the sections: (*a*) The Nature of the Process; (*b*) Passive Metals; (*c*) Higher Metallic Oxides; (*d*) Oxidation by Permanganate; (*e*) Oxidation of Carbon; and deals with the application

of one of the author's (H. E. A.) well-known views on the mechanism of the process of oxidation to the above cases (compare T., 1903, **83**, 1088; A., 1905, ii, 448). The behaviour of various metals in the presence of hydrogen peroxide and acids, when functioning as anodes, is described, the results indicating that higher unstable oxidation products are formed, which may play a part in the phenomenon of passivity. The views of Veley, with respect to the action of nitric acid on copper, of Wieland (A., 1912, ii, 347) on combustion, and of Rhead and Wheeler (T., 1912, **101**, 846) are criticised. T. S. P.

The System Sulphur. ANDREAS SMITS (*Zeitsch. physikal. Chem.*, 1913, **83**, 221—241. Compare A., 1912, ii, 40).—The first part of the paper deals with a consideration of the occurrence of two liquid layers when sulphur is suddenly cooled to below 170° (compare Smith and Holmes, A., 1903, ii, 139, 284; 1905, ii, 382, 580; 1906, ii, 157; Malus, A., 1901, ii, 131; and Kruyt, A., 1908, ii, 1028). Kruyt and Bakhuis Roozeboom were of the opinion that the formation of two layers pointed to a liquid transition point or the separation of both forms of sulphur in different layers. The author has carried out experiments which confirm the view of Smith, namely, that the two layers are due entirely to density differences of molten sulphur at different temperatures, the different temperatures being due to the poor conductivity for heat of the sulphur. It is thus made quite clear that no transition point occurs in the liquid phase. The second part of the paper is theoretical, and deals with the production of a *Tx* diagram for sulphur. The consideration leads to the conclusion that sulphur is certainly a ternary, and not a binary, system. The influence of the addition of $S\mu$ to equilibrium masses of S_R and S_M are considered under many conditions, and experiments are quoted which confirm the results theoretically observed. The diagram finally arrived at is drawn on the sides of a trigonal prism, and represents, according to the author, the simplest arrangement and a first attempt to produce such a diagram. The real diagram is probably much more complicated. J. F. S.

Action of Thionyl Chloride on the Oxides of Metals and Metalloids. HENRY B. NORTH and A. M. HAGEMAN (*J. Amer. Chem. Soc.*, 1913, **35**, 352—356).—Investigations have already been made of the action of thionyl chloride on selenium dioxide (Lenher and North, A., 1907, ii, 255), tellurium dioxide (Lenher and Hill, A., 1908, ii, 484), and on mercuric oxides (North, A., 1910, ii, 296). Darzens and Bourion (A., 1911, ii, 878) have studied its action on certain oxides, particularly those of the rare earth metals.

Experiments have now been made on the behaviour of thionyl chloride with zinc oxide, cadmium oxide, arsenic trioxide, antimony trioxide, bismuth trioxide, ferric oxide, glucinum oxide, calcium oxide, strontium oxide, magnesium oxide, silver oxide, cupric oxide, cuprous oxide, aluminium oxide, chromic oxide, and tin dioxide. These experiments were carried out in sealed tubes at 150—200°.

In general, the action of thionyl chloride on a metallic oxide takes place in accordance with the equation,

$$MO + SOCl_2 = MCl_2 + SO_2.$$

In the case of a metal which has two oxides, the lower oxide when treated with an excess of the reagent is first converted into the lower chloride, and this is then oxidised to the higher chloride, thus:

$$3MCl_2 + 4SOCl_2 = 3MCl_4 + 2SO_2 + S_2Cl_2.$$

Arsenic trioxide yields only the trichloride. Antimony trioxide reacts at the ordinary temperature to form the trichloride, but when it is heated with excess of the reagent, the pentachloride is produced. Glucinum, calcium, strontium, and aluminium oxides, chromic oxide, and tin dioxide are not attacked by thionyl chloride at temperatures up to 200°. Silver oxide is but very slightly affected, only a trace of the chloride being produced. E. G.

Some New Reactions with Thionyl Chloride. Henry B. North and A. M. Hageman (*J. Amer. Chem. Soc.*, 1913, **35**, 543—546).—In an earlier paper (preceding abstract) an account has been given of the action of thionyl chloride on certain oxides. It has now been found that the peroxides also react with this reagent, and that sulphuryl chloride is invariably one of the products.

When barium peroxide is heated with a large excess of thionyl chloride in a sealed tube at 150°, the reaction proceeds thus: $BaO_2 + 2SOCl_2 = BaCl_2 + SO_2 + SO_2Cl_2$, but when the reagents are present in molecular proportions, the following reaction occurs: $2BaO_2 + 2SOCl_2 = BaCl_2 + BaSO_4 + SO_2Cl_2$. By varying the amounts of the reagents, a combination of the two reactions can be obtained. Barium oxide is not attacked by thionyl chloride at 150°. Lead dioxide and manganese dioxide react in the same way as barium peroxide.

Sodium peroxide reacts violently with thionyl chloride at the ordinary temperature in accordance with the equations

$$2Na_2O_2 + 2SOCl_2 = 2NaCl + Na_2SO_4 + SO_2Cl_2,$$

and $Na_2O_2 + 2SOCl_2 = 2NaCl + SO_2 + SO_2Cl_2$, depending on the proportions in which the reagents are used. E. G.

Determination of the Atomic Weight of Selenium. Pierre Bruylants and A. Bytebier (*Bull. Acad. roy. Belg.*, 1912, 856—870).—The method employed by the authors was to determine the density of hydrogen selenide by direct weighing; the compressibility of the gas at 0° was also determined by essentially the same method as that used by Gray and Burt (T., 1909, **95**, 1633) in their experiments with hydrogen chloride. In determining the weight of a litre of the gas under normal conditions at Louvain, the gravitation correction was made by comparison with the weight of a litre of oxygen determined under the same conditions. The results gave 3·6715 grams as the weight of the litre of hydrogen selenide, the error being 3 parts in 10,000. The atomic weight of selenium was found to be 79·18.

The only satisfactory method for the preparation of the hydrogen selenide used was by the action of water on aluminium selenide (compare Fonzes-Diacon, A., 1907, ii, 164). The gas was dried with phosphoric oxide, and condensed in a freezing mixture of solid carbon dioxide and ether. It was purified by distillation and sublimation, and when dry did not attack mercury so long as air was excluded. T. S. P.

The Reaction of Metals and Alloys with Nitric Acid. JOHN H. STANSBIE (*J. Soc. Chem. Ind.*, 1913, **32**, 311—319).—The investigation is a continuation of previous work (A., 1908, ii, 497; 1909, ii, 403), and deals with the metals copper, arsenic, zinc, silver, and bismuth, and their alloys. The apparatus used was an improved form of that previously described. The results previously obtained with the copper–arsenic alloys (*loc. cit.*) were confirmed by a fresh series of experiments; there seems to be an intimate connexion between the amounts of nitric oxide and nitrous acid formed during the reaction, a diminution in the volume of the former corresponding with an increase in the weight of the latter.

With alloys of copper and zinc, using nitric acid, D 1·149, and a temperature of 65°, the amount of acid entering into reaction, using the same weight of alloy and same volume of acid in each experiment, gradually diminishes as the percentage of zinc increases. All the alloys containing copper give a steady evolution of nitric oxide; no nitrous oxide could be detected. All alloys containing zinc give rise to the formation of small quantities of ammonia.

The reactions of bismuth with nitric acid are very similar to those of copper, but under ordinary conditions the rate of solution is slower. If the amount of nitrous acid present in the nitric acid is made as small as possible, bismuth dissolves to a greater extent than copper, but when the nitrous acid is present in the usual proportions the opposite is the case.

In all the above experiments the metals and alloys were used in a finely powdered state; in the following experiments plates of the metals were used, the temperature being that of the room. The rate of solution of silver is considerably reduced by dilution of the acid; acid of density 1·060 has no action within twenty-four hours, although there is action after seventy-six hours. Nitrous acid accelerates the reaction. Approximately half the quantity of acid required to convert silver into its nitrate is converted into nitrous acid, which would be in accordance with Divers' equation: $2Ag + 2HNO_3 = AgNO_3 + AgNO_2 + H_2O$; very little gas is evolved during the reaction with acids varying in density from 1·060 to 1·104. Similar results were obtained with copper, except that more gas is evolved than in the case of silver, probably because the less stable character of copper nitrite enables secondary changes to take place more readily.

As the result of his experiments the author comes to the conclusion that the reactions, for example, in the case of copper, are best represented by the equations: $3Cu + 6HNO_3 = 3Cu(NO_3)(NO_2) +$

$3H_2O$; $3Cu(NO_3)(NO_2) + 2HNO_3 = 3Cu(NO_3)_2 + H_2O + 2NO$. In the reactions of metals and alloys with nitric acid it is necessary to take into account (1) the purity and physical and mechanical condition of the metal or alloy, (2) the purity and concentration of the acid, (3) temperature, (4) the accumulation of the products of reaction in the solutions. T. S. P.

Compounds of Sulphur and Phosphorus. VIII. Tetraphosphorus Trisulphide, P_4S_3, and a New Phosphorus Oxysulphide, $P_4S_3O_4$. ALFRED STOCK and KURT FRIEDERICI (*Ber.*, 1913, **46**, 1380—1387).—Dry tetraphosphorus trisulphide is stable in the air (compare A., 1912, ii, 1166), but solutions in benzene or carbon disulphide become cloudy almost immediately on exposure to the air, giving gradually a yellowish-white, voluminous precipitate of the *phosphorus oxysulphide*, $P_4S_3O_4$. This compound is best prepared by drawing air, laden with carbon disulphide vapour, for twenty-four hours through a solution of tetraphosphorus trisulphide in carbon disulphide. The precipitate thus formed is washed by decantation with carbon disulphide, and freed from the latter first in a vacuum over phosphoric oxide, and then in a current of hydrogen; in all operations it is necessary rigidly to exclude moisture. The oxysulphide forms a yellowish-white, non-crystalline powder, D = 1·96, which is insoluble in the usual solvents, and is decomposed by heat; it shows incipient fusion at 150°, and melts at about 250° to a golden-yellow liquid. It is very sensitive towards moisture, deliquescing in the air as readily as phosphoric oxide.

Ozonised oxygen can be used in the preparation instead of oxygen, when the reaction is complete in half an hour, but there is a tendency to form more highly oxidised products.

A mixture of P_4S_3 and sulphur, when heated at 100°, gives the compound P_4S_7, no matter how great the excess of sulphur. If the temperature is allowed to rise to 130° the heat of reaction further raises it rapidly to 300°, and P_4S_{10} is formed. The compound P_4S_7 is also readily obtained by heating a mixture of P_4S_3 and P_4S_{10} in the proportions of $3P_4S_3 : 4P_4S_{10}$ for twelve hours at 140—150°.

T. S. P.

Applications of Positive Rays to the Study of Chemical Problems. Sir JOSEPH J. THOMSON (*Proc. Camb. Phil. Soc.*, 1913, **17**, 201. Compare A., 1912, ii, 885, 1029).—Two samples of gases obtained from the residues of liquid air have been examined by the positive ray method. The one sample containing the heavier gases was found to be a mixture of xenon, krypton, and argon, and there were no lines on the photograph unaccounted for. The light sample was found to contain helium, neon, and a new gas of atomic weight 22. From the relative brightness of the lines of neon and the new gas, it would seem that the quantity of the new gas present in air is much smaller than that of neon.

The second part of the paper deals with the investigation of a new gas of atomic weight 3, which is found to make its appearance

in discharge tubes under certain conditions. The gas is given out by various metals when these are subjected to bombardment by cathode rays, helium being also liberated during the first stage of the bombardment. The metals used were iron, nickel, zinc, copper, lead, and platinum. It was also found to be given off by calcium carbide. H. M. D.

The Absorption of Neon by the Electrodes of Luminescent Tubes. GEORGES CLAUDE (*Compt. rend.*, 1913, **156**, 1317—1320. Compare A., 1911, ii, 602, 1087).—Neon exhibits a very marked resistance to absorption by the electrodes in luminescent tubes, whilst producing rapid cathodic volatilisation of certain metals without itself entering into this volatilisation. Small quantities of helium and nitrogen present in neon rapidly disappear when the discharge is passing, but small quantities of neon cannot be similarly removed from helium. Tubes thus freed from nitrogen, when submitted to a greatly increased current, become filled with a blue light, which is characterised by the appearance of a continuous spectrum with a strong ray in the green and a series of rays in the violet. W. G.

Experiments on the Alkali Metals. LOUIS HACKSPILL (*Ann. Chim. Phys.*, 1913, [viii], **28**, 613—696).—The preparation of cæsium, rubidium, and potassium by heating the anhydrous chlorides with metallic calcium is described. When the mixture containing a large excess of calcium is carefully heated in an exhausted iron tube placed in an electric oven, it is found that the alkali metals can be obtained in pure condition in nearly theoretical yield. The products have been used in the investigation of the physical properties, including the density, the coefficient of expansion, the vapour pressure, the density of the saturated vapour, and the electric conductivity; in addition the action of the metals on water at low temperatures has been investigated. Corresponding experiments have also been made with sodium.

The densities of the metals at 0° are 0·9723, 0·859, 1·525, and 1·903 for sodium, potassium, rubidium, and cæsium respectively; the coefficients of expansion in the solid state, 0·000216, 0·00025, 0·00027, and 0·000291; in the fused condition, 0·000274, 0·000283, 0·000338, and 0·000345; the percentage increase in volume on fusion, 1·50, 2·42, 2·28, and 2·32. From the coefficient of expansion (α), the critical temperature (T_c) has been calculated from the equation $\alpha = 1/(2T_c - T)$, where T is the temperature at which the expansion is measured. The values so obtained are: sodium, 2025°; potassium, 1965°; rubidium, 1857°; cæsium, 1627°.

In some experiments in which an attempt was made to determine the thermal expansion of the metals immersed in benzene, it was found that this hydrocarbon is acted on by cæsium even at the ordinary temperature. Although no hydrogen is evolved during the reaction, the black, amorphous substance which is obtained corresponds with the formula C_6H_5Cs. This formula is supported by the fact that diphenyl is formed when the substance is acted on

by water or alcohol. It takes fire on exposure to air, and burns with a smoky flame. On heating in carbon dioxide, it decomposes with slight explosion; it reacts violently with chloroform, but is not acted on by carbon tetrachloride, ethyl ether, or pentane.

Measurements of the vapour pressure of the metals were made at temperatures between 250° and 400°, and the results obtained are plotted in the form of vapour-pressure curves. The volatility increases at all temperatures with increase in the atomic weight. The attempts to measure the density of the saturated vapours have not given very consistent results, but they suffice to show that the alkali metals in the state of vapour consist of mon-atomic molecules.

The electric conductivities of the metals were measured in the liquid state and also in the solid state at temperatures ranging from the melting point down to liquid air temperatures. The results seem to show that the ratio of the specific resistances in the solid and liquid states is in the case of all four metals practically 1·5.

In reference to the action of water on the metals at low temperatures, it was found that the reactivity appears to increase as the atomic weight increases. The lowest temperatures at which the action could be detected were: −98° in the case of sodium, −105° for potassium, −108° for rubidium, and −116° for cæsium.

H. M. D.

Solution of the Constituents of Alluvial Sands by Subterranean Waters. F. Dienert (*Bull. Soc. chim.*, 1913, [iv], **13**, 381—394).—As the result of a series of experiments conducted with waters and sands collected in the valley of the Loire between Nevers and Sully-sur-Loire, the author finds that when rain or river water filters through or flows over sand in presence of carbon dioxide, it dissolves calcium carbonate, magnesia, silica, and alkali salts in proportions which are characteristic for a particular sand. If the waters flow over sand in presence of an insufficient quantity of carbon dioxide, they may deposit calcium carbonate, with a little magnesia, but no iron, alumina, silica, or alkali salts will be lost. Analyses of the sands used in these experiments are given, and particulars of the quantities of the soluble constituents in the waters used, before and after their contact with the sands.

T. A. H.

Determination of the Atomic Weight of Calcium. William Œchsner de Coninck (*Bull. Acad. roy. Belg.*, 1913, 222—223).—A weighed amount of pure precipitated calcium carbonate was treated with concentrated sulphuric acid. To the resulting precipitate and solution was added absolute alcohol, after which the calcium sulphate was collected on a tared filter paper, washed with absolute alcohol, and dried at 100°. The resulting atomic weights obtained were 40·16, 40·14, 40·13, 40·19, 40·11, giving an average value of 40·12 for the atomic weight of calcium.

T. S. P.

Preparation of Barium. Camille Matignon (*Compt. rend.*, 1913, **156**, 1378—1380. Compare following abstract).—Barium is

readily obtained by heating barium oxide (3 mols.) with silicon (1 atom) in a vacuum in a steel tube at 1200°. The metal distils off and condenses in the cooler part of the tube, the reaction being:

$$3BaO + Si = BaSiO_3 + 2Ba - 37 \text{ cals.}$$

The silicon can be replaced by ferrosilicon containing 95% silicon. W. G.

Reduction of Magnesia by Aluminium. CAMILLE MATIGNON (*Compt. rend.*, 1913, **156**, 1157—1159).—Aluminium powder heated with heavy magnesium oxide in a vacuum at 1200° in a steel tube, readily and almost completely reduces the oxide, the magnesium being deposited in a crystalline state in the cool part of the tube. W. G.

Lead Tree in a Silicic Acid Gel. ALFRED L. SIMON (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 171. Compare A., 1912, ii, 772).—The reduction of lead acetate in a silicic acid gel with the formation of a lead tree can be readily shown if a piece of zinc foil is supported with its lower edge below the surface of a gel prepared by mixing together a 15% solution of sodium silicate and a slight excess of 50% acetic acid, and then adding to the mixture about 10% of a concentrated solution of lead acetate. The solution is boiled to free it from carbon dioxide, and the zinc introduced into the cold solution. H. M. D.

Colloidal Lead Dioxide. Hydrolytic Method of Preparation. ALEXANDER GUTBIER and E. SAUER (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 171—177).—If small quantities of ammonium plumbichloride are added to a large volume of water, a brown, colloidal solution of lead dioxide is obtained. The reaction may be represented by the equation:

$$(NH_4)_2PbCl_6 + 4H_2O = Pb(OH)_4 + 4HCl + 2NH_4Cl.$$

The solution is unstable, and soon becomes colourless as a consequence of the action of the hydrochloric acid, which is liberated, on the colloid in accordance with:

$$Pb(OH)_4 + 4HCl = PbCl_2 + Cl_2 + 4H_2O.$$

This may be prevented to a large extent if ammonia is added to the water in sufficient quantity to neutralise the acid which is subsequently set free. If, in addition, small quantities of gum arabic are dissolved in the water, it is possible to obtain fairly stable solutions of the dioxide. The best conditions are attained when 20 c.c. of $N/5$-ammonia solution are added to 250 c.c. of a 0·1% solution of gum arabic and 1 gram of the plumbichloride added gradually to the well-stirred solution. When freed from electrolytes by dialysis, the solution can be kept for a considerable time without much decomposition. On evaporation of the solution to dryness, the dioxide becomes insoluble.

The colloidal particles move to the positive pole in an electrical field. When mixed with hydrochloric and nitric acid solutions the brown, colloidal solution is gradually decolorised, the velocity of the reaction increasing with the concentration of the acid. Sodium

hydroxide has a similar action, but the change takes place much less rapidly. Sodium chloride, barium chloride, and aluminium sulphate have no coagulating action, and in presence of these electrolytes the dioxide appears to be approximately as stable as in pure water. H. M. D.

New Method for the Preparation of White Lead. HANS HOF (*Zeitsch. anorg. Chem.*, 1913, **81**, 40—45).—Lead sulphate dissolves in boiling concentrated magnesium chloride solution (mother liquors from potassium deposits), forming magnesium sulphate, which is readily extracted, and magnesium lead chloride. When impure lead sulphate from flue dust is used, copper and silver may be removed by immersing lead plates in the solution.

Magnesium oxychloride, prepared by adding the requisite quantity of milk of lime to magnesium chloride solution and boiling, is collected and mixed with an excess of water. Magnesium lead chloride is then added at 75—80° until the alkaline reaction disappears. The lead oxychloride is then allowed to settle, and the solution, which is now free from lead, is removed by decantation. A further quantity of moist magnesium oxychloride is now mixed with boiling water and saturated with carbon dioxide until the alkaline reaction disappears. The suspension of magnesium carbonate thus obtained is then run into the mixture of lead oxychloride and water, and stirred for an hour at 80°. The product has the composition $2PbCO_3,Pb(OH)_2$, and is completely amorphous.

White lead is completely dissolved in the cold, without decomposition, by a solution of magnesium chloride, D 1·16, the solution becoming alkaline, indicating a reaction:

$$2PbCO_3,Pb(OH)_2 + MgCl_2 = 2PbCO_3,PbCl_2 + Mg(OH)_2.$$

C. H. D.

The Electrochemical Production of Colloidal Copper. T. ROLAND BRIGGS (*J. Physical Chem.*, 1913, **17**, 281—319).—Allotropic copper first described by Schützenberger (A., 1878, 548), and more recently by Benedicks (A., 1907, ii, 548) presents many points of similarity to Carey Lea's gold-coloured allotropic silver, which is generally admitted to be colloidal. The author adduces evidence that Schützenberger's allotropic copper is, in fact, colloidal, and explains its formation on the protective colloid theory.

Copper acetate solution, particularly when heated, is partly hydrolysed with the production of an insoluble basic acetate or hydroxide, some of which remains in suspension. The suspended hydroxide wanders to the cathode during electrolysis, and acts as a protective colloid to the particles of copper electro-deposited, which are thereby prevented from becoming crystalloid, so that the metal remains in the form of a solid gel. The presence of a protective colloid in copper acetate solution is demonstrated by the formation of an emulsion on shaking it with benzene, although the effect is less marked than with ferric acetate. All the properties of Schützenberger's copper, including its dissolution in nitric acid

with evolution of nitrous oxide, can be explained on the colloid hypothesis.

The electrolysis between 50° and 90° of solutions of copper propionate, acetate, and formate in presence of gelatin gives rise to a series of golden to red cathode films. Some of the red films which were lacquered kept their colour for at least twelve months. Electrolysis below 35° gives rise to a pale brown deposit, which weighs 20 to 30% more than Faraday's law requires, and is contaminated with gelatin, copper oxide, and acetic acid or copper acetate. On immersion in one of the above electrolytes, it undergoes a remarkable series of colour changes to golden-brown, reddish-purple, purple, blue, light blue, olive-green. The blue patina is exceedingly beautiful, but unfortunately turns to a pale bluish-grey or olive-green on long exposure, and no means of fixing it could be found.

The production of these colours is analogous to photographic development. Dilute copper sulphate is to some extent active as a developer, and the formate more so, but the full blue colour was only obtained with the acetate and propionate. Other salts of copper are inactive. No appreciable change in weight occurs on development, but the blue colour is only on the surface of the film, which presents the ordinary copper colour at the back when stripped off the copper, brass, or platinum cathode. The blue is temporarily destroyed by hydrazine and by oxidising agents. No colour is developed on an oxidised film, but this can be sensitised again by reduction with hydrazine.

No good colour effects were obtained with films deposited in presence of colloids other than gelatin, but starch in acid solutions is slightly active, since it tends to accumulate at the cathode. The cathode deposits obtained from other salts of copper in presence of gelatin are abnormal, but none develop any colour in acetate solution.

It is supposed that the "development" of these cathode deposits consists in the adsorption of colloidal copper hydroxide from the solution by the deposit of colloidal copper. R. J. C.

Micrographic Notes on Copper. H. BAUCKE (*Intern. Zeitsch. Metallographie*, 1913, **4**, 155—166).—Cold-worked copper undergoes recrystallisation at 200°, at which temperature the size of the crystal grains is a minimum. It increases very slowly up to 700°, and then very rapidly. Prolonged heating at 450° produces the same coarse structure as rapid heating to higher temperatures. Recrystallisation is also well marked after six hundred days at 100°. Superficial conversion of the hardened into annealed material at 160° is greatly accelerated by close contact with an etched, crystalline surface of copper. Prolonged etching with a dilute electrolyte also brings about conversion to the crystalline condition.

The oxide eutectic in copper undergoes segregation at 800° or upwards, but at 450° the effect is imperceptible after thirty days.

C. H. D.

The Rare Earths. Yttrium Chloride and the Atomic Weight of Yttrium. JAMES E. EGAN and CLARENCE W. BALKE (*J. Amer. Chem. Soc.*, 1913, **35**, 365—377).—Rare earths obtained from gadolinite and xenotime have been fractionated by various methods. Fractions obtained by James' bromate method (A., 1908, ii, 190, 499) have been submitted to Muthmann and Böhn's chromate method (A., 1900, ii, 209). It has been found that by this means small quantities of fairly pure yttria can be rapidly prepared from mixtures containing small amounts of erbium and holmium, but that the method cannot be applied to the fractionation of mixtures containing didymium and gadolinium, unless these are first removed by means of potassium sulphate.

The determination of the ratio $Yr_2O_3 : Yr_2(SO_4)_3$ yielded values for the atomic weight which are lower than those obtained by other methods, but a study of the ratio $Yr_2O_3 : 2YrCl_3$ gave values varying from 90·10 to 90·14 (O=16; Cl=35·46). Yttrium material, containing not more than 0·5% of erbium, gave the value 90·12.

E. G.

Yttrium Sodium Sulphate. CHARLES JAMES and H. C. HOLDEN (*J. Amer. Chem. Soc.*, 1913, **35**, 559—563).—In using sodium sulphate for effecting the separation of the cerium and yttrium earths, varying results were obtained, and this has led to an investigation of the system, yttrium sulphate, sodium sulphate, and water. The results have shown that at 25° only one yttrium sodium sulphate exists, namely, $Yr_2(SO_4)_3,Na_2SO_4,2H_2O$, which has been described by Cleve. The solutions showed a tendency to remain in the metastable condition for many months. The efficiency of sodium sulphate for separating cerium and yttrium earths depends on its concentration; if the solution is too concentrated, much of the yttrium earths is precipitated. E. G.

Physico-chemical Researches on the Electrometallurgy of Aluminium. PAUL PASCAL and ALCIDE JOUNIAUX (*Bull. Soc. chim.*, 1913, [iv], **13**, 439—449).—Owing to the discordant and incomplete figures which are given in the literature on the thermal properties of mixtures of cryolite, alumina, and fluorspar, the subject has been systematically studied. About 35 grams of the pure substances were intimately mixed and pressed down in a nickel crucible, and then packed in a graphite crucible with iron filings and heated in a Méker furnace, the thermo-couple being used as a stirrer. Cryolite had the accepted m. p. 977°, but fluorspar was found to have m. p. 1361°, which is much higher than is usually stated. The eutectic mixture of cryolite and fluorspar had m. p. 905°, and was composed of 74·6% of the former, whilst the mixed crystals contained respectively 20·5% and 50% of the fluoride. The eutectic mixture of cryolite and alumina had m. p. 904°, and contained 24% of alumina, whilst the mixed crystals contained 20% and 29%. The mixture of fluorspar and alumina (26·5%) had m. p. 1270°, and gave crystals containing 20% and 28·5% of alumina.

In order to simplify the study of the ternary system the mixtures

were arranged so that two of the constituents were in a proportion studied in the case of the binary mixtures. By triangulation the eutectic point was found to be 868°, the mixture containing 59·3% cryolite, 23·0% fluorspar, and 17·7% alumina. The interpretation of the results was facilitated by the examination of the solidified mass. Mixtures which came within the cryolite section of the triangle presented a sugar-like fracture, those in the fluorspar section showed large cleavage faces with chatoyant reflexion, whilst the mixed crystals isomorphous with alumina were flattened, chiefly hexagonal, and had a grey reflexion.

Isotherms were also plotted. From them it is seen that this case is unusual, but rather ideal in that the maximum lowering of the melting point of a binary mixture is attained by adding the third constituent to the binary eutectic. Temperatures below 950°, which is the point aimed at in the manufacture of aluminium, are represented by a small quadrilateral, from which it is seen that the addition of more fluorspar than 36% of the cryolite must be avoided, whereas more alumina than is commonly used might be added, although the risk of volatilisation of cryolite makes it undesirable.

By measuring the temperature of final solidification it was possible to trace out the solidus with its thermic "landing." This leads to the following compositions for the mixed crystals composing the ternary eutectic:—cryolite: fluorspar: alumina, I, 77 : 16 : 7; II, 60 : 15 : 25; III, 34 : 54 : 12. J. C. W.

The Formation of Aluminium Nitride from Alumina, Carbon, and Nitrogen. I. WALTER FRAENKEL (*Zeitsch. Elektrochem.*, 1913, **19**, 362—373).—The formation of aluminium nitride from alumina and nitrogen was studied with respect to the velocity of formation, temperature at which the reaction occurs, and the influence of the presence of carbon monoxide on the process. The reactions were effected in a carbon tube contained in a large glass vessel; the tube was electrically heated, and temperature readings were made by means of a Holborn-Kurlbaum pyrometer. Alumina and carbon in the form of soot were mixed together in the proportion of $2Al_2O_3$: 1C, and compressed into pellets of 0·5—1 gram. The reaction was carried out on one of the pellets in each case. It is shown that aluminium nitride is formed to a small extent below 1400°, and that at 1500° the velocity of formation becomes very great. The velocity is arrived at in the various experiments by allowing the reaction to proceed for a definite time (thirty minutes) and then boiling the product with alkali and estimating the ammonia evolved. The course of the reaction is expressed by the equation $Al_2O_3 + 3C + N_2 = 2AlN + 3CO$. This reaction is strongly endothermic, and proceeds at about the same rate when the pressure is reduced to 250 mm. of nitrogen. The presence of carbon monoxide diminishes the velocity of the reaction, and as this gas is a product of the reaction, experiments were made to see if the reaction was reversible. It is shown that at 1500° an equilibrium is set up when carbon monoxide is present to 25—40 vol. %; at 1600° the

equilibrium occurs at 50—65 vol. % of carbon monoxide. When alumina is heated alone with carbon in carbon monoxide of 20—65 mm. pressure, reduction occurs at temperatures as low as 1450°, with the formation of aluminium carbide. The experiments show that, qualitatively at least, the formation of carbide runs parallel with the formation of nitride, and it is suggested that the nitride is formed through the carbide. The use of different forms of carbon causes the reaction to occur at different velocities. The authors can find no evidence to support the equation of Peacock and du Pont (U.S.A. Pat. 1031581/82), which represents the reaction in the following way: $Al_2O_3+6C+3N_2=Al_2C_3N_6+3CO$.

J. F. S.

"Liquefaction" of Clay by Alkali. JOHANNES K. NEUBERT (*Koll. Chem. Beihefte*, 1913, **4**, 261—342).—The author has made a detailed investigation of the influence of sodium and calcium hydroxides on the thinning of clay pastes, both in the presence and absence of humus substances. With this object measurements have been made of the adsorption of the alkali by the clay, and also of the electrical conductivity and viscosity of clay suspensions containing alkali hydroxide in varying concentrations.

The results obtained in the investigation of the distribution of the alkali between water and the various clays indicate that the hydroxide is adsorbed in accordance with the ordinary exponential formula. This phenomenon is modified to a greater or less extent in the presence of humus substances, which combine with the alkali to form humates. The thinning of a clay mash in presence of alkali is to a large extent determined by the swelling of the humus substance in the clay particles; this leads to a process of disintegration, whereby larger quantities of alkali humate are formed, and this substance appears to play the part of a protective colloid.

On account of the chemical reaction which thus occurs in presence of humus, the distribution of the alkali between the solid and liquid phases is found to deviate very considerably from the requirements of the exponential formula when the concentration of the alkali hydroxide is very small.

The viscosity measurements indicate that slow changes occur in the character of the clay suspensions, but it seems probable that these can be accounted for on the basis of the swelling and disintegration processes referred to above.

H. M. D.

New Process for the Utilisation of Iron and Manganese Ores Rich in Silicon. NAZARENO TARUGI (*Chem. Zeit.*, 1913, **37**, 511—512).—In Italy and other countries there are considerable deposits of iron and manganese ores containing more than 20% of silicon, and the author proposes the following method for their utilisation. By the action of superheated steam on magnesium chloride, hydrochloric acid is produced, with which the ores are then treated in suitable vessels. The chlorides of iron and manganese thus produced are separated from the silicon compounds by lixiviation, and the solution so obtained treated with the magnesium oxide

from the first process, whereby all the iron is precipitated as hydrated oxide and magnesium chloride regenerated.

The manganese can be separated from the iron by replacing part or all of the magnesium oxide by lime. The calcium chloride thus obtained can be converted into magnesium chloride by the addition of the requisite quantity of magnesia and treatment with carbon dioxide.

The products obtained are free from sulphur and phosphorus, no matter how much of these elements was present in the original ores.

T. S. P.

The So-called Fibrous Structure in Mild Steel. PAUL OBERHOFFER (*Zeitsch. anorg. Chem.*, 1913, **81**, 156—169).—A fibrous structure, due to parallel arrangement of ferrite and pearlite masses, presents itself in all hot-rolled steels, with the exception of pure pearlitic steel. All kinds of hot-working produce the effect, but its degree is dependent on the nature of the working, the temperature, and the rate of heating and cooling. The production of the structure is due to the influence of slag enclosures, which serve as nuclei for the recrystallisation of the ferrite. That part of the steel which is derived from the outside layer of the ingot, and is almost free from slag, does not develop the fibrous structure. The relation between structure and mechanical properties has also been determined.

C. H. D.

The Toughness of Iron [Steel] at Different Temperatures. PAUL GOERENS and G. HARTEL (*Zeitsch. anorg. Chem.*, 1913, **81**, 130—144).—Tests have been made by heating or cooling the specimen beyond the required temperature, placing the bar on the anvil of the testing machine, and starting the test when a thermocouple indicates that the correct temperature has been reached. Charpy's method of shock-testing with notched bars has been used. The two steels contained 0·089 and 0·085% of carbon respectively, but specimens from the heads of the ingots, exhibiting considerable segregation, have also been examined.

The tests extend from $-75°$ to $1000°$, and the curves of work done are very regular, showing distinct maxima at 35° and 600°, and a minimum at 450°. Above 600° the work done in fracture falls off rapidly. At $-75°$ the steel is brittle. Discontinuities at the critical temperatures of the steel are not observed. The curve showing the angle through which the bars are bent has a sharp minimum between 450° and 500°.

C. H. D.

Action of Electrolytes on Metals under Stress. H. BAUCKE (*Intern. Zeitsch. Metallographie*, 1913, **4**, 129—142).—Steel balls used for bearings, when sawn through for microscopical examination and etched with hydrochloric acid (1 : 2), develop numerous cracks, the surface of the metal becoming first corrugated, after which rupture occurs. The effect is due to the action of the electrolyte in accelerating the passage from the metastable to the stable condition. Flaws in steel boiler-plates, in the neighbourhood of rivet-holes, where

the metal is locally strained, are also caused to spread by the action of acids. C. H. D.

The Transformations of Alloys of Iron and Silicon. GEORGES CHARPY and ANDRÉ CORNU (*Compt. rend.*, 1913, **156**, 1240—1243).—A study of the dilatation curves of soft steels, containing varying percentages of silicon, shows that the addition of silicon has no appreciable effect on the dilatation between 0° and 700°. The irregularity in the dilatation curve for ordinary steel observed between 800° and 900° is not displaced on the temperature scale, but the departure from the regular curve becomes less, and finally vanishes with increase of silicon up to 1·3%. Thus with steels containing more than 1·3% of silicon the dilatation curve shows no transformation between 0° and 900°, whereas the cooling curve shows one at 700°. W. G.

The Transformation of Alloys of Iron and Silicon. ÉMILE VIGOUROUX (*Compt. rend.*, 1913, **156**, 1374—1376).—A reply to Charpy and Cornu (preceding abstract), in which the author maintains that it is the point A_2 which is of primary importance either in iron alone or alloyed with silicon, that the point A_3 does not exist, and that the point A_1 only occurs when carbon is present. In the re-heating of iron the transformation A_2 begins at 726° and ends at 746°, the addition of silicon causing an immediate rise in this transformation temperature. W. G.

Influence of Manganese on the Mechanical and Structural Properties of Low Carbon Steels of Commercial Quality. A. STADELER (*Zeitsch. anorg. Chem.*, 1913, **81**, 61—69. Compare Lang, A., 1911, ii, 206).—Experiments with low-carbon steels, containing only 0·008% Si, and low phosphorus and sulphur, show that the tenacity is increased proportionately to the manganese up to 0·7% Mn. The elongation and contraction are not altered by manganese within that limit, and depend only on the carbon content. The presence of manganese is without influence on the microscopic structure. C. H. D.

Reciprocal Behaviour of Alkali Sulphates, Chromates, Molybdates, and Tungstates at Low and at High Temperatures. II. MARIO AMADORI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 453—459. Compare A., 1912, ii, 757).—The paper records the results of the thermal analysis of the systems:

$$K_2SO_4-K_2CrO_4,\ K_2CrO_4-K_2MoO_4,\ \text{and}\ K_2SO_4-K_2MoO_4.$$

The m. p.'s of certain salts were found to be as follows: potassium sulphate, 1070°; potassium chromate, 978°; potassium molybdate, 926°; potassium tungstate, 894°. The transition points of these salts are: potassium sulphate, 585°; potassium chromate, 666°; potassium molybdate, 475°; potassium tungstate, 575°. The results obtained in the system $K_2SO_4-K_2CrO_4$ agree with those of Groschuff (A., 1908, ii, 501). In the system $K_2CrO_4-K_2MoO_4$ the curve of crystallisation is also intermediate between the solidification tem-

peratures of the two salts. Mixtures up to 30 mol. % of chromate crystallise at the m. p. of the molybdate. The curve of the system K_2SO_4–K_2MoO_4 is also continuous, but there is a very flat minimum 6° below the m. p. of the molybdate. The m. p. of the mixture containing 45 mol. % of sulphate is equal to that of the pure molybdate. Analogous curves were obtained for the corresponding sodium salts by Boeke (A., 1906, ii, 750). R. V. S.

Electrochemistry of the Chromium Group. I. Tungsten and Uranium. ARTHUR FISCHER (*Zeitsch. anorg. Chem.*, 1913, **81**, 170—208).—[With A. RODERBURG.]—Rods of metallic tungsten are prepared by Wartenberg's method (A., 1907, ii, 697), using a modified apparatus with a cathode composed of tungsten impregnated with calcium and barium oxides, and an auxiliary tungsten electrode for starting the arc. The electrolyte used is an alcoholic solution of tungsten hexachloride, and the comparison electrode a calomel electrode in contact with an alcoholic solution of lithium chloride. Comparative measurements are made with alcoholic cupric chloride against the same electrode. Tungsten is found to occupy a place in the potential series between antimony and mercury. Passivity is not observed. The normal potential is at least 0·609 volt.

[With ERIC K. RIDEAL.]—It is not possible to obtain rods of uranium of sufficiently high conductivity for fusion by Wartenberg's method, and the material used for potential measurements is that obtained from oxide and carbon, fused in a vacuum furnace. It thus contains carbide. Using an alcoholic solution of uranium hexachloride, uranium is found to have a potential between copper and hydrogen.

It has not been found possible to obtain metallic tungsten by the electrolysis of alcoholic solutions of tungsten salts, or of an aqueous solution of pertungstic acid. Alcoholic tungsten hexachloride yields, in the cathode compartment, green crystals of the compound $WCl_2(OEt)_3$ (this vol., i, 584). Uranium does not yield a similar product.

The electrolysis of solutions of uranium acetate yields a deposit of a hydrated uranium oxide. The conditions of deposition in different electrolytes have been determined. Both acid and alkaline solutions yield the uranium in the same state of oxidation.

C. H. D.

Preparation of Pure Uranium. A. RODERBURG (*Zeitsch. anorg. Chem.*, 1913, **81**, 122—129).—Uranium has not yet been obtained in a sufficiently pure condition for measurements of the electrolytic potential. Uranium tetrachloride is best prepared by grinding the oxide, U_3O_8, with sugar and heating to redness, and then heating the product in a porcelain boat in a current of chlorine. The product always contains aluminium and silicon derived from the porcelain. When reduced by sodium in a closed iron vessel, much iron is always taken up. Nickel, magnesia, graphite, or silver vessels are rapidly destroyed. Nickel steel is more resistant than iron or other steels.

The attempt has been made to reduce uranium tetrafluoride, which is more readily obtained pure. Sodium is not available for this purpose, on account of the sparing solubility of sodium fluoride in water, whilst potassium has been found to escape in the form of vapour, even when the joints of the vessel are tightly made.

C. H. D.

The Equilibrium Tetragonal Tin $\rightleftarrows$ Rhombic Tin. Ernst Cohen (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 839—840).—Polemical against Smits and de Leeuw (this vol., ii, 141).

H. M. D.

Oxidation of Stannous Chloride in the Air in Presence of Ferrous Chloride. T. Warynski and W. Towtkiewicz (*Ann Chim. anal.*, 1913, **18**, 130—132).—Of twenty-five salts experimented with, the only one that strongly accelerates the oxidation of stannous chloride dissolved in dilute hydrochloric acid is ferrous chloride. From the tables given, it is evident that the maximum effect is obtained when 1 mol. of ferrous chloride is added to 100 mols. of stannous chloride. If more is added, the action decreases.

L. de K.

Compounds of Titanium Dioxide with Selenic and Selenious Acids. Hans Brenek (*Zeitsch. anorg. Chem.*, 1913, **80**, 448—452).—A solution of α-titanic acid in hot dilute sulphuric acid is boiled with selenic acid. The white precipitate has the composition TiO_2,SeO_3,H_2O, whilst with one-half the quantity of selenic acid a similar compound, $2TiO_2,SeO_3,H_2O$, is obtained. Selenious acid also yields two compounds, TiO_2,SeO_2,H_2O and $2TiO_2,SeO_2,H_2O$. The selenious compounds dissolve more readily in water than the selenic compounds. All are soluble in hot mineral acids.

C. H. D.

Zirconium Carbonates. Edouard Chauvenet (*Bull. Soc. chim.*, 1913, [iv], **13**, 454—457).—Dry zirconium oxide does not combine directly with carbon dioxide, but at temperatures below 450° it absorbs a small amount of the gas. When a zirconium salt is precipitated by sodium carbonate of any concentration, the *hydrate*, $ZrCO_4,ZrO_2,8H_2O$, is precipitated as a gelatinous, microcrystalline mass (compare Berzelius, *Ann. Chim. Phys.*, 1825, 337; Hermann, *Jahresb.*, 1866, 89, 191), which changes into the *hydrate* with $2H_2O$ in an exhausted desiccator. Above 60° it begins to lose carbon dioxide as well as water, and forms $2ZrCO_4,3ZrO_2,3H_2O$, which, towards 250°, becomes still more basic and agrees with $ZrCO_4,3ZrO_2,H_2O$, and then steadily decomposes, until at 400° pure oxide remains. An anhydrous carbonate seems incapable of existence. Like thorium, zirconium forms ortho-carbonates, but, unlike that metal, it only yields a basic carbonate by precipitation. Under 30 or 40 atmospheres pressure, however, the dihydrated basic carbonate absorbs carbon dioxide, and forms a hydrated normal carbonate, $CO_4Zr,2H_2O$.

J. C. W.

Chemistry of Gold. Victor Lenher (*J. Amer. Chem. Soc.*, 1913, **35**, 546—552).—An examination of the action of various organic

reducing agents on auric chloride has shown that aurous compounds cannot be obtained in this way. In alkaline solutions, numerous compounds, such as formic and lactic acids, formaldehyde, acetone, phenol, and aniline, cause the immediate precipitation of gold, whilst a few substances, such as pyrogallol, quinol, and other photographic developers, produce the same effect in acid solutions. Many organic liquids which are immiscible with water extract auric chloride from its aqueous solutions.

Of inorganic reducing agents, sulphurous acid and arsenious oxide are capable of reducing auric salts to the aurous state, but all other reagents studied cause the precipitation of gold. Sulphurous acid has proved the most satisfactory for the purpose (compare Diemer, following abstract). E. G.

Aurous Chloride. MELVIN E. DIEMER (*J. Amer. Chem. Soc.*, 1913, **35**, 552—559).—When auric chloride, containing hydrochloric acid and water, is heated at 100°, it gradually loses weight, and is converted into the metal. If, however, the auric chloride is prepared by dissolving gold in aqua regia, evaporating the solution, and heating the residue at 200° in a current of chlorine, it is obtained free from hydrogen chloride and water. When such anhydrous auric chloride is heated at 190° and weighed at regular intervals, it is found that at a certain point it is completely converted into aurous chloride. Aurous chloride is rapidly decomposed by water in accordance with the equation $3AuCl = 2Au + AuCl_3$. When a solution of the salt in ammonia is acidified with hydrochloric acid, the *compound*, $AuNH_3Cl$, is obtained as a white, crystalline precipitate, and is very unstable.

When a solution of auric chloride is treated with sulphur dioxide, its colour is reduced to some extent, but, before it becomes colourless, decomposition takes place, and gold separates. If chloride of sodium, potassium, ammonium, calcium, or magnesium is added to an auric chloride solution, the yellow colour can be entirely removed by sulphur dioxide, and this reaction can be used for the volumetric estimation of gold. Determinations have been made of the single potential of gold in an auric chloride solution at various stages of its reduction by sulphur dioxide in presence of each of the chlorides mentioned, and all the curves obtained show a decided break corresponding with the formation of an aurous compound at an intermediate stage of the reduction. Further experiments have afforded evidence that in such solutions aurous chloride exists as a compound of the type $AuCl,NaCl$, which is unstable except in presence of a large amount of the chloride of the alkali metal. When these double compounds suffer decomposition, the solution becomes yellow, owing to the formation of auric chloride, and gold is precipitated. E. G.

Mineralogical Chemistry.

The Melting Points of Some of the Rarer Minerals. ARNOLD L. FLETCHER (*Sci. Proc. Roy. Dubl. Soc.*, 1913, **13**, 443—459).—The melting points were obtained with an improved form of the Joly meldometer, in which the temperatures were determined by measuring the extension of the platinum strip on heating. The instrument was calibrated with substances of known melting point, and could be used for temperatures between 300° and about 1600°. The melting points and behaviour of minerals belonging to the following classes were investigated: fluorides, orthosilicates, subsilicates, titano-silicates, columbates and tantalates, phosphates and arsenates, and uranates.

The results obtained by Cusack (A., 1898, ii, 383) are corrected in the light of the author's results. T. S. P.

Maucherite, a New Nickel Mineral from Thuringia. FRIEDRICH GRÜNLING (*Centr. Min.*, 1913, 225—226).—This new mineral, which was at first mistaken for rammelsbergite, occurs together with niccolite, chloanthite, native bismuth, calcite, barytes, manganite, etc., in veins ("Kobaltrücken") in the copper-shales (Kupferschiefer) at Eisleben, Thuringia. The crystals have the form of rectangular plates (tetragonal or orthorhombic?), and are arranged in fan-shaped groups; compact, fibrous, and cellular masses also occur. The colour is reddish-silver-white, altering to greyish-copper-red, and the streak blackish-grey. D 7·83. Analyses, I by Friedrich, and II by Prandtl, give the formula Ni_3As_2:

	As.	S.	Ni.	Co.	Pb.	Fe.	Insol.	Total.
I.	45·66	—	49·51	0·93	—	—	—	96·10
II.	43·67	0·17	52·71	2·15	0·20	0·40	0·40	99·70

L. J. S.

The Natural Crystalline Carbonates of Calcium, Magnesium, Iron, and Manganese. KARL GRÜNBERG (*Zeitsch. anorg. Chem.*, 1913, **80**, 337—396).—The material employed in this investigation includes ankerites, in which the molecular proportion of calcium carbonates is equal to the sum of the carbonates of magnesium, iron, and manganese; dolomitic rocks, in which the proportion of calcium is lower; and chalybites, containing the carbonates of iron, manganese, and magnesium, with little or no calcium. Determinations of density show that the density of ankerites varies in a linear manner between the limits $CaFe(CO_3)_2$ and $CaMg(CO_3)_2$, whilst the former compound has a density which is the mean of those calculated from calcite and siderite.

By heating the powdered minerals in a silica vessel in a stream of hot air, free from carbon dioxide, the rate of dissociation of the carbonates has been determined. When a mixture of artificial

magnesite, dolomite, and calcite is thus heated, the magnesite is first completely decomposed at 410°; the dolomite loses carbon dioxide corresponding with its magnesium content at 500° and with its calcium content at 530°; finally the calcite is decomposed at 570°. The same order is observed when a stream of carbon dioxide is used. Determinations with ankerite and two dolomitic rocks indicate that in both materials there is no compound of magnesium and calcium carbonates, but that mixtures of ankerite with calcite are present. On the other hand, another dolomitic rock behaves as a mixture of dolomite and magnesite. Microchemical methods of distinguishing the intermixed carbonates in thin sections are described.

Dilute hydrochloric acid attacks chalybite much more slowly than ankerite, and the solution always contains relatively more iron and less manganese than the original mineral. The compound $CaFe(CO_3)_2$ is more readily attacked than $CaMg(CO_3)_2$, with which it is isomorphous, whilst the third component of ankerite, the compound $CaMn(CO_3)_2$, is the most resistant of all. Ankerite and dolomite are decomposed as such, and not fractionally. Similar conclusions are drawn from the action of copper nitrate on the minerals, but the differences of solubility are even greater than with hydrochloric acid. C. H. D.

Certain Sulphates from the Neighbourhood of the Monastery of St. George in the Crimea. SERGEI P. POPOV (*Bull. Acad. Sci. St. Pétersbourg*, 1913, 253—256).—Pebbles on the shores of the Black Sea, near the Monastery of St. George, are coated with white and yellow mineral deposits, which are found to be sulphates of various compositions. One of the purest of these, which was white with a very faint bluish-green tint, gave the following percentage results on analysis:

SO_3.	Al_2O_3.	Fe_2O_3.	MgO.	MnO.	NiO.	CuO.	Na_2O.	H_2O.	Insol. matter.	Total.
36·25	11·42	trace	4·08	0·42	0·38	0·63	0·40	45·78	0·74	100·10

If the CuO, NiO, MnO, and Na_2O are calculated as MgO, the above figures correspond well with the formula $MgAl_2(SO_4)_4,22H_2O$, which is that of pickeringite. Partial replacement of the magnesia by other oxides has been observed in other samples of pickeringite. In other specimens of the white sulphate, the ratio between the oxides R_2O_3 and RO was found to be different from that shown above.

The yellow substances consist of iron sulphates containing free sulphur and various impurities. Gypsum is also found.

The formation of pickeringite and other alumino-sulphates is regarded as due to the action on the alumino-silicates of the pebbles of sulphuric acid resulting from the weathering of pyrites; the latter may also be the source of the copper and nickel. T. H. P.

Attempts to Produce Mixed Crystals of Diopside and Jadeite. VERA SCHUMOFF-DELEANO (*Centr. Min.*, 1913, 227—230).—Mixtures of artificial diopside ($CaMgSi_2O_6$) and jadeite ($NaAlSi_2O_6$)

were fused, and the products examined microscopically. A homogeneous, crystalline mass is obtained only when less than 5% of jadeite is present. The optical characters ($c\gamma = 39°$, $n\gamma = 1·689$) are practically the same as those for pure diopside; m. p. 1150—1200° (that of pure diopside being 1260—1300°). With more jadeite in the mixture, the product contains crystals of two kinds and some glass; and with still richer mixtures, only glass. Jadeite could not be crystallised artificially.

Diopside, when fused with sodium aluminate, $NaAlO_2$, takes up some alumina, with a slight increase in the angle of optical extinction. L. J. S.

Chemical Constitution of Nephelite. V. V. KARANDEEV (*Bull. Acad. Sci. St. Pétersbourg*, 1913, 267—277).—The author describes a specimen of elæolite from Mias, near the shores of Lake Ilmen. The mineral, which has a pale rose colour and a fatty lustre, has $D_4^{15·25-17}$ 2·6295, and gives the following results on analysis:

SiO_2.	Al_2O_3.	CaO.	Na_2O.	K_2O.	Loss on heating.	Total.
43·64	33·84	0·41	16·14	5·82	0·83	100·68

These figures are discussed in relation to the various views which have been expressed concerning the chemical structure of nephelite (compare Thugutt, A., 1895, ii, 358; Rammelsberg, A., 1896, ii, 189; Clarke, A., 1897, ii, 51; Morozewicz, A., 1908, ii, 201; Wallace, A., 1909, ii, 665; Foote and Bradley, A., 1911, ii, 122; Bowen, A., 1912, ii, 176, 774). T. H. P.

Chemical Investigation of Certain Minerals from Ceylon Gravel. II. GEORGEI P. TSCHERNIK (*Bull. Acad. Sci. St. Pétersbourg*, 1913, 365—376. Compare this vol., ii, 421).—The gravel from the Sabaragamuwa province of Ceylon contains a mineral which occurs in the form of dull, greyish-black pebbles, D 4·68, with a velvety-black, flat conchoidal, glassy fracture. It shows neither cleavage nor crystalline form, and exhibits but slight transparency, thin chips transmitting yellowish-brown light at their edges. It gives a dark brown streak, and scratches apatite, but not orthoclase. Its percentage composition is as follows:

SiO_2.	TiO_2.	Ce_2O_3.	Y_2O_3.	Al_2O_3.	Fe_2O_3.	ThO_2.	ZrO_2.	FeO.	MnO.
23·73	19·55	33·35	1·56	0·58	3·07	2·61	3·42	6·07	2·00

CaO.	MgO.	GlO.	$K_2O + Na_2O$.	H_2O.	Total.
2·91	0·12	0·04	little	trace	99·01

These results are expressed by the formula: $6Ce_2O_3(SiO_2)_3 + Fe_2O_3(SiO_2)_3 + 6FeO(TiO_2) + 3CaO(TiO_2) + 2ZrO_2(TiO_2)_2$, which, together with the physical properties, indicate that the mineral belongs to the tscheffkinites. T. H. P.

Application of Colloidal Chemistry to Mineralogy and Geology. Nature of Meerschaum. H. MICHEL (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 165—170).—An examination has been made

of the microscopic structure, the optical properties, and the behaviour towards dyes of different samples of meerschaum obtained from various sources. The observations seem to show that the meerschaums consist of mixtures of a fibrous, crystalline silicate with constant optical properties, and of a gel. The crystalline constituent is basic and absorbs acid dyes, whilst the isotropic substance is acidic and absorbs basic dyes. When a finely powdered sample of meerschaum is subjected to the action of a solution containing methylene-blue and magenta, it is found that the mineral becomes blue and the solution red. This is attributed to the much greater rate at which the basic dye is absorbed by the gel. The variable water content of the meerschaums is probably connected with the varying proportion of the two constituents, for the constancy of the optical properties of the crystalline constituent would seem to show that the proportion of water in this is quite constant. H. M. D.

Behaviour of Cimolite before the Blowpipe with Cobalt Solution. HERMANN STREMME (*Centr. Min.*, 1913, 313—318).—A further criticism and reply to Thugutt (A., 1912, ii, 267) on the constitution of the minerals of the allophane group. The cimolite from Bilin, Bohemia, examined by Thugutt, does not become blue when ignited with cobalt solution, and he consequently drew the conclusion that this mineral represents a definite compound of alumina, silica, and water. His analysis showed, however, 2·49% FeO, and this is sufficient to mask any coloration. L. J. S.

Cancrinite- and Nephelite-bearing Bombs from the Laacher See District. REINHARD BRAUNS and JOHANNES UHLIG (*Jahrb. Min.*, 1913, *Beil.-Bd.*, **35**, 119—220, 723—752).—The first part, by R. Brauns, gives a detailed petrographical description of these ejected volcanic-blocks, with an account of their contained minerals; and the second part, by J. Uhlig, gives an account of the chemical examination of the materials. Details are given of the methods of analysis, especially with regard to the detection of traces and the estimation of small amounts of the rare elements (tantalum, glucinum, etc.), the presence of which have not before been detected in these minerals. Analysis I of the nephelite gives the ratio $SiO_2 : Al_2O_3 : (Na,K)_2O = 2·25 : 1 : 1·02$ (compare Morozewicz, A., 1908, ii, 201). Analysis II of cancrinite agrees with the formula $Na_{20}Al_{20}Si_{22}O_{84},Ca_4Na_2(CO_3)_5,5H_2O$. Analysis III of davyne gives $Na_{20}Al_{20}Si_{22}O_{84},5CaCl_2,10H_2O$. A sodium-potassium felspar (microperthite) gave IV. These analyses and formulæ are discussed in detail; and bulk analyses of the rocks are also given.

	SiO_2.	Ta_2O_5.	Al_2O_3.	Fe_2O_3.	GlO.	MnO.	CaO.	Na_2O.	K_2O.	Cl.	CO_2.	H_2O.	Total.	Sp. gr.
I.	44·10	trace	32·60	0·86	0·58	trace	0·52	17·16	4·27	0·06	—	—	100·15	2·60
II.*	36·29	0·74	27·43	0·59	0·59	,,	6·61	17·38	1·09	0·19	6·33	2·77	100·01	2·415
III.†	35·66	0·14	27·07	0 57	0·10	0·14	5·76	9·84	8·09	6·40	0·28	5·75	101·83	2·34
IV.‡	66·40	trace	19·38	0·30	—	trace	0·38	8 09	5·48	—	—	0·34	100·37	—

* Also TiO_2 trace, UO_2 trace ?, Ce_2O_3 trace, Li_2O trace. † Also UO_2 trace ?, SO_3 1·93, MgO 0·10
‡ Also Cb_2O_5, MgO traces.

L. J. S.

Meteorite from near Cullison, Kansas. GEORGE P. MERRILL (*Proc. U.S. Nat. Mus.*, 1913, **44**, 325—330).—This stone, weighing 10·10 kilos., was found in 1911 near Cullison, in Pratt Co., Kansas, and is stated to have fallen on December 22nd, 1902. On the broken surface it is black and very dense, showing no apparent structure, but on a polished surface it exhibits abundant metallic specks, numerous chondrules, a large, light-coloured patch, and an obscure banded structure suggestive of shearing. Under the microscope is seen a dense aggregate of small chondrules of various shapes; the recognisable minerals are olivine, orthorhombic and monoclinic pyroxenes, and fragmentary plagioclase felspars, together with metallic iron and iron sulphide. D 3·65. Chemical and mechanical analyses by J. E. Whitfield yielded the following results. A separation by means of an electromagnet and treatment of the residue with iodine gave: iron sulphide (troilite or pyrrhotite), 6·00; metallic iron, 19·40; silicates, 74·50; schreibersite, 0·10%. The metallic portion yielded I, and the silicate portion II, from which the bulk composition under III is calculated:

	Si.	S.	P.	Ni.	Co.	Cu.	Cr.	C.	Mn.	Fe.	Mo, W, V.	Total.
I.	0·129	trace	0·071	9·207	0·507	0·040	0·160	0·088	0·080	89·700	absent	99·982
III.	—	2·184	0·014	1·80	0·098	0·008	0·029	0·017	0·015	21·270	—	—

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	MnO.	Na_2O.	K_2O.	TiO_2.	Total.
II.	47·36	5·67	0·10	11·25	0·84	31·72	0·36	2·42	0·23	nil	99·95
III.	35·30	4·24	0·75	8·38	0·62	23·631	0·268	1·804	0·171	—	100·599

The powdered stone, when digested with distilled water, gave a trace of calcium, and with very dilute hydrochloric acid 0·28% CaO, 0·05% SO_3, and 1·14% MgO (the last, no doubt, derived from the olivine). These results suggest the presence of the mineral oldhamite (CdS) or of its weathered representative gypsum. L. J. S.

The Minor Constituents of Meteorites. GEORGE P. MERRILL (*Amer. J. Sci.*, 1913, [iv], **35**, 509—525).—The elements well known to be present in meteorites are silicon, aluminium, iron, chromium, manganese, nickel, cobalt, magnesium, calcium, sodium, potassium, sulphur, phosphorus, and carbon. In addition to these, the following have been reported, some of which are doubtful (a summary of the literature is given): arsenic, antimony, copper, gold, lead, lithium, palladium, platinum, iridium, tin, titanium, tungsten, uranium, vanadium, and zinc. Samples of not less than 50 grams of each of the following eleven meteorites have been specially examined by J. E. Whitfield for the presence of these rarer elements. The occasional presence of platinum is confirmed, and of vanadium in two instances; palladium and ruthenium were found in one sample. I, Iron from Canyon Diablo, Arizona; anal. I, also, $FeCl_2$, 0·097. II, Iron from Casas Grandes, Mexico. III, Iron from Mount Joy, Pennsylvania; Cr, 0·006; Mn, 0·075; Cu, 0·008; Cl, 0·255; Pt, trace. IV, Iron from Perryville, Missouri (this vol., ii, 424). V, Stony iron (pallasite) from Mt. Vernon, Kentucky; also, Cr, 0·300; V, trace.

	Si.	S.	P.	Mn.	Cu.	Ni.	Co.	C. (Combined.)	C. (Graphitic.)	Iron oxides.	Fe.	Total.
I.	trace	0·009	0·261	nil	0·015	7·335	0·510	0·105	0·028	2·520	89·167	100·047
II.	0·010	0·029	0·166	—	0·012	7·742	0·604	0·145	0·032	0·794	90·470	100·004
V.	—	—	—	0·151	0·016	2·960	0·090	—	—	—	—	—

VI, Stone from Selma, Alabama; also, V_2O_3 trace. VII, Stone from Ness County, Kansas; also, loss on ignition 3·50, Fe 13·86, Ni 1·05, Co 0·03, Cu 0·05. VIII, Stone from Cullison, Kansas (see preceding abstract). IX, Stone from MacKinney, Collin Co., Texas, consisting of troilite (FeS) 6·26, schreibersite 0·58, metal 5·70, chromite 0·11, silicates 87·35; the silicate portion gave anal. IX, and the metallic portion contained Ni 13·16, Co 0·92, Cu 0·08, Fe [85·84]=100·00. X, Stone from Holbrook, Arizona (this vol., ii, 71). XI, Stony iron (pallasite) from Krasnojarsk, Siberia, specially examined for arsenic and tin, but no trace of these detected. Comparisons are made between the chemical composition of these meteorites and of the ultra-basic terrestrial rocks.

	SiO_2.	Al_2O_3.	Fe_2O_3.	Cr_2O_3.	CaO.	MgO.	MnO.	NiO.	CaO.	Total.
VI.	32·40	4·88	37·00	0·19	1·52	21·05	0·27	1·88	0·12	99·31
VII.	38·34	8·259	8·551	0·587	1·18	24·04	—	—	—	99·447
IX.	43·30	15·18	8·45*	—	1·88	30·48	0·25	0·51	—	100·05

* FeO.

L. J. S.

Analytical Chemistry.

A Refined Method of Obtaining Sublimates. ARNOLD L. FLETCHER (*Sci. Proc. Roy. Dubl. Soc.*, 1913, **13**, 460—466).—The sublimation chamber is a cylindrical, wooden or porcelain box, 5—6 cm. in diameter and 3 cm. in height, with walls about 1 cm. in thickness. A pair of forceps is fitted internally on each side of the box, and connected through the walls with terminals for the source of current; they are hinged at a short distance from the internal face, and are of sufficient length to reach nearly to the top of the box when bent at right angles at the hinge. The forceps carry a carbon rod (in some cases a platinum strip is used), on which the substance to be heated is placed. The sublimation chamber is closed above and below by cover-plates, and is fitted with inlet and outlet tubes, so that the heating process may be carried out in any desired atmosphere. The cover-plates may consist of glass, clear or opaque silica, biscuit ware, plaster of Paris, or even white paper, and may be raised if necessary by circular washers. A glass cover-plate is conveniently cooled by a drop of water on its upper surface.

With the above apparatus it is possible to examine the effect of heat on substances in different atmospheres, sublimates being formed

with the same facility in these atmospheres as they are in air. Mixtures or alloys, such as brass, or even steel, may be dealt with to a certain extent by fractional volatilisation, the deposits produced being removed on separate cover glasses. Very small quantities of impurities in metals can thus be detected, the cadmium present in commercial zinc being easily distinguishable.

This method of analysis possesses a range of action enormously superior to that of the blowpipe, and is limited only by the volatility of the carbon; only very small quantities of material are necessary.

The results of experiments with the various solid elements in the periodic system are given. T. S. P.

Removal of Fusions in Alkali Carbonates from the Crucible. R. HOWDEN (*Chem. News*, 1913, **107**, 232).—At the end of the fusion a pinch of powdered nitre is added to the still liquid mass. This causes the same to become more porous on cooling, owing to gases being evolved, and to be more readily disintegrated by water. L. DE K.

The Use of Extract of Red Cabbage as an Indicator for Colorimetric Estimation of the Hydrogen Ion Concentration. L. E. WALBUM (*Biochem. Zeitsch.*, 1913, **50**, 346. Compare this vol., ii, 237).—Reply to a claim for priority by E. Fuld. S. B. S.

Theory of Indicators. JOHN WADDELL (*Chem. News*, 1913, **107**, 206).—According to the ordinary theory of indicators, it is strange that methyl-orange, a strong acid, should act towards weak acids in exactly the same way as phenolphthalein, a weak acid, acts towards weak bases. This anomaly is removed if methyl-orange is considered to be a weak base, and not a strong acid, and the author gives experiments which indicate the basic behaviour of methyl-orange. According to the ordinary theory, the pink colour is due to the undissociated substance, and the yellow colour to the dissociated ion; all means of diminishing the dissociation, however, tend to change the colour from pink to yellow; for example, glacial acetic acid to which methyl-orange is added gives a red colour, which may be lessened, if not destroyed, by the addition of acetates, and is easily changed to yellow by the addition of alcohol. Other experiments are quoted, of a similar nature, indicating that the yellow colour of methyl-orange is that of the undissociated compound, the red being due to the dissociated cation (compare Noyes, A., 1910, ii, 746). T. S. P.

The Development of Electro-analysis. REMIGIUS FRESENIUS (*Zeitsch. anorg. Chem.*, 1913, **81**, 4—23).—An historical account of the introduction of electrolytic methods of analysis, with bibliographical references. C. H. D.

New Electrode for Electrolytic Analysis. L. BERTIAUX (*Ann. Chim. anal.*, 1913, **18**, 129—130).—A slight modification of the

Hollard apparatus, so as to render it more stable. The electrode consists of a cylinder of perforated foil composed of an alloy of platinum with 10% of iridium, to which has been sealed a rigid stem of the same alloy. The spiral used with this electrode is about the same as that in Hollard's apparatus, only is a little more cylindrical in form. L. DE K.

Estimation of Water in the Volatile Products Obtained in the Distillation of Fuels. GUSTAV LAMBRIS (*Zeitsch. anorg. Chem.*, 1913, **81**, 24—39).—Phosphoric oxide is the only drying agent available for the estimation of water in the products of distillation of fuels, as sulphuric acid or salts either combine with hydrocarbons and other impurities, or again give up the water at the temperature necessary to expel tarry products. The only impurities retained by phosphoric oxide are ammonia, pyridine bases, and phenol. These substances are retained quantitatively, and may be estimated by the following method. The phosphoric oxide must be free from lower oxides. After absorption and weighing, it is dissolved in water, made strongly alkaline, and distilled. The distillate is absorbed in a known quantity of sulphuric acid, and the excess of acid titrated with sodium hydroxide, using Congo-red as an indicator, and evaporated to dryness. The residue is heated to 130° to expel pyridine, and the sulphuric acid thus set free is titrated. Unless the ammonia present is largely in excess of the pyridine, it is necessary to add a known quantity of ammonium sulphate to the residue before heating; otherwise the expulsion of pyridine is incomplete. Pyridine bases are estimated in similar manner, but longer heating is required, and the result obtained must be multiplied by a corresponding factor. Phenol is estimated by the usual bromide-bromate method, metaphosphoric acid being without disturbing influence. These methods allow of a complete correction for impurities in the aqueous distillate. C. H. D.

Estimation of the Water Formed in the Combustion of Substances containing Sulphur and Nitrogen in the Calorimetric Bomb. O. RAU (*Zeitsch. anorg. Chem.*, 1913, **81**, 116—121). —The estimation of nitric and sulphuric acids is necessary in order to determine the proper correction of gross to net calorific values. The method recommended is that of mixing a small quantity of dry sodium carbonate with the fuel before combustion. After combustion, the bomb is immersed in an oil-bath at 110°, and the gas allowed to escape slowly through a large absorption apparatus, a current of air, free from moisture and carbon dioxide, being then passed through. Water and carbon dioxide are thus estimated. The residue in the bomb is washed out with water, titrated with $N/5$-hydrochloric acid and methyl-orange, warmed, and precipitated by means of $N/5$-barium chloride. After the precipitate has settled, $N/5$-sodium carbonate is added, the solution is cooled, diluted to a definite volume, filtered through a dry filter, and a measured quantity of the filtrate titrated with $N/5$-hydrochloric acid. The nitric and sulphuric acids may thus be calculated. The

correction of the calorific value for water and acids amounts, in the case of coal, to about 1·5%, whereas the sodium peroxide method involves a correction of 30%.

The carbon dioxide estimated in this way is always about 1% low.

C. H. D.

Estimation of Iodine in Syrup of Iodotannin. M. EMMANUEL POZZI-ESCOT (*Bull. Soc. chim.*, 1913, [iv], **13**, 403—404).—Twenty-five c.c. of the syrup, diluted with 50 c.c. of water, are placed in a "bromine tube" with 10 c.c. of chloroform, and then 2 c.c. of sulphuric acid and excess of a saturated solution of potassium permanganate added. The mixture is shaken to dissolve the iodine in the chloroform, and the latter is decanted and the extraction continued with two further portions of chloroform, each of 10 c.c. The united chloroform solutions are then titrated with sodium thiosulphate solution.

T. A. H.

Estimation of Oxygen in Metallic Tungsten Powder and Some Notes on the Estimation of Oxygen in Steel. CHARLES MORRIS JOHNSON (*J. Ind. Eng. Chem.*, 1913, **5**, 295—297).—A detailed description is given of the method of estimating oxygen in tungsten powder, which involves heating the metal in a current of hydrogen. The hydrogen employed is passed through vessels containing potassium hydroxide solution, alkaline pyrogallol solution, calcium chloride, potassium hydroxide, and phosphoric oxide respectively, before it enters the quartz combustion tube, in which the metal is heated to a temperature of 950—1000° by means of an electric furnace. The metal is dried at 105° previous to the estimation, and the necessary precautions are taken to remove all air from the apparatus before the heating part of the process is commenced. The water produced is collected and weighed in a tube containing phosphoric oxide. The presence of excessive amounts of free carbon in tungsten oxide does not affect the results obtained, but low results are found in the case of ferric oxide when this contains more than 5% of free carbon. Attention is drawn to the fact that steel undergoes decarbonisation when heated in a current of hydrogen; for instance, a steel containing 1·08% of carbon was found to contain only 0·83% after having been heated for three and a-half hours in hydrogen.

W. P. S.

Estimation of Ozone and Hydrogen Peroxide. VICTOR ROTHMUND and A. BURGSTALLER (*Monatsh.*, 1913, **34**, 693—704).—Although molybdic acid catalyses the reaction between hydrogen peroxide and hydriodic acid (potassium iodide in acid solution), it does not catalyse the oxidation of hydriodic acid by dissolved oxygen or air (compare Luther and Inglis, A., 1903, ii, 406). It can consequently be used as a catalyst in the iodometric estimation of hydrogen peroxide in acid solution, accurate results being obtained.

Attempts to estimate a mixture of ozone and hydrogen peroxide by a direct method, using potassium iodide, were not successful.

The following indirect method gives good results. The slightly acid (0·01*N*) solution of ozone and hydrogen peroxide is added to excess of potassium bromide at 0°, whereby bromine is liberated by the ozone (compare Inglis, T., 1903, **83**, 1010; Treadwell and Anneler, A., 1906, ii, 123); an excess of potassium bromide is necessary in order to prevent further action between bromidion and hydrogen peroxide. A slight excess of potassium iodide is then added, and the liberated iodine titrated, after which the solution is acidified with dilute sulphuric acid, and ammonium molybdate and more potassium iodide added. After five minutes, the liberated iodine is again titrated, this giving the amount of hydrogen peroxide present. T. S. P.

Estimation of Sulphur Dioxide in the Air. CARL KULLGREN (*Arkiv. Kem. Min. Geol.*, 1913, **4**, No. 31, 1—20).—While investigating the conductivities of very dilute solutions, the author made the observation that in certain cases the conductivity increased to some extent (about 1%) at the commencement of the experiments. Similar results were obtained when conductivity water was used. It was ultimately found that sulphur dioxide present in the air, especially in a room where gas was burning, was the cause of these anomalous results. During the drying of the electrodes the sulphur dioxide is absorbed by the platinum black and oxidised catalytically to sulphuric acid, which then dissolves in the solutions or water under investigation, and increases the conductivity. Carbon dioxide or ammonia does not have a similar effect.

On the above observations the author has based a method for estimating the amount of sulphur dioxide in the air. About 40 litres of the air are drawn through platinum black placed on a platinum sieve at the bottom of a tube of platinum, the time necessary being about 15 minutes. The tube and black are then immersed in water to dissolve out the sulphuric acid, and the conductivity of the solution measured. Preliminary experiments with known quantities of sulphur dioxide showed that the conductivity of the solution formed is directly proportional to the amount of sulphur dioxide when no allowance is made for the conductivity of the water used. T .S. P.

Titration of Sulphurous Acid, also in Presence of Thiosulphuric Acid. EMIL BOSSHARD and W. GROB (*Chem. Zeit.*, 1913, **37**, 465—466).—*Sulphite + Acid Sulphite.*—Fifty c.c. of the solution (about 0·5 gram of solid salts) are titrated with *N*/5-hydrochloric acid, with methyl-orange as indicator; the result = half the amount of sulphite. Three hundred c.c. of saturated mercuric chloride are now added, also a little sodium chloride, and the liquid titrated with *N*/5-sodium hydroxide until again neutral; the result = total sulphur dioxide. After making allowance for the normal sulphite, the acid sulphite is obtained.

If *thiosulphate* is also present, the sulphite is first titrated with *N*/5-hydrochloric acid, with methyl-orange as indicator. After adding phenolphthalein, the solution is titrated with *N*/5-sodium

hydroxide until neutral; the result is total sulphur dioxide, and the acid sulphite is then found by difference. To another 50 c.c. of the solution is now added an excess of mercuric chloride, also 1 gram of sodium chloride, and the hydrogen chloride liberated is titrated, after adding 30 c.c. of $4N$-ammonium chloride, with $N/5$-sodium hydroxide, with methyl-orange as indicator. After deducting the alkali necessary for the neutralisation of the acid sulphite, the result = thiosulphuric acid. L. DE K.

Iodometric Estimation of Persulphuric Acid. ERICH MÜLLER (*Zeitsch. anal. Chem.*, 1913, **58**, 299—303).—The following process is recommended in the absence of hydrogen peroxide. Twenty c.c. of persulphate solution (about 0·36 gram of solid salt) are added to 25 c.c. of N-sodium hydroxide containng 1 gram of potassium iodide, and after waiting for at least five hours the liquid is acidified with $2N$-sulphuric acid; the iodine liberated, which represents the available oxygen, is then titrated with thiosulphate as usual.

The reaction may be accelerated by heating the alkaline mixture for ten to twenty minutes on the water-bath. L. DE K.

Colour Reaction for the Detection of Thiosulphates. M. EMMANUEL POZZI-ESCOT (*Bull. Soc. chim.*, 1913, [iv], **13**, 401—402).—To 1 or 2 c.c. of the solution to be tested, an equal amount of a 10% solution of ammonium molybdate is added, and 5 c.c. of sulphuric acid are poured carefully down the side of the tube to form a separate layer, when, if a thiosulphate is present, a bluish-coloured zone forms between the two liquids. The test will detect 0·0005 gram of sodium thiosulphate. T. A. H.

Occurrence of Selenium in the Mother Liquors from the Preparation of Sulphite Cellulose. PETER KLASON and HJALMAR MELLQUIST (*Arkiv. Kem. Min. Geol.*, 1913, **4**, No. 34, 1—10).—The qualitative detection and quantitative estimation of selenium in the mother liquors from the preparation of sulphite cellulose is made difficult by the colour of these liquors, due to the organic substances present, and by the quantity of calcium salts present. After numerous experiments the authors recommend the following method. Three to five litres of the liquor, in portions of one litre at a time, are evaporated in an air-bath until the free sulphur dioxide is expelled. As soon as calcium sulphite begins to separate, sufficient hydrochloric acid is added to dissolve the crystals. This process is repeated from time to time until the volume of liquid is 200—300 c.c., when it is transferred to a smaller vessel of appropriate size, taking care to transfer any selenium which may have precipitated out. The solution is then strongly acidified and boiled to remove the last traces of sulphur dioxide, after which stannous chloride is added, and the solution again boiled for a few minutes. After keeping in the warm for one to two days, the selenium has settled to the bottom of the containing vessel, and can be filtered off and estimated according to the method previously described (A., 1912, ii, 201, 990). The presence of selenium is indicated by

the fact that it forms a red deposit on the sides of the combustion tube whilst the organic matter is being burned off.

Experiments made by the authors show that no matter how carefully the gases from the pyrites burners are washed and cooled, the selenium oxide contained in them cannot be completely removed.

T. S. P.

Direct Estimation of Gaseous Nitrogen by means of Calcium Carbide. B. NATUS (*Zeitsch. anal. Chem.*, 1913, **52**, 265—292).—A special apparatus is described, in which a gaseous mixture containing nitrogen is passed over a red-hot mixture of 10 parts of calcium carbide and 1 part of fused calcium chloride. The operation is carried out in an atmosphere of hydrogen, using a porcelain boat.

The mass, which absorbs practically all the nitrogen if precautions have been taken to ensure absence of moisture, readily yields it as ammonia on treatment with sulphuric acid and a drop of mercury (Wilforth's modified Kjeldahl process).

The calcium carbide should be purified by heating in a current of hydrogen. As it generally contains some nitrogen, this should be estimated and allowed for.

L. DE K.

Estimation of Ammonia by Titration. LUDWIG W. WINKLER (*Zeitsch. angew. Chem.*, 1913, **26**, 231—232).—Instead of absorbing the ammonia in excess of sulphuric or hydrochloric acid and titrating back the excess, the author recommends that a solution of boric acid be used. The ammonia can then be titrated directly with standard hydrochloric acid, using methyl-orange or Congo-red, preferably the latter, as indicator, the colour change being quite sharp.

In an ordinary Kjeldahl nitrogen estimation about 5 grams of boric acid in 100 c.c. of water should be used to collect the ammonia; no condenser is necessary. For very accurate work it is advisable to take a saturated solution of boric acid, add one drop of ammonium hydroxide solution, then sufficient indicator to give a colour, and finally run in 0·1*N*-hydrochloric acid until the colour change occurs; this solution is then used to absorb the ammonia.

T. S. P.

Apparatus for the Distillation of Ammonia in the Kjeldahl Process. G. DELATTRE (*J. Pharm. Chim.*, 1913, [vii], **7**, 395—397).—A "baffle," consisting of a loose siphon tube of special form, is inserted in the leading tube from the distilling flask. This serves to break any bubbles which form in the tube, so that the distillation can be conducted more rapidly than in the forms of leading tube in general use. The apparatus is figured in the original. T. A. H.

Detection and Estimation of Ammonia in Cerebro-spinal Fluid. PIERRE THOMAS (*Bull. Soc. chim.*, 1913, [iv], **13**, 398—400).—It is shown that the colour reaction already described (A., 1912, ii, 991) is suitable for the detection of ammonia in cerebro-spinal

fluid, since it is not affected by the presence of proteins or sugars. The amount of ammonia present may be estimated colorimetrically.

T. A. H.

Detection of Nitrous Acid in the Presence of Ferric Salts [in Waters]. PAUL ARTMANN (*Chem. Zeit.*, 1913, **37**, 501).—To 100 c.c. of the sample are added 8 grams of crystallised disodium hydrogen phosphate, and 0·2 gram of potassium iodide is then added. Five c.c. of 4*N*-sulphuric acid are added, and 2 c.c. of starch solution.

If nitrites are present, even in minute quantities, a blue coloration is noticed.

L. DE K.

Influence of Chlorine on the Determination of Nitrates by the Phenoldisulphonic Acid Method. ROBERT STEWART and JOSEPH E. GREAVES (*J. Amer. Chem. Soc.*, 1913, **35**, 579—582).—In an earlier paper (A., 1910, ii, 652) it has been shown that the estimation of nitrates in soil extracts by the phenoldisulphonic acid method is affected by the presence of chlorides. It has now been found that accurate results can be obtained in such cases by means of the lime method proposed by Lipman and Sharp (*Univ. Cal. Publ. in Agric. Sci.*, 1912, **1**, 12). Chloroform is sometimes added to the soil extract to inhibit the action of bacteria. In the case of extracts prepared by the lime method, however, reaction takes place between the calcium hydroxide and the chloroform with formation of calcium chloride, and the use of chloroform is therefore excluded.

E. G.

The Quantity of Nitric Acid Present in Fruit Juices and Fruit Juice Statistics for 1911 and 1912. JOSEF TILLMANS and ARTHUR SPLITTGERBER (*Zeitsch. Nahr. Genussm.*, 1913, **25**, 417—429). —Fruit juices contain small quantities of nitric acid, the amount being usually less than 1 mg. (N_2O_5) per litre. Two samples examined, one a raspberry juice and the other a strawberry juice, contained 5 mg. per litre, but this may have been due to the berries having been washed with water containing a large quantity of nitrate. Apart from this source of contamination, the presence of considerable quantities of nitric acid in fruit juices affords some indication or suspicion that water containing nitrates has been added to the juice. The diphenylamine–sulphuric acid reaction was employed for estimating the nitric acid, and the process was applied, preferably, after the juice had been treated with animal charcoal to remove interfering substances (compare A., 1911, ii, 930), and then cooled by means of a freezing mixture. It is also advisable to cool the reagent before adding it to the juice, and in certain cases the treatment with animal charcoal may be omitted, provided that both the reagent and juice are strongly cooled.

Tables are given showing the chemical composition of various fruit juices examined during the years 1911 and 1912.

W. P. S.

Estimation of Phosphorus in Ferro-tungsten, Metallic Tungsten Powder, Tungsten Oxide, and Tungstic Acid by Direct Solution. CHARLES M. JOHNSON (*J. Ind. Eng. Chem.*, 1913, **5**, 297—298).—Ferro-tungsten is heated with concentrated nitric acid and hydrofluoric acid, then evaporated, dissolved in hydrochloric acid, again evaporated, and the greater part of the tungsten separated by filtration. The filtrate is then evaporated with nitric acid, and the residue repeatedly treated with nitric acid and evaporated, insoluble substances being separated by filtration. The phosphorus is, finally, obtained in nitric acid solution, and is precipitated by the addition of molybdate solution after the solution has been treated with potassium permanganate and the manganese dioxide dissolved by the addition of ferrous sulphate. Tungsten ores are first treated with hydrochloric acid and potassium chlorate, and the phosphorus subsequently obtained in nitric acid solution. Metallic tungsten powder must be converted into oxide by roasting before the phosphorus is estimated, as in the case of ores, whilst tungstic oxide and tungstic acid are treated directly with hydrochloric acid and potassium chlorate and afterwards with nitric acid. W. P. S.

Removal of Phosphoric Acid by means of Metastannic Acid in Qualitative Analysis. WERNER MECKLENBURG (*Zeitsch. anal. Chem.*, 1913, **58**, 293—298).—To the solution, which should be practically free from chlorine but contain 15 vol. % of nitric acid, is added a sufficiency of metastannic acid, and the whole is boiled for fifteen minutes. In this way the phosphoric acid is completely removed, and the filtrate is then analysed as usual.

The metastannic acid is prepared in the form of paste as follows: 150 grams of granulated tin are introduced into a cooled (0°) mixture of 750 c.c. of nitric acid (D 1·4) and 750 c.c. of water, and when all is dissolved, the liquid is poured into 10 litres of water. The deposit is washed, first by decantation and then on a filter, and bottled moist.

Besides phosphoric acid, the deposit may also retain iron and titanium; the first is tested for with ferrocyanide, the latter with hydrogen peroxide. Scarcely any tin passes into solution.

L. DE K.

Detection and Estimation of Arsenic by the Marsh Apparatus. GEDEON MEILLERE (*J. Pharm. Chim.*, 1913, [vii], **7**, 425—431).—The author describes the manner in which he carries out this process. He employs zinc, which has been treated with platinum chloride or copper sulphate, for evolving the hydrogen; on leaving the evolution flask, the gases are passed through a tube containing zinc, and then through a tube containing anhydrous sodium sulphate or sodium phosphate; the end of the capillary in which the arsenic mirror is collected is bent downwards and immersed in silver nitrate solution in order to ascertain whether any of the arsenic has escaped being deposited in the capillary. In the case of comparatively large quantities of arsenic, the capillary

may be replaced by a weighed tube containing copper foil on which the arsenic is collected and weighed, or the gases may be passed into silver nitrate solution and the quantity of arsenic estimated gravimetrically. W. P. S.

Modification of the Liebig Combustion Furnace. Hugo Brach and Emil Lenk (*Zeitsch. angew. Chem.*, 1913, **26**, 230—231).—An ordinary Liebig combustion tube is surrounded by a wider tube, which is also packed with copper oxide over a length corresponding with that taken up in the inner tube. The inner tube is connected in the usual way with a sulphuric acid tube and a soda-lime tube, and leading from the latter is a length of tubing opening into the outer concentric tube at the end nearest the oxygen gas-holder. At the other end of this outer tube are fitted a soda-lime tube, a calcium chloride guard-tube, and a sulphuric acid bubbler.

A combustion can be completed in about half an hour, any carbon monoxide escaping from the inner tube being completely oxidised to carbon dioxide in the outer tube. T. S. P.

Estimation of Zinc in Ores. D. J. Demorest (*J. Ind. Eng. Chem.*, 1913, **5**, 302—304).—The method proposed depends on the fact that ammonium carbonate separates zinc (and copper) from iron, aluminium, manganese, lead, and cadmium; the zinc and copper remain in solution, and the former is titrated with ferrocyanide after the copper has been precipitated as sulphide. One gram of the ore is heated with 5 c.c. of hydrochloric acid, D 1·12, 20 c.c. of concentrated nitric acid are then added, and the heating is continued until all brown fumes are expelled. After the addition of 1 gram of potassium chlorate, the mixture is evaporated to dryness, and the residue is treated with 50 c.c. of hot water and 0·5 gram of potassium hydroxide; 6 grams of ammonium carbonate are now added, the mixture is boiled for a few minutes, and the solution filtered, the insoluble portion being washed with hot 5% ammonium carbonate solution. The insoluble portion is then dissolved in hydrochloric acid, potassium nitrite added to reduce manganese dioxide which may be present, the solution neutralised with potassium hydroxide, and again treated with ammonium carbonate. The united filtrates and washings are acidified with hydrochloric acid, 20 c.c. of concentrated hydrochloric acid are added, the solution is heated to 70°, and the copper precipitated as sulphide. When the copper is practically all precipitated, 20 c.c. of ammonia (1 : 1) are added, and hydrogen sulphide is passed through the solution for a further short period. The zinc is then titrated at 70° with standardised potassium ferrocyanide solution, without previous removal of the copper sulphide. W. P. S.

Method for the Qualitative Analysis of the Zinc Group. Richard Edwin Lee, Roy H. Uhlinger, and Frank O. Amon (*J. Amer. Chem. Soc.*, 1913, **35**, 566—579).—The methods usually employed for the qualitative analysis of the zinc group are discussed,

and various inaccuracies are pointed out. The complete precipitation of zinc, manganese, nickel, and cobalt can be effected by passing hydrogen sulphide into a weak, ammoniacal solution. By this means, the dissolving of the nickel sulphide is prevented, and the nickel is but rarely precipitated in the colloidal condition. The method renders it possible to precipitate and detect 0·0005 gram of any metal of the group in presence of large quantities of any or all of the other metals. Methods are also proposed for the subsequent analysis of the group precipitates, which are capable of confirming the presence of any of the metals even in quantities of 0·0005 gram. E. G.

Some Quantitative Separations of Neodymium. TODD O. SMITH and CHARLES JAMES (*Chem. News*, 1913, **107**, 205—206; *J. Amer. Chem. Soc.*, 1913, **35**, 563—566).—Quantitative separations of neodymium from titanium, glucinum, uranium, and barium may be made by precipitating the neodymium as oxalate from boiling solutions. Oxalic acid is used as the precipitant, and after precipitation the solution is digested until the precipitate becomes granular.

In the separation of neodymium from zirconium according to the above method, the results are slightly high, some of the zirconium probably being carried down with the neodymium, zirconium oxalate being insoluble in water, but soluble in an excess of oxalic acid. T. S. P.

Detection of Mercury in "Kyanised Wood." CHARLES GROFFIER (*Bull. Soc. chim. Belg.*, 1913, **27**, 137—138).—The mercury sulphide obtained in due course after submitting the wood to the well-known destruction process of Fresenius and Babo still contains organic matters which render the further identification of the mercury a matter of great uncertainty.

The author overcomes this difficulty by boiling the well-washed precipitate with dilute nitric acid (2 : 1). This removes the foreign matters. The residue is dissolved in aqua regia, and the usual reactions will then be obtained readily. L. DE K.

Precipitation of Aluminium Hydroxide and its Separation from Chromium. W. JAKÓB (*Bull. Acad. Sci. Cracow*, 1913, *A*, 56—62).—Alumina may be obtained as a dense precipitate, readily washed, by adding to the aluminium salt solution (about 0·2 gram of the oxide in 100 c.c.) sufficient aqueous sodium hydroxide to redissolve the precipitate and then boiling with addition of excess of bromine water. Attention is called to the hygroscopic nature of the ignited precipitate.

Chromium, if present, is oxidised to chromate. The precipitated alumina must, however, be freed from adhering chromate by decanting the liquid and boiling the deposit with a solution of ammonium nitrate containing ammonia.

Traces of zinc or magnesium do not interfere, but in the presence of sulphates or borates the method is less suitable. L. DE K.

Estimation of Manganese in Irons and Steels by von Knorre's Process. MAURICE HUYBRECHTS and N. JOASSART (*Bull. Soc. chim. Belg.*, 1913, **27**, 130—137).—A modification of von Knorre's process, ensuring a more complete precipitation of small quantities of manganese. Four grams (or less) of the sample are treated with about 50 c.c. of cold water, 7*N*-nitric acid (11 c.c. for each gram) is added, and the whole is heated for twenty to thirty minutes on the water-bath, when the last particles are dissolved by boiling for a minute. To the solution are now added 250 c.c. of water, 8 grams of ammonium persulphate, and 4 grams of sodium carbonate; after boiling for twenty minutes the manganese will be completely precipitated.

The precipitate is collected and drained (not washed). It is then dissolved in just a sufficiency of hydrochloric acid, boiled, and diluted. The iron is now precipitated by cautiously adding zinc oxide, the liquid is heated to nearly 100°, and then titrated as usual for manganese with standard permanganate. L. DE K.

Colorimetric Method for the Estimation of Chromium in Steel. FRANK GARRATT (*J. Ind. Eng. Chem.*, 1913, **5**, 298—300).—The process described by Koenig (A., 1911, ii, 337), which depends on the coloration which is produced when chromic salts are treated with sodium 1 : 8-dihydroxynaphthalene-3 : 6-disulphonate, is recommended as being trustworthy. Tungsten and molybdenum do not interfere with the process, but vanadium imparts a brown tint to the pink chromium coloration. The red coloration given by titanium is destroyed on the addition of hydrofluoric acid or by strongly acidifying the solution with mineral acids. Concentrated sulphuric acid solutions of titanium, however, yield pink coloured solutions with the reagent. W. P. S.

Potassium Iodide and Mercurous Nitrate as a Delicate Reagent for Tungsten and Molybdenum. M. EMMANUEL POZZI-ESCOT (*Bull. Soc. chim.*, 1913, [iv], **13**, 402—403).—The explanation of this reaction, described by Kafku (A., 1912, ii, 693), is that mercurous iodide is first formed, which is reduced to mercury by the excess of potassium iodide. The mercury then reduces the tungstate, producing the blue coloration. The reaction is given by sodium tungstate in presence of mercury and hydrochloric acid. In the case of molybdates the reaction is of very little value. If much molybdate is present, the mercury is oxidised by it, and a yellow precipitate of mercurous molybdate is formed. With dilute solutions, a pale blue, fugacious coloration is produced. T. A. H.

Study of Certain Confirmatory Tests for Tin. LOUIS J. CURTMAN and MAX MOSHER (*J. Amer. Chem. Soc.*, 1913, **35**, 357—365).—The test for tin, which consists in reducing an acid solution of stannic chloride with an iron nail, and subsequently treating the stannous chloride with mercuric chloride, is not altogether trustworthy as usually carried out. It has been found that certain nails are not suitable because of the irregularity of their action.

The best procedure is to add one $1\frac{1}{2}$ inch cut nail to a total volume of 5 c.c. with an acidity equivalent to 2·5 c.c. of concentrated hydrochloric acid, and to heat for three minutes in a boiling water-bath. Under these conditions, 0·2 mg. of tin can be detected either alone or in presence of 250 mg. of antimony. When the amount of tin is small, a blank experiment must be made.

The ammonium molybdate test for stannous salts can be applied to stannic salt solutions after reduction with zinc. With a total acidity of 2·5 c.c. of concentrated hydrochloric acid in a volume of 10 c.c. the test is capable of detecting 0·01 mg. of tin in the absence of antimony, or 0·05 mg. in presence of 250 mg. of antimony. The presence of 5 mg. of antimony does not affect the sensitiveness of the test. E. G.

The Electrolytic Separation of Tin and Tungsten. W. D. TREADWELL (*Zeitsch. Elektrochem.*, 1913, **19**, 381—384).—The author gives a critical resumé of the processes of separation of tin and tungsten which are in use for quantitative purposes, including those of Donath and Müller (A., 1888, 531), Talbott (*Zeit. für Analyt. Chem.*, 1871, **10**, 343), Rose, and Angenot (A., 1906, ii, 496). The two electrolytic methods of precipitating tin from ammonium sulphide and sodium sulphide solutions respectively are investigated by the author; he shows that with ammonium sulphide solution the deposited tin is generally contaminated with sulphur, and at times contains as much as 2 mg. of platinum. The deposit obtained from sodium sulphide solutions which contain a little free alkali are not so contaminated, particularly if the current is only allowed to pass for a very short time after all the tin has been deposited. From these experiments he has devised the following method for quantitatively separating tin and tungsten. The cathode consists of a cylinder of platinum gauze, 35 mm. diameter and 49 mm. high. The anode is a cylinder of platinum foil, 41 mm. diameter and of the same height as the cathode; this is perforated by a number of holes to avoid the presence of a dead space at the back of the anode. The cathode is generally arranged so that it can be rotated, but stationary cathodes may be employed. The solution, which contains about 0·1—0·2 gram of tin and 1 gram of sodium tungstate, is mixed with 5 grams of pure sodium sulphide and 15 c.c. of commercial sodium hydrogen sulphite solution, which has been made alkaline with sodium hydroxide. The electrolysis is then carried out with a current strength of 0·5—1·7 ampere and a terminal P.D. of 2·5 volts, the temperature being preferably between 50° and 60°. The current must only be allowed to pass for a few minutes after the amount, theoretically required for the deposition of all the tin, has passed through. If molybdenum is present, the results are too high, owing to its deposition along with the tin. Attempts were made to effect the separation from oxalic acid solution, but there was found to be a tendency of the tungsten to deposit with the tin. J. F. S.

Rapid Methods for the Estimation of Antimony. H. NISSENSON (*Zeitsch. anorg. Chem.*, 1913, **81**, 46—48).—The titration

of antimony by potassium bromate and indigotin (A., 1903, ii, 697; 1904, ii, 292) may be employed as a rapid method, and in the separation of arsenic and antimony. Other known methods are described. C. H. D.

The Direct Estimation of Caoutchouc as Tetrabromide. F. WILLY HINRICHSEN and ERICH KINDSCHER (*Zeitsch. anorg. Chem.*, 1913, **81**, 70—82).—The direct estimation of caoutchouc by means of bromine is liable to a number of errors, and experiments have now been carried out to determine the sources of error. The proportion of bromine in the product increases with the time of reaction at the ordinary temperature, but is almost constant when the reaction is carried out in chloroform solution cooled by ice. This method is also applicable to vulcanised rubber, which is readily dissolved by a solution of bromine in chloroform, even in presence of large quantities of inorganic matter.

In the analysis of the bromides obtained in these experiments, the solution in chloroform is precipitated by means of light petroleum, and the precipitated bromide is washed, first with alcohol and then with hot water and dried, and then fused with a mixture of sodium and potassium carbonates below a red heat. C. H. D.

Estimation of Phenols in "Creolines." ALBERT J. J VANDEVELDE (*Bull. Soc. chim. Belg.*, 1913, **27**, 128—129).—Two hundred and fifty c.c. of the sample of creoline ("soluble creosote") are treated in a separating funnel with 500 c.c. of water, acidified with sulphuric acid, and 100 c.c. of benzene added. After twenty-four hours, the supernatant liquid is submitted to distillation until the temperature rises above 240°. The distillate, which contains, beside the benzene added, the phenols and part of the hydrocarbons, is then shaken three times in succession with 50 c.c. of 10% sodium hydroxide. The united liquids are acidified with dilute sulphuric acid, and the phenolic layer is measured in a graduated tube; 1 c.c. may be taken to represent 1·055 gram. L. DE K.

The Heat Test. ALFRED C. EGERTON (*J. Soc. Chem. Ind.*, 1913, **32**, 331—341).—The author has submitted the heat test to an exhaustive examination in the case of guncotton, nitroglycerin, and cordite. The theory of the connexion between the time of colouring of the indicator and the concentration of nitrogen peroxide in the heat test-tube is also discussed (compare Robertson and Smart, *ibid.*, 1910, **29**, 130).

The details and results of the many experiments carried out do not admit of a short summary; the author, however, emphasises the following points: To obtain a trustworthy and satisfactory stability test by which the actual tendency of the explosive to decompose can be accurately measured, it is necessary to carry out a continuous test, the results of which should be plotted graphically. The paper indicator usually used is open to certain errors, to obviate

which the author has devised a drop test. A solution of α-naphthylamine and sulphanilic acid in acetic acid is placed in a small cell supported at the top of the heat test-tube. The time necessary for this to colour to a standard tint, under the action of the nitrogen peroxide evolved from the explosive, forms the new drop test. It is said to be simpler than the ordinary heat test.

A single heat test is untrustworthy and therefore valueless, because of the nitric acid formed in the explosive during the test. The author is of the opinion that a state of equilibrium is attained during a continuous test, and hence the value of this test.

T. S. P.

Improved Apparatus for the Estimation of Carboxyl Groups in Organic Acids. William H. Hunter and J. D. Edwards (*J. Amer. Chem. Soc.*, 1913, **35**, 452—461).—Fuchs (A., 1889, 463) has described a method for estimating carboxyl groups, which depends on the fact that organic acids liberate hydrogen sulphide from solution of potassium hydrogen sulphide saturated with hydrogen sulphide. An account is now given of an improved form of apparatus for carrying out the estimation.

A wide-mouthed reaction vessel is fitted with a rubber stopper with three holes. In one hole is placed a sample-holder of the type used in the Victor Meyer vapour density apparatus. Another hole carries a tube for the admission of hydrogen sulphide, and fitted with a glass stopcock. In the third hole is inserted a three-way tap, enabling the reaction vessel and the air-chamber standing above it to be put into communication with one another or either of them to be opened to the air. On the outlet from this tap to the air is a narrow rubber tube provided with a pinchcock. A loose plug of glass wool is placed half-way down the air-chamber, and in the upper end is fitted a rubber stopper with two holes, one with a glass stopcock opening to the air, and the other bearing a delivery tube, without a stopcock, which is connected to the gas-burette.

The solution of potassium hydrogen sulphide is placed in the reaction vessel, and hydrogen sulphide is passed in until it is completely saturated and all the air has been expelled from the vessel. After the apparatus is ready, connexion is made between the reaction vessel, air chamber, and burette. The level of the water in the burette is noted, and the weighed sample of the organic acid is dropped into the reaction vessel. As the hydrogen sulphide is evolved, the level in the gas-burette must be followed closely by the levelling bulb. When the evolution ceases, the reading is taken, the reaction vessel shaken vigorously for three minutes, and the final reading noted. The weight of carboxyl (W) is found by the following equation: $W = V(b - w)0{\cdot}000002632/1 + 0{\cdot}00367t$, where V is the volume of gas evolved, b the barometric pressure, and w the vapour pressure of water at t°

Experiments are recorded which show that by this method monobasic organic acids give results 2—2·5% below the calculated, whilst dibasic acids yield results about 0·7% too high. E. G.

Estimation of Formic Acid in Urine. HENRY D. DAKIN, N. W. JANNEY, and ALFRED J. WAKEMAN (*J. Biol. Chem.*, 1913, **14**, 341—354).—See this vol., i, 679.

Solubility of Certain Metallic Salts of Volatile Fatty Acids in Organic Solvents. Application to the Qualitative Estimation of these Acids. HENRI AGULHON (*Bull. Soc. chim.*, 1913, [iv], **13**, 404—406).—A scheme for the detection of propionic, butyric, valeric, and hexoic acids is described depending on the fact that the cupric and ferric salts of these acids show increasing solubility and a greater range of solubility in organic solvents as the molecular weight of the acid increases. The corresponding salts of formic and acetic acids are insoluble in the organic solvents used.

T. A. H.

Estimation of Solid Fatty Acids by Hehner and Mitchell's Method. HERMANN SERGER (*Zeitsch. öffentl. Chem.*, 1913, **19**, 131—132).—A special filter for use in this method (A., 1897, ii, 289) is described. A Gooch crucible containing asbestos is fitted by means of a rubber ring into the top of a funnel, and the crucible and funnel are surrounded by a vessel containing ice. A flat dish filled with ice forms a cover for the apparatus. After the Gooch crucible has been cooled for thirty minutes by means of the ice-jacket, the solution containing the stearic acid precipitate is passed through the filter, and, when the liquid has been removed as much as possible by a suction pump, the collected stearic acid is dissolved in hot alcohol, the solution evaporated, and the residue weighed.

W. P. S.

The Estimation of Lactic Acid in Urine. HIROMU ISHIHARA (*Biochem. Zeitsch.*, 1913, **50**, 468—482).—By means of Ryffel's process of distillation of urine with 50% sulphuric acid, and the titration of the aldehyde thus produced by Ripper's iodometric method, about four-fifths of the lactic acid present can be found. For urines containng sugar, the process is not applicable. To get accurate results, the acid must be extracted from the urine by ether, after precipitation of certain constituents of the former by phosphotungstic acid; the phosphotungstic acid is then precipitated by barium hydroxide, excess of the latter precipitated by carbon dioxide, and the urine then concentrated and extracted for twenty-four hours. The lactic acid thus extracted can be then estimated by a slight modification of the von Fürth and Charnass method. Lactic acid is thus found to be a by no means negligible constituent of normal urine, which contains about 0·08 gram per litre.

S. B. S.

Estimation of Adrenaline. THOMAS R. ELLIOTT (*Proc. Physiol. Soc.*, 1913, xv—xvii; *J. Physiol.*, **46**).—See this vol., i, 674.

General and Physical Chemistry.

Constancy of the Refraction Equivalents. KARL VON AUWERS and FRITZ EISENLOHR (*Zeitsch. physikal. Chem.*, 1913, **83**, 429—441).—The authors have re-determined the refraction equivalents for the atoms carbon, hydrogen, and oxygen, and for the methylene group, using carefully purified substances. They show that for practical purposes the values are constant, although strictly this is not the case. Constitutive influences make themselves noticeable to a slight extent. Thus, in the case of the *cyclo*paraffins, it is shown that the entrance of a methylene group raises the refraction equivalent; this increase is noticeable in every case except when the methyl groups are in the *gem*-position. Thus, for the substances *cyclo*hexane, methyl*cyclo*hexane, 1 : 4-dimethyl*cyclo*hexane, and 1 : 3 : 5-trimethyl-*cyclo*hexane, the values are H_a : 4·597, 4·620, 4·638, 4·644. The 1 : 2-derivatives give lower values than the 1 : 3, and these lower than the 1 : 4, whereas the *gem*-compounds give still lower values.

J. F. S.

Further Remarks on a Formula for the Index of Refraction of Binary Mixtures. FRÉDÉRIC SCHWERS (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 513—517. Compare this vol., ii, 453).—Polemical. A further reply to Mazzucchelli (this vol., ii, 165). R. V. S.

Character of the Double Refraction of Pleochroic Liquid Crystals. DANIEL VORLÄNDER and M. E. HUTH (*Zeitsch. physikal. Chem.*, 1913, **83**, 424—429. Compare A., 1906, ii, 337; 1908, ii, 88; 1911, ii, 165; also Dorn, A., 1910, ii, 809).—The authors have examined the double refraction of a number of substances forming liquid crystals, and in most cases it is shown that two or more liquid crystal forms exist. The change of one form to another by heating and cooling is indicated diagrammatically. Thus, for the active amyl ester of *p*-anisylideneamino-*a*-methylcinnamic acid, the changes are:

Amorph. liquid ← Cryst. liquid II ← Cryst solid I.

Cryst. liquid I → Cryst. liquid II → Cryst. solid II.

Crystalline liquids I and II are pleochroic.

Active amyl ester of *p*-ethoxybenzylideneamino-*a*-ethylcinnamic acid gives the changes:

Amorph. liquid ← Cryst. solid.

Cryst. liquid I → Cryst. liquid II ⇄ Cryst. liquid III.

Crystalline liquids I and II are pleochroic.

Active amyl ester of *p*-ethoxybenzylideneamino-α-methylçinnamic acid gives the changes:

$$\begin{tikzcd} \text{Amorph. liquid} \arrow[r, shift left] & \text{Cryst. liquid II} \arrow[l, shift left] \arrow[r, shift left] & \text{Cryst. liquid I} \arrow[l, shift left] \arrow[r, shift left] \arrow[d, shift left] & \text{Solid} \arrow[l, shift left] \\ & & \text{Cryst. liquid III} \arrow[u, shift left] \arrow[ur] & \end{tikzcd}$$

Crystalline liquids I and II are pleochroic.

Cholesteryl chloride gives the changes:

$$\begin{tikzcd} \text{Amorph. liquid} \arrow[d] & \text{Cryst. solid} \arrow[l] \\ \text{Cryst. liquid I} \arrow[r] & \text{Cryst. liquid II.} \arrow[u] \end{tikzcd}$$

Crystalline liquids I and II are pleochroic. From the examination of the double refraction the authors are able to confirm the result of Vorländer (*loc. cit.*) that the double refraction is negative in those cases where two pleochroic liquid crystal phases are found for the same substance. J. F. S.

Magnetic Birefraction of Liquid Mixtures. A. COTTON and HENRI MOUTON (*Compt. rend.*, 1913, **156**, 1456—1459. Compare this vol., ii, 288).—The law of additivity cannot be rigorously applied to the magnetic birefraction of a mixture of liquids. Nitrobenzene, when diluted with inactive liquids, such as carbon tetrachloride or alcohol, gives values far below the calculated, whereas α-bromonaphthalene similarly diluted gives values above those calculated. A mixture of equal volumes of nitrobenzene and α-bromonaphthalene gives values fairly closely in accord with those calculated. W. G.

The Goldstein Method of Producing Fundamental Spectra and the Spectra of Air, Nitrogen, and Oxygen in Geissler Tubes. JOSEPH SCHARBACH (*Zeitsch. wiss. Photochem.*, 1913, **12**, 145—205. Compare Goldstein, A., 1910, ii, 669).—The object of the present paper is to control the work of Goldstein (*loc. cit.*) with regard to the spectra of salts in Geissler tubes. It was necessary before this could be done that the spectra of air, oxygen, and nitrogen should be determined. The author has therefore determined the spectra of air, oxygen, and nitrogen in Geissler tubes, and also the spark spectra of air, using aluminium poles. The measurements were made by means of a concave Rowland grating of 1·80 metre radius of curvature, and the spectra photographed. It is shown that lines appear in spark spectrum of air which are not to be found in the spectrum from the Geissler tube, and vice versâ; also many lines are found strengthened in the Geissler tube, whilst the strengthening of tube lines in the spark is rarely found. The second part of the paper deals with the spectra of cæsium bromide, potassium chloride, fluoride, iodide and bromide, sodium chloride, bromide, iodide and fluoride, lithium chloride, bromide and iodide, barium chloride, and silver nitrate in Geissler tubes

between λ 3000 and λ 5900. The measurements were made in the same manner as Goldstein's, but the results differ from his in essential points. The air lines are to be found in all the spectra, and the metal and non-metal lines are not new, but correspond with hitherto measured lines of these elements. The lines termed by Goldstein "Fundamental Spectrum" lines therefore do not exist under the conditions of these experiments. Tables of all the wave-lengths measured are given, and these are compared with the values of other observers. J. F. S.

The Origin of Bands in the Spectrum of Active Nitrogen. E. PERCIVAL LEWIS (*Phil. Mag.*, 1913, [vi], **25**, 826—832. Compare A., 1900, ii, 702; also Strutt and Fowler, A., 1911, ii, 678).—The author shows that with approximately pure nitrogen the spectrum of the third group of nitrogen bands could not be obtained in any circumstances, but when a small percentage of oxygen was admitted they invariably appeared when the discharge was weak, and in addition the β-group of Strutt and Fowler also appeared whenever the third group was present. In studying the after-glow, it was seen that the spectrum contained every band observed by Strutt and Fowler, as well as the "fourth positive group of bands" first observed by the author and Strutt and Fowler. The fourth positive group bands are only found in the spectrum of the discharge which produces the after-glow, and not in the spectrum of the after-glow itself. A series of photographs of the spectra are given, and from these it appears that the second group of bands belong entirely to the discharge and not to the after-glow, whilst the third group and the β-groups are relatively more intense in the after-glow. The author doubts whether pure nitrogen has ever been used in the work on nitrogen spectra. J. F. S.

An Undescribed Spectrum Probably Belonging to Helium. EUGEN GOLDSTEIN (*Ber. Deut. physikal. Ges.*, 1913, **15**, 402—412).—The author describes a spectrum which he has observed with helium drawn from many sources. The spectrum is best seen and photographed in an "end on" tube which has a wide cross section. Details and photographs are given of the spectrum obtained in a 12 mm. wide tube at pressures of 30—50 mm., using a condenser or spark gap in the circuit. The spectrum appears to have the same relationship to the series spectrum that the second hydrogen spectrum has to the hydrogen series spectrum. J. F. S.

Electric Behaviour of Certain Vapours with Banded Absorption. JOHANNES STARK (*Physikal. Zeitsch.*, 1913, **14**, 454—456).—Polemical against Burger and Koenigsberger (this vol., ii, 85). H. M. D.

Distribution of the Light Emission in an Arc Between Metal Poles for Wave-lengths Below λ = 4000. HEINRICH KÖNEMANN (*Zeitsch. wiss. Photochem.*, 1913, **12**, 65—76, and 123—143).—The arc spectra of a number of metals were photo-

graphed by means of a quartz spectrograph, and the intensity of the lines compared at the poles and the centre. A full description of the instrument and method is given. The following metals were examined: tin, zinc, lead, calcium, thallium, cadmium, magnesium, aluminium, copper, and silver. The presence of many spark lines are found in all the spectra, and this fact, which had previously only been observed in a few cases, may be taken as general for arc spectra. It is shown that in a given spectrum, taking the lines along their length from pole to pole, that some are of uniform intensity; others have an intensity which is greater at one or other or both poles; the strengthening at the poles may or may not be the same. It is also shown that all types may occur in a given spectrum. The relative intensity of the various elements in different parts of the lines can be seen from the comparative scheme:

(*a*) Sn 0, Ag 2·3, Cu 3·5, Tl 4·4, Pb 9·5, Cd 21·9, Ca 28·6, Mg 34·2, Zn 40·7, and Al 100·0 indicates the percentage of lines which are strengthened at the positive pole.

(*b*) Al 0·0, Cd 7·1, Zn 7·4, Mg 7·9, Pb 15·6, Ca 39·0, Cu 51·7, Sn 70·4, Ag 84·7, and Tl 87·0 indicates the percentage of lines which are strengthened at the negative pole.

(*c*) Al 0·0, Ag 12·9, Tl 17·4, Sn 31·5, Ca 32·4, Cu 44·7, Zn 51·8, Mg 57·9, Cd 74·0, and Pb 78·2 indicates the percentage of lines which are of equal intensity at both poles.

The lines which are not strengthened are mainly arc lines. The lines which show the greatest differences, or only appear at the poles, are all enhanced lines of the spark spectra. The majority of the lines which are strengthened at the poles are to be found in the extreme ultra-violet. The intensity ratio of the spark lines in the arc spectrum is different from the ratio of the enhanced lines in the spark spectrum. The author shows that the enhanced lines are to be divided into several groups, and he is of the opinion that the appearance of spark lines near the poles explains the differences in arc spectra of other observers. The spectral relationships are compared with the melting points, boiling points, specific gravities, atomic weights, electro-potential and chemical properties of the elements examined, but no definite relationship is to be found. In the case of the electro-potential, there is a partial similarity in the order of the elements. The various reasons for the differences in the intensity are discussed, and lead the author to the conclusion that neither the potential fall distribution, temperature distribution, nor any other single cause can explain the appearance of the spark lines. J. F. S

Measurement of the Spark and Arc Spectrum of Calcium on the International Normal. OSWALD HOLTZ (*Zeitsch. wiss. Photochem.*, 1913, **12**, 101—123).—The spectrum of calcium was determined, using a concave Rowland grating of 6·4 metre radius of curvature and 20,000 lines per inch. The spectrum was photographed, and the wave-lengths determined by a measuring machine. For the arc spectrum, hollow carbon poles filled with calcium carbonate, or solid carbon poles with calcium chloride laid on the

lower carbon, were used, and for the spark spectrum calcium poles were employed. The arc was fed with a current of 7 amperes at 220 volts, and the spark obtained from a resonance transformer fed by alternating current. In the earlier work it was found that a given line did not give the same value for the wave-length when measured on different occasions. Investigation into the cause of this showed that temperature changes in the grating room were responsible, hence in the work precautions were taken to keep the temperature constant. A full list of the lines is given, and compared with the values of Kayser, Rowland, Exner and Haschek, Eder and Valenta, and Saunders. A complete bibliography is appended to the paper. J. F. S.

Arc Spectrum of Iron. KEIVIN BURNS (*Zeitsch. wiss. Photochem.*, 1913, **12**, 207—235).—The object of this paper is to measure all lines of the iron spectrum which can be easily photographed. The stronger lines were photographed and measured four times; the lines above 5434 are not included in the paper owing to the absence of a sufficiently accurate normal. The measurements are made with a Rowland grating of 635 cm. focus and 787 lines per cm. Many pairs are found the distance of which apart is not greater than λ/n. 110,000 of the theoretical dispersing power, and in numerous pairs with twice this distance the single lines are separated clearly by a bright space. The lines are given in tables together with some manganese and nickel lines. J. F. S.

Spectrum Absorption and Polymorphism. KARL SCHAUM (*Zeitsch. wiss. Photochem.*, 1913, **12**, 143—144).—The author indicates the possibility of deciding between chemical polymorphism and physical polymorphism by means of absorption or luminescence spectra, and he sees in this method a means of deciding between the views of Tammann (this vol., p. 193) and Smits (A., 1910, ii, 195, 400; this vol., p. 393) with regard to polymorphism. J. F. S.

Absorption Spectra of Manganese Salts in Different States of Oxidation. WALTER JAESCHKE and JULIUS MEYER (*Zeitsch. physikal. Chem.*, 1913, **83**, 281—289).—An attempt is made to find a relationship between the colour of derivatives of manganese compounds and the valency it is exhibiting in these compounds. For this purpose the absorption spectra of potassium permanganate, potassium manganate, the doubtful manganese tetrachloride, manganic chloride, manganic sulphate, manganic phosphate, manganous chloride, and manganous sulphate are determined. The absorption spectra of all the compounds show great similarity, particularly in respect of the band in the red; this band is very persistent, and only disappears with the very dilute solutions of permanganate and manganous chloride. The central band appears, however, to be influenced by the valency, in the sense that it moves toward the red end of the spectrum with increasing valency. The authors state that the violet end of the spectrum is most sensitive to changes in valency, but they were unable to make any

measurements in that region or in the ultra-violet portion of the spectrum. J. F. S.

Absorption Spectra of Six Blue, Green, and Violet Dyes Sanctioned for Use in Confectionery. GUSTAVE MASSOL and A. FAUCON (*Bull. Soc. chim.*, 1913, [iv], **13**, 513—519).—The method of investigation used is that already described (this vol., ii, 264). Malachite-green, acid-green-J and patent-blue show three bands, one in the visible spectrum, one at the point between the visible and invisible portions of the spectrum, and one in the ultra-violet. Water-blue-6B is characterised by a large band ($\lambda = 320$ to 275) in the ultra-violet, similar to that shown by acid-magenta. Paris-violet and acid-violet-6B have a single absorption band in the visible portion of the spectrum. The limits of the bands for each dye are shown by tables and graphs. T. A. H.

Absorption of the Ultra-violet Rays by the Alkaloids of the Atropine Group. MARCEL GOMPEL and VICTOR HENRI (*Compt. rend.*, 1913, **156**, 1541—1544).—A quantitative study of the absorption of the ultra-violet rays by the three alkaloids atropine, *apo*atropine, and cocaine. The measurements were made with alcoholic solutions, and the molecular constants of absorption calculated for the maxima and minima of absorption. The spectrum of atropine presents three absorption bands at $\lambda = 2645$, 2580, and 2505 respectively. Above $\lambda = 2493$ the absorption steadily increases. These three bands correspond with three in the benzene spectrum moved slightly towards the red. This alkaloid can be detected at a dilution of 5 parts in 10,000. *apo*Atropine has a much stronger absorption than atropine. Its spectrum exhibits one band at λ 2626, and by means of it the alkaloid can be detected at a dilution of 2 parts in 10,000. The spectrum of cocaine is sharply distinguished from the two previous ones. It possesses three absorption bands at $\lambda = 2814$, 2722, and 2314 respectively, the one at λ 2314 being extremely intense, having a molecular constant of absorption greater than 20,000. These three bands correspond with three in the spectrum of benzoic acid moved slightly towards the red. The band at λ 2314 permits of the detection of 1 part of cocaine in 200,000 of solution. W. G.

The Relationship Between the Absorption, Dispersion, and Fluorescence of Light. BENKT SÖDERBORG (*Ann. Physik*, 1913, [iv], **41**, 381—402).—A description is given of measurements of the extinction-coefficient, absorption spectra, and refractive index of solutions of eosin (sodium salt), fluorescein, and erythrosin in water and acetone–water solutions. The experiments were carried out at ordinary temperatures, and in case of the absorption spectra of eosin in water solution, also at 40°, 60°, and 80°. It is shown that the absorption bands of the non-fluorescent solutions can be resolved into two elementary bands, which the author numbers 1 and 3; No. 1 lying toward the violet, and No. 3 toward the red end of the spectrum. The absorption bands of the fluorescent

solutions exhibit two maxima; the one maximum *B* dominates the spectrum, and can be resolved into three elementary bands, No. 2 lying between 1 and 3, and this new band together with 3 together constitute the maximum *B*. Solutions, which on dilution pass from the non-fluorescent to the fluorescent condition, do not obey Beer's Law. At greater concentrations, when the absorption gives no indication of the passage to fluorescence, and also when the fluorescence is strongly marked, the solutions obey Beer's law. The absorption bands of erythrosin and fluorescein solutions show a somewhat higher maximum for *B* than for *A*. This indicates that they are in the condition when they are about to pass into the fluorescent condition, although there is no indication of elementary band 2. On the other hand, this band makes itself very noticeable in the dispersion curve. The presence of band 2 in the absorption spectrum is made probable on the assumption that the absorption is neutralised by the fluorescence. The absorption bands of a 10·7% eosin water solution shows two equal maxima, and its observed dispersion curve agrees well with the calculated curve. From this it is concluded that there is no band 2 or at most only a very weak one, and that here there is no latent fluorescence. The following general conclusions are deduced: (1) Fluorescence is occasioned by absorption in the elementary band 2. (2) Fluorescence can be strong but latent in concentrated solutions. (3) On dilution the latent fluorescence shifts toward the red, the elementary band 2 appears, and the fluorescence becomes visible. These results are in accordance with Stark's theory of the coincidence of the absorption and fluorescence spectra for short wave-length bands. Both the dispersion formulæ of Ketteler and Helmholtz are in accordance with the view of latent fluorescence. J. F. S.

Rotational Optical Activity of Solutions. G. H. Livens (*Phil. Mag.*, 1913, [vi], **25**, 817—826).—A theoretical paper in which the author, from the electromagnetic theory, deduces an equation which expresses the rotatory power of a dissolved substance. The three equations of Landolt are shown to be approximations of the formula evolved, and to represent special cases. A few discrepancies between experimental facts and those deduced from the formula are indicated. These occur particularly at the minimum value of the rotation. J. F. S.

Studies of the Processes Operative in Solutions. XXVII. The Causes of Variation in the Optical Rotatory Power of Organic Compounds and of Anomalous Rotatory Dispersive Power. Henry E. Armstrong and E. E. Walker (*Proc. Roy. Soc.*, 1913, *A*, **88**, 388—403).—The authors summarise their views as follows: The variations in rotatory power met with in optically active compounds may be ascribed (*a*) to alterations in molecular size, and to the formation of compounds between solvent and solute; (*b*) to the occurrence of changes giving rise to the presence of reversibly related isodynamic forms.

The changes included under (*a*) are common to all optically

active substances; those included under (*b*) can occur only in special cases. In these special cases, if the change involve the formation of compounds so different in chemical type that they not only differ in rotatory power in sign but also in rotatory dispersive power, the product might have anomalous dispersive power; in other cases it would behave normally.

The above conclusions are drawn from a consideration of the specific rotations in solution of lævulose, methyl and ethyl tartrates, *o*-nitrobenzoyltetrahydroquinaldine, and 2-nitrotoluene-4-sulphonyltetrahydroquinaldine. T. S. P.

Magneto-chemical Researches. III. PAUL PASCAL (*Ann. Chim. phys.*, 1913, [viii], **28**, 218—243).—A continuation of the résumé already abstracted (A., 1912, ii, 426). This portion gives in greater detail a discussion of the results obtained with acetylenic compounds, and corrects certain of the values already given (A., 1912, ii, 734). An examination of a number of allyl compounds shows that the mean value of λ for the double linking in the allyl group is $+47 \times 10^{-7}$, as compared with $+57 \times 10^{-7}$ for the ordinary ethylenic linking. The figures for allyl alcohol and for diacroleinacetylene, $CH_2{:}CH{\cdot}CH(OH){\cdot}C{:}C{\cdot}CH(OH){\cdot}CH{:}CH_2$, are anomalous. T. A. H.

Variations of the Magnetic Rotatory Power with Changes of State. J. CHAUDIER (*Compt. rend.*, 1913, **156**, 1529—1532. Compare this vol., ii, 368).—A comparative study of the magnetic rotatory power of substances in the gaseous and liquid states and in the liquid and solid states. The magnetic rotatory power in the gaseous state, as calculated from the values in the liquid state, supposing that the phenomenon varies as the density, is found to be higher than the observed value in the case of oxygen, carbon dioxide, and carbon disulphide, substances for which the magnetic rotatory dispersion is in wide disagreement with the law of the inverse square of the wave-length, whilst in the case of nitrogen, sulphur dioxide, and chloroform, which obey this law, the observed and calculated values agree fairly closely. In the passage from the liquid to the solid state the magnetic rotatory power disappears completely in the case of active liquids, which solidify to crystalline solids, but is preserved unaltered where the liquids give amorphous, vitreous solids. W. G.

Determination of the Order of a Photochemical Reaction. A. TIAN (*Compt. rend.*, 1913, **156**, 1758—1761).—A theoretical paper, in which the author shows that it is possible to deduce mathematically the order of a photochemical reaction. W. G.

The Decomposition of Lactic and Tartaric Acids in Ultraviolet Light. HANS EULER and S. RYD (*Biochem Zeitsch.*, 1913, **51**, 97—106).—Lactic acid, in the presence of the short ultra-violet rays, undergoes a decomposition, analogous to a fermentation, with evolution of carbon dioxide. This reaction is less influenced by

temperature than other photochemical reactions. The rate of evolution of carbon dioxide is not accelerated by the presence of either ferrous or ferric salts, but the latter are reduced. Tartaric acid undergoes similar changes in the ultra-violet light, with the formation of carbon dioxide and reducing substances. In this case ferric (but not ferrous) salts increase the rate of gas evolution, being reduced themselves at the same time. S. B. S.

Chemical Action of Light. XXVI. Autoxidations. IV. GIACOMO CIAMICIAN and PAUL SILBER (*Ber.*, 1913, **46**, 1558—1565; *Atti R. Accad. Lincei*, 1913, [v], **22**, 539—547. Compare A., 1912, i, 174, 645; this vol., i, 350).—The authors have studied the spontaneous oxidation of aqueous solutions of hydroxy-acids in light in the absence of other substances, such as salts of iron or uranium (contrast Neuberg, A., 1908, ii, 915; Benrath, A., 1911, ii, 681).

Lactic acid, in these circumstances, yields carbon dioxide and acetaldehyde, identified as the *p*-nitrophenylhydrazone, m. p. 127—128°. Acetic acid is also formed.

Mandelic acid gives carbon dioxide, benzaldehyde (characterised by its semicarbazone, m. p. 216°), salicylaldehyde, benzoic acid, and salicylic acid.

Carbon dioxide, formaldehyde (*p*-nitrophenylhydrazone, m. p. 180°), acetaldehyde, formic and acetic acids are formed by the oxidation of malic acid.

The volatile products of the oxidation of tartaric acid consist of carbon dioxide and formic acid. From the non-volatile products, the osazone of hydroxypyruvic acid, m. p. 208—209° (*sodium* salt, orange-yellow needles, m. p. 239°), and glyoxalosazone, m. p. 175°, were obtained by means of phenylhydrazine acetate.

Citric acid yields carbon dioxide and acetone (*p*-bromophenylhydrazone, m. p. 92°).

Quinic acid (tetrahydroxy*cyclo*hexanecarboxylic acid) gives quinol and 3:4-dihydroxybenzoic acid in accordance with the equations: (1) $C_6H_7(OH)_4CO_2H + O = C_6H_3(OH)_2 + CO_2 + 3H_2O$, and (2) $C_6H_7(OH)_4{\cdot}CO_2H + O = C_6H_3(OH)_2CO_2H + 3H_2O$.

Carbon dioxide, formic acid, and the semialdehyde of maleic acid are formed from pyromucic acid. The latter product was identified in the form of its phenylhydrazone, m. p. 157° (which was identical with the product obtained by the action of phenylhydrazine on the semialdehyde of maleic acid obtained by treatment of pyromucic acid with bromine in alkaline solution), and also as the oxime, m. p. 130°, which was subsequently converted into methyl fumarate, m. p. 102°.

Cinnamic acid yields α-truxillic acid, benzaldehyde, benzoic, and formic acids.

The authors are unable to confirm Inghilleri's statement (A., 1911, i, 354) that a sugar-like substance (sorbose) is formed when formaldehyde (40%) and crystallised oxalic acid are exposed to sunlight. H. W.

Chemiluminescent Reactions with Physiological Substances. F. ALEX. McDERMOTT (*J. Amer. Chem. Soc.*, 1913, **35**, 824—826)

—When solid potassium cyanide is introduced into urine, a faint luminescence is produced, which is greatly increased by the addition of a strong, alkaline solution of hydrogen peroxide. Potassium formate and formaldehyde produce the same effect as potassium cyanide. If Witte's peptone is hydrolysed by boiling it with alkali in an atmosphere of hydrogen, and strong alkaline hydrogen peroxide is added, a faint light is emitted. If formaldehyde is introduced before adding the hydrogen peroxide, a much more intense light of a pale green colour is produced. Glue gives a faint luminescence when treated in the same way, but egg-albumin, casein, glutenin, leucine, asparagine, glutamic acid, nucleic acids, and phytin give negative results. These experiments support the view that in living organisms the emission of light is due to the oxidation of a waste-product. E. G.

Production of Fluorescent Radiation. J. CROSBY CHAPMAN (*Phil. Mag.*, 1913, [vi], **25**, 870).—Polemical, in answer to Bragg's criticism (this vol., ii, 373). J. F. S.

Chemical Production of Light. WILDER D. BANCROFT (*J. Franklin Inst.*, 1913, **175**, 129—152).—The author discusses and classifies different forms of luminescence with the action of cathode rays on numerous oxides and salts and the probable influence of the acidic and basic ions contained on the colours of the light emitted. He considers that if the reaction velocity is sufficiently high, light will always be emitted, and that in describing this phenomenon the spectrum of a reaction should be spoken of, and not that of a substance. F. M. G. M.

Uni-, Bi-, and Ter-valent Lines of Albumin in the Canal-Ray Spectrum (JOHANNES STARK, R. KÜNZER, and GEORG WENDT (*Sitzungsber. K. Akad. Wiss. Berlin*, 1913, 430—441. Compare this vol., ii, 172, 360).—It is shown that aluminium furnishes uni-, bi-, and ter-valent positive ions in the canal rays, and consequently gives canal-rays of three velocity intervals. With a fall of potential at the cathode of less than 8000 volts, the uni- and bi-valent aluminium ions are present in canal-rays in far larger numbers than the tervalent ions, but with a potential fall of over 8000 volts measurable numbers of tervalent aluminium ions are present. The uni-, bi-, and ter-valent aluminium ions are the carriers of different spectral lines. Thus, for example, the doublet λ 3961·7—3944·2 Å is due to the univalent aluminium ions, the line λ 4663·5 Å is due to the bivalent aluminium ions, and the lines λ 4529·7, 4513·0, and 4480·0 Å to the tervalent aluminium ions. J. F. S.

The Purification and Concentration of Crude Radium-Barium Chlorides by Fractional Precipitation with Hydrochloric Acid. ERICH EBLER and W. BENDER (*Ber.*, 1913, **46**, 1571—1573).—The method used is based on the practical insolubility of barium chloride in approx. 10*N*-hydrochloric acid (Ebler, A., 1909, ii, 347). Soddy ("Chemistry of the Radioelements") has

pointed out that radium is carried down with the barium in the precipitation.

The authors find that when an aqueous solution of radium barium chloride is fractionally precipitated by leading into it hydrogen chloride gas, the first fractions are richer in radium than the salt started with; moreover, practically all the radium is precipitated with the first two-thirds of the barium chloride.

The above gives a much simpler fractionation method than that usually employed, since all the salts used are soluble in water.

T. S. P.

Occluded Gases and Radium and Uranium Contained in the Radioactive Tufa of Fiuggi. C. PORLEZZA and G. NORZI (*Gazzetta*, 1913, **43**, i, 504—510. Compare Nasini and Levi, A., 1908, ii, 401).—The rock contains only very minute traces of helium. The quantity of radium per gram (measured by Strutt's method) is 5×10^{-12}, whilst the uranium amounts to $0{\cdot}76 \times 10^{-5}$ per gram of rock.

R. V. S.

Concentration of the Radioactive Emanation of the Gas of the Boraciferous "Soffioni" by means of Carbon at a Low Temperature. C. PORLEZZA and G. NORZI (*Gazzetta*, 1913, **43**, i, 510—514).—When the gas from the "soffioni" of Larderello is passed over charcoal at $-77°$, it becomes inactive, and on heating the charcoal a gas is obtained from it which is thirty-four times more active (activity $6{\cdot}8 \times 10^6$ volt-hour) than the natural gas.

R. V. S.

The Constancy of the Potassium Activity. WILHELM BILTZ and E. MARCUS (*Zeitsch. anorg. Chem.*, 1913, **81**, 369—377).—The examination of potassium salts from a large variety of natural minerals shows that the β-ray activity of potassium is very closely a constant, and the activity of the minerals is, within wide limits of the potassium content, proportional to that content. The evidence is against the assumption of an unknown active alkali-metal.

The minerals examined are: carnallite and sylvite from the Stassfurt deposits; orthoclase, muscovite, lepidolite, leucite, spodumene, and beryl, specimens of different origin being available in several cases. The Stassfurt minerals are converted into perchlorate, purified by recrystallisation, and then converted into sulphate. The silicates are either decomposed by hydrofluoric acid or by means of calcium carbonate and ammonium chloride, the latter method giving the better yield. The presence of lithium, rubidium, and cæsium has been detected in several of the minerals, and an approximate estimation has been made in the case of Norwegian beryl.

C. H. D.

Ionisation in Gases and Gaseous Mixtures by Röntgen and Corpuscular (Electronic) Radiations. CHARLES G. BARKLA and A. J. PHILPOT (*Phil. Mag.*, 1913, [vi], **25**, 832—856).—The

relative ionisations of air, hydrogen, nitrogen, oxygen, carbon dioxide, hydrogen sulphide, sulphur dioxide, ethyl bromide vapour, and methyl iodide vapour, by the complete absorption of corpuscular radiations set free by *X*-radiations have been determined by the authors. It is shown that there is no change in the relative ionisation with the velocity of the ionising corpuscles. The relative ionisations due to complete absorption of the corpuscular radiation are found to agree closely with the relative ionisations brought about by complete absorption of Röntgen radiation and its secondary radiations. The results indicate that the complete adsorption of a given *X*-radiation by different gases causes the emission of the same number of corpuscles. The ionisation coefficients for homogeneous *X*-radiations in a number of gases and vapours are determined, and the general laws stated by Barkla are confirmed. The ionisations in various gaseous and vapour mixtures due to complete absorption of corpuscular radiation are determined, and the values indicate that in the air–ethyl bromide mixture the relative absorptions of energy were very closely in agreement with the relative masses of the constituent gases. The ionisation by *X*-rays of gaseous mixtures has been shown to differ considerably from the sum of the ionisations of the constituent gases. The difference shows the effect of corpuscles from one gas being absorbed by the other, the general nature of the deviation being such as could be inferred from earlier experiments, although the amount of the difference is less than was to be expected on the theory of ionisation by ejected corpuscles. J. F. S.

Collisions between Gas Molecules and Slow Moving Electrons. J. FRANCK and GUSTAVE HERTZ (*Ber. Deut. physikal. Ges.*, 1913, **15**, 373—390).—The paper deals with an investigation of the phenomena which occur when electrons collide with gas molecules at velocities at which they are unable to ionise the gas. It is shown that the free path of electrons, which are emitted with velocities corresponding with voltages between 2 and 10 volts, is of the order $4\sqrt{2}$ times the free path of the gas through which they are passing; this result is in agreement with the value previously found by Lenard. It appears therefore that at these velocities the electron-affinity and the electric charge have no noticeable influence on the free path. It is also shown that when electrons, moving at these velocities, collide with helium or hydrogen molecules, they are reflected with comparatively little loss of energy. From these results the authors put forward an hypothesis of the changes occurring at these collisions. They also state that at the reflection of electrons an energy change occurs between the molecule and the electron which does not take place in whole quanta as has been stated by Sommerfeld. J. F. S.

The Electronic Theory of the Metals. KARL F. HERZFELD (*Ann. Physik*, 1913, [iv], **41**, 27—52).—A theoretical paper which starts from the hypothesis that in good conducting metals the transport of heat and electricity is brought about by the free

electrons alone. The various points considered are: (*a*) the calculation of the electron energy from the Wiedemann-Franz law; (*b*) calculation of the product of the number of electrons per c.c. and the free path ($n\lambda$) from the electro-conductivity; (*c*) calculation of the relationship of temperature and number of electrons from the Thomson effect; (*d*) the relationship between temperature and the free path of the electrons. It is shown in the paper that for good conducting metals the ratio $x/\sigma T$ can be expressed by the formula $x/\sigma T = 0{\cdot}07244 \,.\, 4N^2 \,.\, dE/dT \,.\, E/T$, in which T is the absolute temperature, E the energy of the electrons, N the number of atoms per gram molecule, σ the electrical conductivity, x the thermal conductivity. The value of E in the above equation is replaced by $E = \frac{1}{2}hv/e^{hv/kT} - 1$, in which e is the charge of the electron, and hv/k for copper is 57·77, for aluminium, 104·5, for silver, 41, and for zinc, 28. From the Thomson effect, the relationship between n, the number of electrons in 1 c.c. of metal, and the temperature is given by the equation: $(n/n_0)^A = Te^{a - q_0/\sigma}$ For copper the values are $\alpha = 0{\cdot}9711$ and $q_0 = 34{\cdot}05$, and for aluminium, $\alpha = 1{\cdot}001$ and $q_0 = 55{\cdot}4$. From a discussion of the formula, the value of A is shown to be approximately 2/3. It is also shown that Lindemann's formula, $1/\lambda = (B\sqrt{E} + C)^2$, does not represent the relationship between the free path and the temperature. J. F. S.

Radioactivity of Some Minerals and Rocks. EMIL F. BELLMER (*Jahrb. Min.*, 1913, i, Ref. 184; from Pamphlet, *Freiburg, Schweiz*, 1911, 49 pp.).—Attempts were made to separate the various radioactive substances by a new method. In the case of orthite, the radioactivity is due solely to the small amount of thorium present. This mineral is widely distributed in the granites and gneisses of the Black Forest, and its presence accounts for the radioactivity of these rocks. Granites and other igneous rocks from Sumatra, Baden, and elsewhere were found to contain from $5{\cdot}10^{-6}$ to $6{\cdot}10^{-4}$ grams of thorium per gram of the rock. The radioactivity of samarskite is due to the presence of uranium, thorium, radium, and mesothorium-II. L. J. S.

Electrical Conductivity of Some Pure Liquids: Ammonia, Acetone, Methyl and Ethyl Alcohol. JACQUES CARVALLO (*Compt. rend.*, 1913, **156**, 1755—1758. Compare A., 1910, ii, 1026; 1912, ii, 119).—The author has determined the electrical conductivity of chemically pure specimens of these substances, when submitted to an electric current, a constant potential difference being maintained between the cell electrodes, with a view to determining the purifying effect and the apparent specific conductivity of the pure liquids. His results show that the prolonged passage of a current, through a liquid which is a bad conductor, leads to a conductivity limit, which may, according to the conditions and for the same liquid, be greater or less than the original conductivity. This method of purification does not apply to the two alcohols. W. G.

Electrical Resistance of a Few Metals Through a Wide Range of Temperature. Edwin F. Northrup and V. A. Suydam (*J. Franklin Inst.*, 1913, **175**, 153—161).—A preliminary account of work undertaken for the purpose of perfecting a method whereby the electrical resistance of metals and alloys can be measured with ease, precision, and rapidity through a range of temperature between that of liquid air and a point a little below the boiling point of the substance in question; the same method is stated to be applicable to the case of molten salts.

To obtain data from which the relationship of resistance to temperature for metals, alloys, and molten salts which boil below 1500° can be expressed in curves, the following substances have been investigated by this method: mercury, lead, cadmium, zinc, tin, bismuth, and antimony, and their resistance in microhms per cm.-cube at various temperatures are tabulated. F. M. G. M.

Electrical Dispersion in Benzene, Toluene, and Petroleum. N. Linnitschenko (*Physikal. Zeitsch.*, 1913, **14**, 543—555).—The author has examined the dispersion and dielectric constants of benzene, toluene, and petroleum by three methods, which are modifications of the Drude method. It is shown that in the region of half wave-length 330—350 mm., there are no dispersion bands in benzene, toluene, or petroleum. The bands found by Colley (A., 1908, ii, 909) and Obolenski (A., 1910, ii, 562) are shown to have arisen from experimental errors. It is shown that the so-called methyl bands, which were supposed to be characteristic of the methyl group, have no existence. J. F. S.

Silicon and Its Position in the Thermoelectric Series. Franz Fischer, Richard Lepsius, and Ernst Baerwind (*Zeitsch. anorg. Chem.*, 1913, **81**, 243—256. Compare Koenigsberger and Weiss, A., 1911, ii, 578).—An apparatus is described by means of which irregular pieces of commercial silicon may be clamped between two masses of copper, one of which is heated and the other cooled. Some specimens of silicon are positive to copper, and others as strongly negative, and a thermo-couple composed of the two varieties may have a thermo-*E.M.F.* as high as 820 microvolts per 1°. The two varieties do not differ characteristically in electrical conductivity. The difference is due to the presence of silica. Melting silicon in contact with magnesia, lime, or alumina renders it positive, silica being removed. On the other hand, melting silicon so that a part of it burns and the oxide thus formed dissolves renders it negative. Several methods of bringing about the conversion are described. C. H. D.

Disturbing Influence of Air in Observations on the Concentration Cell. Charles M. van Deventer (*Chem. Weekblad*, 1913, **10**, 472—477).—In a concentration cell with zinc and zinc sulphate, exclusion of air prevents change of polarity on dilution of the second liquid, and the *E.M.F.* of the cell corresponds with

that indicated by theory. If air is not excluded, accuracy of observation is impossible. A. J. W.

Electromotive Force of Silver Nitrate Concentration Cells. JAMES M. BELL and ALEXANDER L. FEILD (*J. Amer. Chem. Soc.*, 1913, **35**, 715—718).—Measurements of the *E.M.F.* of concentration cells containing silver nitrate in aqueous and in alcoholic solutions have been made at 25° over a wider range of concentrations than have been used previously.

Determinations made with aqueous solutions accord with Nernst's formula for dilute solutions, $E=(2v/u+v)(RT/nF)\log_e c_1/c_2$, where c_1 and c_2 denote the concentration of the silver ions, and u and v the migration ratios of $Ag^{\cdot}$ and NO_3'. In the case of higher concentrations, however, the calculated value of the *E.M.F.* is greater than the observed value, since the migration ratio v is smaller at such concentrations. This affects the factor $2v/u+v$, and also affects the factor $\log c_1/c_2$, because the ratio c_1/c_2 is determined from conductivity measurements, and this method of determination is only valid when the migration velocity remains constant. The calculated value of the migration ratio for dilute solutions agrees closely with that found experimentally.

In the case of alcoholic solutions, the migration ratio seems to vary even at concentrations below $0{\cdot}1N$. The value of v calculated from the most dilute solution was 0·62. E. G.

The Nature of Overvoltage. JOHN I. CRABTREE (*J. Soc. Chem. Ind.*, 1913, **32**, 521).—A statement of what is usually meant by overvoltage, and a discussion of its applications. T. S. P.

The Influence of the Addition of Colloids on the Anode and Cathode Reactions in the Electrolysis of Metal Salt Solutions (Lead and Zinc). I. ROBERT MARC (*Zeitsch. Elektrochem.*, 1913, **19**, 431—444).—The influence of the addition of small quantities of gum arabic, starch, albumin, and gelatin on the nature of the cathode and anode products of the electrolysis of solutions of the following salts of lead is examined: acetate, silicofluoride, formate, benzoate, and salicylate, and of acetate, and silicofluoride, of zinc. It is shown all additions produce a finer grained deposit on the cathode, but that there is no relationship between the tendency to produce fine-grained deposits and the tendency to give coherent deposits. In many cases it is shown that the contrary is the case, and that with high current densities the coherence is much reduced by the addition of a colloid, whilst the size of the particles remains the same. The process depends evidently on two actions detrimental to one another. A coherent layer has a large plasticity and small particles as necessary conditions. From a pure solution the plasticity is at its maximum, as also is the tendency to form large crystals. With electrolytes which have great tendency to form large crystals, so much of a colloid must be added that the brittleness of the deposit naturally becomes too great of a coherent layer. It is shown that only

in special circumstances can a beneficial action of colloid additions be possible, and that colloids which are only slightly adsorbed by the deposit are more likely to have a favourable effect on the deposit than strongly adsorbed colloids. The author observed that lead crystals obtained by electrolysis showed Brownian movement up to crystals 15μ long and 2μ broad in colloid solutions, but not in pure water. He made experiments with barium and strontium carbonates and with barium sulphate, and found in these cases that the Brownian movement persists longer, and occurs with larger crystals (up to $0{\cdot}5\mu$—1μ) in a dilute solution of a colloid than in pure water. The reasons for the increased Brownian movement in colloidal solutions are stated to be that the presence of the colloid diminishes the adsorption by the glass of the solid particles. The excessive size of the lead crystals is explained by the fact that they are extremely thin; in some cases they are stated by the author to be transparent. The influence of the colloid on the cathode in addition to a change in the nature of the deposit is always hydrogen production, whilst on the anode several actions take place, among which the author notes formation of lead peroxide, evolution of oxygen, and formation of crusts of insoluble organic lead compounds. The last action is observed in the case of lead benzoate and salicylate, but the compounds have not yet been identified. Microphotographs of the various lead and zinc deposits are appended to the paper. J. F. S.

The Coefficient of Magnetisation of Water and Oxygen. AUGUSTE PICCARD (*Arch. Sci. phys. nat.*, 1913, [iv], **35**, 458—482. Compare this vol., ii, 473).—A detailed account of work published previously (this vol., ii, 17, 100). The values given, however, are slightly different. At 20° the coefficient of magnetisation and the susceptibility of water are respectively $-0{\cdot}7193 \times 10^{-6}$ and $-0{\cdot}7180 \times 10^{-6}$, the temperature-coefficient of magnetisation being $+0{\cdot}00012$. The susceptibility shows a flat maximum between 10° and 20°. The susceptibility of oxygen at 20° and 760 mm. is $+0{\cdot}14073 \times 10^{-6}$; there are 7 magnetons to the atom of oxygen. T. S. P.

The Magnetism of Aluminium Bronze. ROBERT C. GRAY (*Proc. Roy. Phil. Soc., Glasgow*, 1911-12, **43**, 104—106).—The α-solid solutions of aluminium in copper become more retentive on quenching from 900°, whilst alloys containing the compound Cu_3Al become less retentive under the same treatment, in this respect resembling the Heusler alloys. C. H. D.

Relation Between the Magnetic Field and the Passive State of Iron. III. HORACE G. BYERS and SETH C. LANGDON (*J. Amer. Chem. Soc.*, 1913, **35**, 759—767).—Byers and Darrin (A., 1910, ii, 579) and Byers and Morgan (A., 1911, ii, 1057) have shown that when iron or nickel is used as an anode in certain electrolytes, the current density required to produce passivity is increased if the apparatus is placed in a magnetic field. It is now shown that

this retardation of the establishment of passivity is due to agitation of the electrolytes caused by the magnetic field, and that the same effect can be produced by mechanical stirring or by rotation of the anode. No satisfactory explanation of this effect of stirring can be offered. E. G.

Some Physical Properties of Alloys of Iron and Copper. ALEXANDER D. ROSS (*Proc. Roy. Phil. Soc. Glasgow*, 1911–12, **43**, 62—66).—The magnetic properties of iron deteriorate with increasing copper up to 0·15%, the hysteresis loss increasing. Beyond this, the quality improves up to 0·4%, at which composition the alloy is almost equal to standard iron. Higher proportions of copper again diminish the susceptibility. The difference between the Ar_2 and Ac_2 points is greater in these alloys than in pure iron. C. H. D.

The Magneto-chemistry of Some Ferric Salts and the Theory of the Magneton. B. CABRERA and ENRIQUE MOLES (*Arch. Sci. phys. nat.*, 1913, [iv], **35**, 425—457; *Anal. Fis. Quim.*, 1912, **10**, 394).—The measurements of the coefficient of magnetisation were carried out according to the method given by Piccard (this vol., ii, 17).

The results obtained for the specific susceptibilities of solutions of ferric chloride, ferric nitrate, and sodium ferric pyrophosphate give a value for the atomic susceptibility of iron which varies with the concentration. This variation is probably due to changes which take place in the dissolved salt, as, for example, dissociation and hydrolysis, and consequently it is impossible to draw conclusions from measurements made with one concentration only, as has been done previously by some investigators.

When the number of magnetons is calculated for infinite dilution the law of whole numbers put forward by Weiss is confirmed, these numbers being either 25 or 27 for the compounds mentioned above. In the case of ferric chloride, which was the only substance which could be investigated in very concentrated solutions, the number of magnetons tends to approach the value 29 for the most concentrated solutions, which value is the same as that obtained by Feytis for sublimed ferric chloride. The curve for ferric nitrate, showing the relation between the number of magnetons and the concentration, also tends to the same value at high concentrations. The solutions of sodium ferric pyrophosphate are somewhat unstable and viscous, but the limiting value for high concentrations is apparently 27. It follows that the number of magnetons for the atom of iron is always 25, 27, or 29.

A study has also been made of the influence of the addition of the corresponding acid, or of salts with the same anion, to the above ferric salts. The results indicate that hydrion and anion exert separate influences; the hydrion tends to restore the molecule to its original condition, the number of magnetons approaching 29, whilst the anion apparently increases the susceptibility in a continuous manner. T. S. P.

Magnetic Study of the Constitution of Some Alloys of Antimony. P. LEROUX (*Compt. rend.*, 1913, **156**, 1764—1766).—The author has determined the specific coefficients of magnetisation of alloys of antimony-tin and antimony-lead, and curves are given showing the variations of these coefficients with the composition of the alloys. The results are in agreement with those obtained by Pouchine (*Rev. Metallurgie*, 1907, **4**, 933) from the measurements of the *E.M.F.* of these alloys, and point to the existence of an antimony-tin compound containing 50% antimony. There is a second angular point at 95% antimony corresponding perhaps with a limit solid solution. The alloys antimony-lead are more complicated, and the existence of a compound containing 85—86% antimony is probable. W. G.

Relationship of the Coefficient of Expansion and the Coefficient of Compressibility of Water Vapour to Pressure and Temperature. ÉMILE WERTHEIMER (*Zeitsch. physikal. Chem.*, 1913, **83**, 260—268).—A mathematical paper, in which the above-mentioned relationships are considered. It is shown that over the temperature interval 96—220° the coefficient of expansion at constant temperature increases with the pressure, and at constant pressure decreases with increasing temperature. It approaches the ideal value with increasing superheating. The maximum divergence from the ideal value, in the region considered, amounts to 30%. With regard to the coefficient of compressibility, it is shown that the divergence from the ideal value increases with increasing pressure at constant temperature, and decreases with increasing temperature at constant pressure. The maximum divergence amounts to 7% in the region considered. The equations deduced for water vapour are shown to hold generally for saturated vapours. J. F. S.

Improvement in Gas Thermo-Regulators. A. WHITAKER (*Chem. News*, 1913, **107**, 242—243).—The improvement consists in a modification of the gas inlet and the mercury outlet tubes, which ensures that the mercury seals by entering the comparatively narrow orifice of the inlet tube. The end of the inlet tube is ground internally to form a cone, the edges of which are either sharp or slightly expanded. This is brought close up to the end of the capillary outlet tube, which is countersunk by grinding, so as to present an obtuse and symmetrical aperture. With this arrangement there is no danger of external sealing. H. M. D.

Comparison of the Optical and Thermal Methods for the Determination of Melting Points. RICHARD NACKEN (*Centr. Min.*, 1913, 328—337).—The optical method used consists in the observation of a thin plate of the substance between crossed nicols. The substance is heated in a horizontal electric furnace, the ends of the inner tube of which are closed by quartz; the temperature is measured by means of a thermocouple. The melting point is taken as the temperature at which the substance loses the optical

properties of a crystal, as indicated by examination between the nicols.

Experiments with anorthite, albite, adular, and sanidine showed that the optical and thermal methods gave results which agreed satisfactorily. Former differences which have been found are considered to be due to errors inherent in the optical methods used; for example, the disappearance of the sharp edges of a crystal is a very unsatisfactory sign of melting. T. S. P.

Behaviour of Solids Under Unevenly Distributed Pressure. HENDRIK E. BOEKE (*Centr. Min.*, 1913, 321—324).—Johnston's theory (A., 1912, ii, 129; this vol., ii, 290) is discussed with a view to inciting further experimental work on the subject. T. S. P.

Matter in the Superfused State and the Discontinuity in Some of its Physical Properties in the Neighbourhood of the Melting Point. RAFFAELE NASINI and U. BRESCIANI (*Mem., R. Accad. Lincei.*, 1913, [v], 9, 341—401).—The authors have studied the rate of cooling of a considerable number of superfused substances, and from the results they have constructed not only the ordinary curves in which the abscissæ are times and the ordinates temperatures, but also differential curves, in which the abscissæ are temperatures and the ordinates are the differences between the times taken for the mercury to fall 0·1° at these temperatures (respectively) and the time it takes to fall 0·1° at the beginning of the cooling. The latter curves show a discontinuity, corresponding with a diminution in the rate of cooling, in the neighbourhood of the melting point of the substance. This phenomenon the authors propose to name the "Moreschini effect" (compare Moreschini, A., 1900, ii, 465). The effect is pronounced only in some cases, but slight anomaly is almost always to be observed. In the case of the substances which exhibit the phenomenon best, the contraction in volume during the cooling was determined, and the changes in volume were measured pyknometrically, but no corresponding peculiarity was observable with certainty. It was found, however, that these substances show a maximum specific heat at the corresponding temperature, and they also show, to a greater or lesser degree, peculiarities in the value of the surface tension about the melting point.

The experimental results are given in a large number of tables and curves. Among the substances showing the effect most are thymol, anethole, acetic acid, and palmitic acid. The observations of the rate of cooling were carried out with the aid of an apparatus similar to that of Beckmann for measuring depression of the melting point, but it was provided with a mechanical stirrer, and with an arrangement to ensure a dry atmosphere in contact with the superfused substance. The rate of cooling was measured with the aid of a stop-watch for each alternate interval of 0·1°. The specific heats were determined by means of Pfaundler's apparatus, and the surface tension with that of Ramsay and Shields.

R. V. S.

Calculation of Latent Heats of Vaporisation. L. GAY (*Compt. rend.*, 1913, **156**, 1464—1466).—The author modifies Clapeyron's formula $(v_1 - v_2)dP = ELdT/T$, where v_1 and v_2 are the molecular volumes of the vapour and liquid respectively, to $(Pv_1/RT - Pv_2/RT)d\log P = ELdT/RT^2$, and determines the values of $(Pv_1/RT - Pv_2/RT)$ in terms of the reduced pressure P/π according to Amagat (this vol., ii, 188). This he has done in the case of fluorobenzene, *iso*pentane, stannic chloride, and methyl alcohol, using the physical constants given by different workers.
W. G.

The Temperature of Sublimation. JOHN JOLY (*Phil. Mag.*, 1913, [vi], **25**, 856—869; *Chem. News*, 1913, **107**, 241—242).—The author has determined the temperatures at which sublimation occurs when various finely powdered minerals containing arsenic, antimony, and tellurium are heated in contact with the air. From the results obtained with the minerals containing arsenic, it would appear that the sublimation of the arsenic is definitely related to the structure, the various minerals falling into groups which are characterised by very different sublimation temperatures. This behaviour is also shown by the tellurides, whereas the antimony-containing minerals of the type $n\mathrm{RS},m\mathrm{Sb_2S_3}$ are found to sublime over a range of temperature which is but little influenced by R, n or m.
H. M. D.

Trouton's Ratio. ROBERT DE FORCRAND (*Compt. rend.*, 1913, **156**, 1439—1443).—A theoretical paper in which the author advocates a further modification of Nernst's revision of Trouton's law, in order to account for the values found for substances, such as zinc, lead, copper, silver, boiling at above 1000° absolute. The new equation given is:

$$L/T = 10{\cdot}1 \log T - 1{\cdot}5 - 0{\cdot}009T + 0{\cdot}0000026T^2.$$
W.G.

Trouton's Ratio and the Molecular Heat of Vaporisation of Pure Substances Boiling at High Temperatures. ROBERT DE FORCRAND (*Compt. rend.*, 1913, **156**, 1648—1651).—A theoretical paper, in which the author gives further evidence in support of his equation modifying Trouton's law (compare preceding abstract).
W. G.

New Formulæ for Representing the Vapour Pressure of Water Vapour. II. P. H. HOFBAUER (*Zeitsch. physikal. Chem.*, 1913, **83**, 336—338. Compare A., 1912, ii, 735).—A mathematical paper, in which additions are made to the formulæ already quoted (*loc. cit.*), and instances quoted to confirm the formulæ.
J. F. S.

A Law of Tonometry and its Consequences Relative to the Ionic Theory. EUGENE FOUARD (*Compt. rend.*, 1913, **156**, 1761—1763).—A theoretical paper, in which the author deduces that for each solvent at a temperature T, between 0° and 25°, the molecular diminution of the vapour tensions of its solutions tends,

as the dilution increases indefinitely, towards a limit value, represented by the physical molecular weight, M_T, of the liquid solvent. Further, that the degree of electrolytic dissociation of a normal solution of a substance, such as potassium chloride, when determined by the tonometric method of Raoult-Arrhenius, varies with the temperature in an absolutely discordant manner, not shown by electrical conductivity measurements. W. G.

The Law of Volatility in Chemical Reactions. CAMILLE MATIGNON (*Compt. rend.*, 1913, **156**, 1536—1538).—Berthollet's law with regard to the reaction of non-volatile substances (compare *La Statique Chimique*) is capable of generalisation. All systems of non-volatile solid or liquid substances capable of giving rise, by a new grouping of the atoms, to a system containing volatile substances must enter into reaction at a suitable temperature. This has recently found application in the reduction of magnesium oxide by aluminium (compare this vol., ii, 505), and the reduction of barium oxide by silicon (compare this vol., ii, 504). It also explains the reducing action of carbon. The law can be further extended to systems containing volatile substances. A reaction which contains volatile substances in its initial and final systems is facilitated when the volatile molecules are more numerous in the final than in the initial system. W. G.

New Thermodynamical Results from the Theory of Quanta. MICHAEL PÓLÁNYI (*Zeitsch. physikal. Chem.*, 1913, **83**, 339—369).—A theoretical paper, in which the entropy relationships for various systems are mathematically considered. J. F. S.

Precision Viscometer for the Measurement of Relative Viscosity, and the Relative Viscosities of Water at 0°, 18°, 25°, and 50°. EDWARD W. WASHBURN and GUY Y. WILLIAMS (*J. Amer. Chem. Soc.*, 1913, **35**, 737—749).—With a view to undertake a comprehensive study of the relation between the conductivities of ions and the viscosity of the medium in aqueous solutions, an effort has been made to improve the Ostwald type of viscometer, so as to render it more convenient and more accurate.

An improved apparatus is described which is made of fused quartz, and possesses the following advantages. Its water-constant at a given temperature is not changed by cleaning it with hot liquids or subjecting it to large variations of temperature. The water-constant at 25° is 580 seconds, and is reproducible to about 0·03 second under given conditions, so that a precision of at least 0·01% is attainable in measurements of relative viscosity. For effective pressures between 130 and 300 mm. of water, the deviation from the requirements of Poiseuille's law is less than 0·03%. An error of 1 c.c. in the liquid introduced into the viscometer does not change the time of flow by as much as 0·05%. A single instrument can be used for a large range of temperature, as its dimensions do not change with the temperature.

The relative viscosity of water at different temperatures was found to be:

$\eta_{18°}/\eta_{0°} = 0{\cdot}58978$; $\eta_{25°}/\eta_{0°} = 0{\cdot}49741$; $\eta_{50°}/\eta_{0°} = 0{\cdot}30640$; $\eta_{50°}/\eta_{25°} = 0{\cdot}61599$.

The relative viscosity of *N*-potassium chloride at 18° is 0·98130.

E. G.

Importance of Viscosity for the Study of the Colloidal State. WOLFGANG OSTWALD (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 213—222).—A general theoretical paper, giving a résumé of the factors which govern the viscosity of colloids and the various facts which may be deduced from viscosimetric measurements. It is shown that in a colloidal system the viscosity is affected by ten variables, namely, concentration, temperature, dispersity, solvate formation, electric charge, previous thermal treatment, previous mechanical treatment, inoculation with small quantities of more viscous colloids, time (that is, age of the colloids), and additions of both electrolytes and non-electrolytes. The measurement of viscosity is shown also to be a good method of determining the points at which "changes of state" occur; among the changes of state for which it has been used the author mentions, changes in dispersity, solvate formation, peptisation, coagulation, gelatinisation, and imbibition. Each of these changes is discussed for special cases. It is also pointed out that viscosity measurements would afford valuable evidence in many industrial problems, for example, in the case of caoutchouc sols. In this case the "nerve" of caoutchouc corresponds with a higher viscosity of its solutions; "killed" or depolymerised caoutchouc, which has been rendered less elastic, gives lower viscosities at the same concentrations than caoutchouc which has not been treated mechanically. J. F. S.

The Viscosity and Electrochemistry of Protein Solutions. WOLFGANG PAULI (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 222—230). —The paper deals with the relationships between the viscosity and the electrochemical properties of colloids. For this consideration it is divided into two parts: 1, which deals with the relationships at the isoelectric point, that is, the point at which the acid and basic ionisations of the proteins are identical, and 2, the relationship after the isoelectric point has been passed. It is shown that the isoelectric point is independent of the protein concentration, and that the swelling of glutin is a minimum at this point. Further, the coagulation of albumin solutions by alcohol has its maximum at the isoelectric point. The isoelectric point corresponds exactly with a maximum of dehydration and a minimum of viscosity for albumin solutions. As soon as the isoelectric point is passed by driving back the concentration of hydrogen ions by means of acid, it is shown that the hydrogen ions become fixed up to a certain concentration of acid, but that the chlorine ions only become fixed beyond this concentration. The viscosity of acid albumin is shown to rise to a maximum with increase of acid, which then falls off as the acid becomes excessive. In connexion with these relationships, the work of a large number of investigators is examined. It is shown finally that by viscosity measurements it has been pos-

sible to indicate the formation of an albumin caffeine hydrochloride complex, which is characterised by a greater hydration than the albumin chloride itself. The effect observed is a rapid increase of the viscosity with the addition of caffeine up to a maximum, after which the viscosity decreases. This result has only been observed for albumin, and is not given by gluten or fibrin or the direct decomposition products of albumin. J. F. S.

General Theory of Viscosity of Two-Phase Systems. EMIL HATSCHEK (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 238—248).—The general theory of two-phase colloidal systems put forward by the author (A., 1911, ii, 19, 98) is discussed, and the formula obtained by him, $\eta' = \eta(1 + 4{\cdot}5f)$, compared with the formula of Einstein (*Ann. Physik*, 1906, [iv], **19**, 289), $\eta' + \eta(1 + f)$. These formulæ are examined in connexion with viscosity measurements made by various observers on suspensoids. The question of the effective volume of the disperse phase is considered, and it is shown that it is the sum of two factors, the volume of the actual disperse phase (probably but not necessarily proportional to the weight), and the volume of the adsorption envelope. The authors, using figures obtained by Odén for sulphur sols (A., 1912, ii, 1143), calculate that the thickness of this layer is $0{\cdot}87\mu\mu$. It is shown that with two-phase colloids it is advantageous to study the viscosity changes by a method which allows of a varying "rate of shear." This is not possible with the Ostwald viscometer, where the rate of shear is determined by the diameter of the capillary and the density of the liquid, but is possible by means of Couette's apparatus, which is described. A few preliminary measurements are given for a paraffin soap solution emulsion. J .F. S.

Viscosities and Conductivities of Aqueous Solutions of Raffinose. EDWARD W. WASHBURN and GUY Y. WILLIAMS (*J. Amer. Chem. Soc.*, 1913, **35**, 750—754).—In continuation of the investigation of the relation between ion conductivities and the viscosity of the medium (A., 1911, ii, 862), raffinose has been selected as the first non-electrolyte to be employed for changing the viscosity.

An account is given of a method of preparing pure raffinose, and the conductivities at 0° and 25°, and the densities and relative viscosities at 0°, 25°, and 50°, of its aqueous solutions of various concentrations are recorded. E. G.

Experiments on Wetting, and on the Adhesion of Solid Particles at the Surface of Two Liquids. F. B. HOFMANN (*Zeitsch. physikal. Chem.*, 1913, **83**, 385—423. Compare Stark, *Ann. Phys. Chem.*, 1898, [iii], **65**, 287; Pickering, T., 1907, **91**, 2001).—Experiments are described showing that when a fine powder is shaken with two liquids which are not completely miscible, the powder is entirely retained at the surface of contact of the two liquids. This action is shown to be due to the partial wetting of the particles by both liquids. The wetting of glass surfaces was studied in the case of a number of liquids and mixtures of liquids. It is shown in this case that the partial wetting of a glass

surface by a mixture of two liquids runs parallel with the adhesion of small glass particles at the surface of contact of the same two liquids. Experiments were then made with thin plate crystals and powders of a number of substances, and it is shown that in those cases where the thin crystal adheres strongly to the surface the powder also, on shaking with the liquid, will adhere to the surface; in those cases where the thin crystals adhere only slightly, a part only of the powder adheres to the surface; and finally, where the thin crystals do not adhere, neither does the powder. A table is given of the action of water and one of the following liquids on a number of inorganic substances: ether, chloroform, *iso*butyl alcohol, benzene, xylene, petroleum, *iso*amyl alcohol, and paraffin oil. J. F. S.

Determination of the Surface Tension of Molten Lead in Contact with Molten Mixtures of Lead and Potassium Chlorides. (Theory of Metal Fog Formation.) RICHARD LORENZ and ALFRED LIEBMANN (*Zeitsch. physikal. Chem.*, 1913, **83**, 459—480).—The authors have measured the surface tension of molten lead in contact with molten lead chloride, and mixtures of lead chloride and potassium chloride by the rise in capillary tubes. The capillary apparatus was of Jena glass and of the usual form; a quantity of pure lead was placed in the wider tube, and covered with a layer of a molecular mixture of potassium chloride and lead chloride to preserve it from oxidation. The apparatus was then sunk in a bath of molten lead chloride, so that the capillary tube was completely immersed, whilst the wider tube was open to the air. The heating was electric, and the temperature measurements were obtained by means of a platinum, platinum-rhodium thermocouple. The measurements fell into three groups: (1) the measurement of the surface tension of a molecular mixture of molten lead and potassium chlorides in contact with the air at temperatures 457—616°; (2) measurement of the surface tension of molten lead against the molecular mixture of lead chloride and potassium chloride at temperatures 605—448°; and (3) measurement of the surface tension of lead in contact with a series of potassium and lead chloride mixtures (varying from 100% $PbCl_2$ to 78·39% $PbCl_2$) at temperatures 555°, 508°, and 600°. The necessary density values were taken from the measurements of Lorenz, Frei, and Jabs (A., 1908, ii, 156). From the results it is shown that the theory of Lorenz and Kaufler (A., 1908, ii, 1023), which states that the surface tension of molten liquids, in contact with molten salts, changes, is in accord with facts. The surface tension of lead in contact with $PbCl_2$ increases at 600° by the addition of 16% KCl from 170·1 dyne/cm. to 203·4 dynes/cm. Temperature plays a considerable part in the increase; thus, at 600°, the increase in the case quoted is 12—14%, whilst at 550° it is 20%, and at 510°, 30%. The disappearance of metal fog by the addition of potassium chloride is similar to the disappearance of precipitates in colloidal solutions, although of a fundamentally different nature. It is shown that the fog formation of metal decreases with the increasing

surface tension as occasioned by the molten electrolyte in contact with the metal. This is explained on the assumption that the fog formation is due in some way to the solution pressure, inner pressure, and vapour pressure of the metal, and that the forces at work on the surface, that is, those which condition the surface tension, act against the internal forces. J. F. S.

The Nature and Cause of Sorption from Aqueous Solutions. GEORG VON GEORGIEVICS (*Zeitsch. physikal. Chem.*, 1913, **83**, 269—279).—A theoretical paper, in which the results of previous papers (A., 1911, i, 537; ii, 1070; 1912, ii, 140, 236, and the following abstracts) are considered. It is shown that the x value of the expression for the partition relationships $\sqrt[x]{c_1}/c_2 = K$ runs parallel with the strength of the acid used, and consequently the adsorption is determined by the strength of the acid. Of two acids of equal strength, the one with the greater viscosity is more strongly absorbed by wool. Hence a large viscosity brings about a greater solubility of the acid in the absorbent; so that it follows that the sorption (adsorption and solution) of acids in wool is determined by the strength of the acid and the viscosity. The usual method of considering adsorption as a concentration of the adsorbed material on the surface of the absorbent is shown to be unsatisfactory, and it is shown that experiment indicates that a concentration of the adsorbed substance takes place on all the molecules of the adsorbent, as far as this is not rendered impossible by any hindrance of the diffusion. A hypothesis is put forward to show how the adsorption can pass over to chemical reaction between the adsorbed material and the adsorbent. J. F. S.

Adsorption in Solutions. IV. The Significance of the x in the Distribution Formula and the Causes of Sorption. GEORG VON GEORGIEVICS (*Monatsh.*, 1913, **34**, 733—749. Compare A., 1912, ii, 140, 236).—The interpretation of the meaning of x in the ordinary distribution formula, $\sqrt[x]{c_1}/c_2 = K$, has hitherto been a matter of difficulty. When the range of concentrations varies greatly it is often necessary to have different values of x for different ranges of concentration in order to obtain a constant value of K. In order to interpret the meaning of x, the author proceeds as follows. In any given series of concentrations, the value of x is calculated for each consecutive pair of concentrations; the mean of the various values of x is then taken for the series. It is then found that if a number of acids is arranged in the order of their strengths, then the mean values of x, calculated from experiments on the distribution of these acids between water and wool, also follow the same order. If the value of x were 1, no adsorption would take place, the acid merely dissolving in the adsorbent (wool); when, however, a hindrance to sorption (adsorption + solution) takes place, adsorption occurs to a greater or lesser extent, and the value of x increases. It follows that the stronger an acid is, the more it is adsorbed by wool, since the value of x increases with the strength of the acid.

Comparison of the values of x and the viscosity of the aqueous solutions of the various acids shows that within one and the same group of acids, that is, mineral acids, or fatty acids, etc., the adsorption is all the greater the smaller the viscosity. Acids, therefore, which have the smallest value of x are dissolved by the wool in the greatest proportion during the process of sorption.

Considerations such as the above lead the author to the conclusion that the strength of acids and the viscosity of their solutions are the two chief factors which regulate the whole process of sorption.

Apparently there is no relation between adsorption and surface tension. If, however, the acids are arranged in the order of descending values of x, that is, in the order of decreasing adsorption, the same order is obtained as for their toxic action towards bacilli; the reverse order is obtained for the hæmolytic action of these acids.

The distribution coefficient of the following acids between water and wool was measured: formic, malonic, and adipic acids.

T. S. P.

Adsorption in Solutions. V. Solution, Adsorption, Chemical Combination, Adhesion. GEORG VON GEORGIEVICS (*Monatsh.*, 1913, **34**, 751—757).—Arguments are adduced against the assumption that the process of sorption is essentially chemical. Various considerations, which depend to a great etxent on those given in the previous abstract, lead the author to account for the process of sorption between wool and acid solutions as follows: The acid dissolved in the water diffuses into the wool fibre and distributes itself uniformly. As further diffusion takes place and the concentration of the sorbed substance in the adsorbent becomes greater, the chemical attraction of the molecules of the adsorbent comes into play, and adsorption, which consists in the gradually increasing accumulation of the sorbed substance round the individual molecules of the adsorbent, occurs. As the adsorption increases, the attraction of the molecules of the adsorbent for those in the sorption solution decreases, and consequently a retardation of the sorption occurs, which retardation is a characteristic sign of adsorption.

T. S. P.

The Determination of the Chlorine and Sulphur Trioxide Pressures in the Case of Chlorides and Sulphates. LOTHAR WÖHLER and M. GRÜNZWEIG (*Ber.* 1913, **43**, 1587—1590).—The authors describe an improvement of the apparatus previously used by Wöhler and Plüddemann (A., 1908, ii, 290) for the determination of the sulphur trioxide tension of sulphates, whereby the vapour tension of chlorides can also be determined.

With the new apparatus, the measurements on ferric sulphate gave results in agreement with those obtained by Bodenstein and Suzuki (A., 1910, ii, 1042). The results obtained previously for cerous sulphate were confirmed, at all events for the higher temperatures, and a fresh calculation of the sulphur trioxide partial pressures given.

T. S. P.

Studies on Osmosis. C. FERDINAND NELSON (*J. Amer. Chem. Soc.*, 1913, **35**, 658—671).—Kahlenberg (A., 1906, ii, 337) and Wilcox (A., 1910, ii, 693) have determined the osmotic pressures of solutions of certain substances in pyridine when separated from pure pyridine by a caoutchouc membrane. This work has now been extended.

It has been found that pyridine solutions of metallic abietates readily pass through the membrane without producing any considerable rise of liquid in the osmometer tube. The oleates, palmitates, and stearates, camphor, phenol, thymol, and benzoic acid all behave similarly. All these compounds are easily soluble in hydrocarbons, such as benzene and petroleum, and are therefore also soluble in caoutchouc and thus pass through the membrane. On the other hand, certain compounds also soluble in pyridine, such as silver thiocyanate, copper chloride, lead nitrate, copper formate, dextrose, lævulose, "saccharin," and hippuric acid, do not pass through the membrane so easily nor in such large quantities, and these are insoluble, or nearly so, in hydrocarbons. The effect of adding water in various amounts to the inner and outer liquids of an osmotic cell, either separately or simultaneously, has been determined for several compounds. Of the compounds examined with the object of determining their suitability for use in direct osmotic pressure measurements, lead nitrate and dextrose have been found to approximate most closely to sucrose and silver nitrate with regard to semi-permeability towards a caoutchouc membrane when pyridine is used as solvent.

The results support Kahlenberg's chemical theory of osmosis, according to which the phenomenon is selective and depends on the specific natures of the solvent, solute, and membrane, instead of being due to the purely physical factors of porosity, capillarity, and surface tension. E. G.

Diffusion in Solids. CECIL H. DESCH (*Rep. Brit. Assoc.*, 1912, 348—372).—A summary of knowledge on this subject, arranged under the following heads: diffusion in glasses; devitrification; electrolysis of glass and porcelain; diffusion of gases through metals; passage of liquids through metals; solid diffusion in metals; cementation and decarburisation of iron; segregation and crystallisation; influence of the amorphous modification in metals; electrolysis of crystalline solids; diffusion in minerals, artificial crystals and colloidal gels, Liesegang's phenomenon. C. H. D.

Diffusion of an Electrolyte in Gelatin. L. WILLIAM ÖHOLM (*Chem. Zentr.*, 1913, i, 1648; from *Med. Vetenskapsakad. Nobelinstitut*, 1913, **2**, 30, pp. 8).—The diffusion-coefficient of potassium chloride in gelatin solutions of different concentrations has been measured in a vessel composed of four superposed brass cylinders, the solution being placed in the bottom section and the solvent in the others, such a system being especially adapted to viscous solutions. The coefficient decreases with increasing concentration exactly like the conductivity, so that it can be calculated from measurements of

the latter. Gelatin therefore influences the ionic velocity, but not the degree of dissociation. J. C. W.

The Dependence of Diffusion on the Viscosity of the Solvent. L. WILLIAM ÖHOLM (*Chem. Zentr.*, 1913, i, 1648—1649; from *Med. Vetenskapsakad. Nobelinstitut.*, 1913, **2**, 26, pp. 21).—The diffusion-coefficients of glycerol and bromoform in ether, benzene, acetone, methyl, ethyl, propyl and amyl alcohols, and aqueous alcohol have been obtained, the concentrations being measured refractometrically. Except in the case of glycerol in amyl alcohol, the solutions are more viscous than the solvents. The percentage increment of the viscosity on the addition of the same quantity of glycerol is irregular for different solvents, but in the case of bromoform the increase is greater the smaller the initial viscosity. The diffusibility of glycerol decreases with increasing viscosity and concentration; $k\eta$ is about 0·46 in the case of methyl, ethyl and propyl alcohols, but varies widely between 50% alcohol and amyl alcohol. Glycerol is much less complex in alcoholic than in aqueous solution. The diffusibility of bromoform varies less with viscosity, but the values of $k\eta$ are irregular, decreasing with increasing molecular weight of the solvent. The product $k_x\sqrt{M}$ is greater for bromoform than for glycerol. J. C. W.

Free Diffusion of Non-Electrolytes. II. Diffusion of Some Organic Substances in Water. L. WILLIAM ÖHOLM (*Chem. Zentr.*, 1913, i, 1649—1650; from *Med. Vetenskapsakad. Nobelinstitut.*, 1912, **2**, 23, pp. 52. Compare A., 1910, ii, 273).—The diffusion-coefficients of a number of inactive substances have been measured, the concentrations being arrived at by refractometric means. The values rise with increasing dilution, but for different substances the variation is widely different, and the coefficients for solutions of equal concentration are very far apart. The temperature-coefficients of diffusion are about the same as in the former paper. The variations of the diffusion-coefficients at 20° for the extreme limits of concentration employed are as follows: glycerol, 0·645 to 0·717 for $2N$ to $0·125N$; acetamide, 0·685 to 0·900 for $10N$ to $0·25N$; carbamide, 0·986 to 1·022 for $2N$ to $0·25N$; mannitol, 0·459 to 0·500 for $0·5N$ to $0·125N$; quinol, 0·640 to 0·665 for $0·7N$ to $0·25N$; resorcinol, 0·524 to 0·654 for $2N$ to $0·125N$; alloxan, 0·531 to 0·570 for $1N$ to $0·125N$; pentaerythritol, 0·573 to 0·589 for $0·4N$ to $0·2N$; saligenin, 0·521 to 0·619 for $1N$ to $0·25N$; ecgonine, 0·528 to 0·604 for $1N$ to $0·1N$; dicyanodiamide, 0·860 to 0·895 for $0·4N$ to $0·2N$; salicin, 0·402 to 0·422 for $0·12N$ to $0·06N$; caffeine, 0·488 for $0·05N$; inulin, 0·132 to 0·138 for $0·01N$ to $0·005N$; gum arabic, 0·193 to 0·203 for 4·9% to 2·4%; starch paste, 0·207 to 0·214 for 8% to 5%, and starch powder, 0·058 to 0·0676 for 4·98% to 1·23%.

The product $k_\infty\sqrt{M}$ is again about 7. From this expression the molecular weight of gum arabic must be about 1050, of starch paste, 970, and starch powder, 10,000. The diameter of the molecule has also been calculated, and is of the order 10^{-8} cm. for ordinary compounds, and 10^{-7} cm. for colloidal substances. J. C. W.

Diffusion of Some Organic Substances in Ethyl Alcohol. L. WILLIAM ÖHOLM (*Chem. Zentr.*, 1913, i, 1650—1651; from *Med. Vetenskapsakad. Nobelinstitut.*, 1912, **2**, 24, pp. 34. Compare preceding abstract).—The diffusion of a large number of organic compounds in ethyl alcohol has been studied with analogous results. The diffusibility falls from 1·08 and 0·98 for chloroform and acetone to 0·60 for camphor, 0·25 for aconitine, and 0·16 for carminic acid, and rises on dilution as in aqueous solution. The product $k_{\infty}\sqrt{M}$ is about 4·4 for acetamide, glycerol, resorcinol, and quinol, but for saligenin, acetin, and eosin-sodium it is 5·7. Assuming that the diffusion-coefficient for the same substance and same concentration is proportional to the viscosity of the solvent, the constant, calculated from the value 7 for aqueous solutions, should be 5·24. This assumption is not always justified, however (see above), and some of the values obtained in the present instance, when recalculated for aqueous solutions, would become as much as 15.

J. C. W.

Solubility. II. J. VARGAS EYRE (*Rep. Brit. Assoc.*, 1912, 795—871).—The report deals with work on solubility published between 1895 and 1911, under the following headings: I, Introduction; II, Methods of Determination; III, Influence of Nature of Solvent; IV, Influence of Nature of Solute; V, Solubility in relation to (*a*) temperature, (*b*) pressure, (*c*) influence of other substances; VI, Mutual solubility and distribution coefficients; VII, Theoretical considerations; VIII, Chronological bibliography; IX, Authors' index.

C. H. D.

Dissociation Constant of Weak Acids and Bases from Solubility Data. NILRATAN DHAR (*J. Amer. Chem. Soc.*, 1913, **35**, 800—802).—The solubility of an acid is increased in presence of the salt of a weak base and a strong acid, benzoic acid, for example, being more soluble in a solution of sodium acetate than in the same volume of water. It is shown that, assuming the dissociation constant of benzoic acid, the dissociation constant of acetic acid is given by the formula $(6 \times 10^{-5} \times a)(c-6+a)/(b-a)^2$, where a is the solubility of benzoic acid in water, and b its solubility in a solution of sodium acetate of concentration c. Philip (T., 1905, **87**, 987) and Philip and Garner (T., 1909, **95**, 1466) have determined the solubility of cinnamic, benzoic, salicylic, and nitrobenzoic acids in solutions of sodium acetate, sodium butyrate, sodium formate, sodium monochloroacetate, and sodium salicylate. Calculations have been made from these data, and fairly concordant results have been obtained with cinnamic and benzoic acids. Similar results are obtainable from the potassium salts. In the case of salicylic and nitrobenzoic acids, difficulty arises owing to ionisation, as these are fairly strong acids.

E. G.

Dissociation Constants of Monobasic Acids. NILRATAN DHAR and ASWINI KUMAR DATTA (*Zeitsch. Elektrochem.*, 1913, **19**, 407—409).—Carbon dioxide is more soluble in solutions of sodium

salts of weak acids than it is in water. This fact is made the basis of a method of determining ionisation constants of weak acids. A small Erlenmeyer flask, containing about 100 c.c. of an aqueous solution of the sodium salt of a weak acid, is connected with two U-tubes containing calcium chloride; these are connected with a second flask containing 100 c.c. of distilled water, and this to two U-tubes. Each flask with its contents and accompanying U-tubes is weighed; carbon dioxide is then slowly bubbled through for about an hour, and the two sets are re-weighed, and from the weighings the increased solubility of carbon dioxide in the salt solution calculated. Using the dissociation constant of carbonic acid determined by Walker (A., 1900, ii, 268), the authors have determined the dissociation constants of the following acids at 25°: hippuric acid, $2{\cdot}5 \times 10^{-4}$; nitrous acid, $5{\cdot}6 \times 10^{-4}$; cacodylic acid, $6{\cdot}27 \times 10^{-7}$; formic acid, $2{\cdot}4 \times 10^{-4}$; butyric acid, $1{\cdot}55 \times 10^{-5}$; propionic acid, $1{\cdot}33 \times 10^{-5}$; acetic acid, $1{\cdot}95 \times 10^{-5}$; and benzoic acid, $6{\cdot}07 \times 10^{-5}$. The method obviously makes it possible to determine the dissociation constants of acids which cannot easily be obtained pure, for example, nitrous acid (see also Sand, A., 1904, ii, 612; Bauer, A., 1906, ii, 649). J. F. S.

Degree of Dissociation of a Dissolved Substance in Saturated Solutions of Different Solvents. PAUL WALDEN (*Bull. Acad. Sci. St. Petersbourg*, 1913, 427—448. Compare A., 1906, ii, 527).—The author has determined the solubility of tetramethylammonium iodide in the following solvents at 25°: water, 50% water-ethyl alcohol mixture, methyl alcohol, methyl thiocyanate, acetonitrile, cyanoacetic ester, propionitrile, ethyl alcohol, epichlorohydrin, and acetylacetone. The solubilities in grams per 100 grams of solvent are: 5·268, 3·107, 0·337, 0·229, 0·183, 0·0897, 0·0578, 0·0478, 0·0367, and 0·0275, taking the solvents in the order given above. It is shown that the solubility is parallel with the dielectric constants of the liquids. The electroconductivity of the solutions over a large range of concentration is measured, and the value of λ_∞ obtained by extrapolation. It is shown that the degree of ionisation of tetramethylammonium iodide in saturated solutions as obtained from $\alpha = \lambda_v/\lambda_\infty$ is the same for all the solvents, and has the value $\alpha = 0{\cdot}666$. The value of α for saturated solutions is compared with the corresponding values for tetraethylammonium iodide and tetrapropylammonium iodide, and it is found that the value decreases with increasing molecular weight, but that the product $\alpha \,.\, \Sigma n$, where Σn represents the number of atoms in the molecule, is practically constant, and equal to 12—14. The value of α for saturated solutions is shown in the case of tetrapropylammonium iodide to decrease with increasing temperature; thus, at 0°, $\alpha = 0{\cdot}305$, whilst at 25°, $\alpha = 0{\cdot}270$. The paper concludes with a series of orienting experiments on saturated solutions of potassium iodide in water, methyl alcohol, and ethyl alcohol. In this case it is also shown that α is constant and equals 0·423.

J. F. S.

Molten Salts as Solvents. III. The Degree of Dissociation of Dissolved Salts. OTTO SACKUR (*Zeitsch. physikal. Chem.*, 1913, **83**, 297—313. Compare A., 1912, ii, 233, 744, 836).—The study of solutions in fused salts is continued in the present paper. It is shown that solutions of silver chloride and cuprous chloride in molten potassium or sodium chlorides lower the freezing point normally up to concentrations of 1 gram-mol. per litre. Further concentration elements of the type Cu | CuCl(dil.) | CuCl(conc.) | Cu in molten sodium and potassium chloride were measured, and these showed strict adherence to the Nernst hypothesis. All the results showed that these solutions agree with the laws of ideal dilute solutions to within 1% for concentrations up to 1 volume normal. The dissociation of the dissolved substance is independent of the concentration, and is of the order of 10% for the cases investigated (compare Schulze, A., 1913, ii, 193). The difference in the normal potential of silver and copper has the same value in molten potassium chloride solutions at 800° as it has in aqueous solutions at the ordinary temperature. The thermoelectric power of a copper silver couple was measured, and found to be very small; it changes its sign from negative to positive at 675°. J. F. S.

The Dissimulated State in Hydrates. ROBERT DE FORCRAND (*Compt. rend.*, 1913, **156**, 1506—1509).—A theoretical discussion of the work of Feytis (compare A., 1911, ii, 1058; this vol., ii, 381), Lebeau (A., 1911, ii, 403), and Chauvenet and Urbain (this vol., ii, 479) on the constitution of hydrates, and in particular of the crystalline hydrates formed by a large number of salts. The author suggests that the stability of these hydrates should be expressed in terms of their heats of solution, referred to one molecule of water. This mode of expression would give a scale varying from 0 to 50 calories, and capable of being determined to 0·1 calorie. W. G.

The Crystallisation of Metals. CECIL H. DESCH (*Proc. Roy. Phil. Soc. Glasgow*, 1911—1912, **43**, 107—120).—The structure of crystal skeletons in metals may be examined in three dimensions by the device of photographing serial sections and reconstructing the crystal as a model. The structure of alloys is largely determined by the power of crystalline orientation possessed by their respective components, and the form of a eutectic generally depends on the crystallising power of one component, the other serving as a mere filling material. This is illustrated by the alloys of copper with antimony, and of copper with phosphorus. C. H. D.

Determination of the Size of Colloidal Particles. VICTOR HENRI (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 246—250).—A general résumé of the methods which have been adopted for the determination of the dimensions of colloidal particles. The following methods are noted, and the difficulties and necessary precautions peculiar to each discussed: (1) Direct measurement by means of the ultra-microscope; (2) density determinations of the disperse

system at various heights; (3) measurement of the Brownian movement; (4) measurement of the velocity of settling; (5) diffusion measurements; (6) measurement of the light absorption; and (7) measurement of the intensity of the light dispersed by the particles. J. F. S.

The Behaviour of Gels towards Liquids and their Vapours. Ludwig K. Wolff and Ernst H. Büchner (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 1078—1085).—The authors confirm Schroeder's observation (A., 1903, ii, 721) that gelatin, swelling in water vapour, behaves differently from gelatin swelling in liquid water; in the first case, it absorbs much less water than in the second. Agar-agar behaves in a similar manner, as also does celloidin towards ethyl alcohol.

The explanations given by Bancroft (A., 1912, ii, 838) and Freundlich ("Kapillarchemie," p. 494) are discussed; that of Bancroft is considered to be untenable, whilst that of Freundlich is neither very clear nor very convincing; at the same time the authors can offer no better explanation. T. S. P.

Protein Sols of Continuously Varying Dispersity. Walter Ramsden and N. G. Chavasse (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 250—252).—The authors have obtained, by denaturating strong albumin solutions with carbamide, a series of protein colloids which vary from a clear, coagulated protein gel to a series of weak solutions of metaproteins. The differences in the various metaproteins are brought about by suitable changes in the concentration of the carbamide and the albumin. The part played by the carbamide in the denaturating is considered. The authors consider that the main difference between the coagulated protein and the metaproteins consists in a difference in size of the individual aggregates. On comparing a series of sols, the authors note that the greater the concentration of the protein during the denaturating the greater the opalescence, the viscosity, and the influence of acid or alkali on neutral sols with respect to lowering or raising the viscosity. Further, the rate of sedimentation is greater the greater the concentration of the protein during denaturating. From the observations the authors draw the conclusion that the greater the original concentration the greater the size of the individual aggregates, and from the viscosity measurements it is rendered probable that the disperse system consists of small hydrogel protein particles, which, on the addition of acid, shrink, and on the addition of alkali return to their former dimensions, without losing their individuality. J. F. S.

Precipitation of Colloids by means of Aluminium Hydroxide. John Marshall and William H. Welker (*J. Amer. Chem. Soc.*, 1913, **35**, 820—822).—Moist aluminium hydroxide, in the form of a thin jelly, has been found capable of completely removing the following substances from their colloidal solutions: copper, gold, platinum, sulphur, nickel sulphide, cobalt sulphide, cupric hydroxide (in sodium hydroxide), Prussian-blue, Congo-red,

azolitmin, litmus (neutral, red, and alkaline), starch (from starch paste and soluble starch), erythrodextrin, starch iodide, fat (from emulsion with water and with soap solution), egg-albumin, globulin (edestin in 5% sodium chloride), gelatin, casein (in half-saturated lime water), glutenin (in 0·5% sodium carbonate), nucleoprotein (in 0·5% sodium carbonate), gliadin (in 70% alcohol), ovomucoid, acid metaprotein (in 0·1% hydrochloric acid), primary proteose, secondary proteose, fat and protein from milk, and protein from blood serum. Oxyhæmoglobin is the only protein tested which was not removed by aluminium hydroxide, and this reagent is therefore well adapted for use in the preparation of oxyhæmoglobin from erythrocytes. E. G.

The Velocity of Coagulation of Aluminium Hydroxide Sols as Measured by Changes in the Viscosity. HERBERT FREUNDLICH and N. ISHIZAKA (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 230—238).—The rate of coagulation of aluminium hydroxide sols by the addition of electrolytes was followed by viscosity measurements. The results confirm those of Paine (A., 1912, ii, 337) obtained in connexion with copper sols. It is shown that the precipitation time curves exhibit a point of inflexion, and that there is little or no change in the sol immediately the electrolyte is added. The curves obtained from solutions containing different concentrations of the electrolytes are similar, from which it follows that the point of inflexion corresponds with the same value in the increase of the viscosity. Further, it is shown that one curve can be deduced from another by multiplying the time periods of the various degrees of precipitation by the factor for the rate of coagulation. This factor bears a relationship to the concentration of the electrolyte, which is expressed by the equation $V=Lc^p$, where L and p are constants, the value of p varying between 3 and 6. The form of the curves and the high numerical value of p offer a reason for (*a*) the fact that sols below a given concentration are insensitive to electrolytes, (*b*) for the frequently observed sudden coagulation. It is further shown that the rate of coagulation of aluminium hydroxide by potassium salicylate can be expressed by the equation $dx/dz=2kz(1+bx)(1-x)^2$, which, when integrated, gives $k=1/z^2(1+b)\{b/(1+b).\log(1+bx)/(1-x)+x/(1-x)\}$, in which x represents the fraction precipitated, z the time, b and k constants, b being independent of the concentration of the electrolyte, and a function of the x value for the point of inflexion, and k being a function of the concentration of the added electrolyte. The rate of coagulation constant k is related to the concentration of the electrolyte as indicated by the equation $k=\lambda c^q$. The maximum viscosity of an aluminium hydroxide sol, which is completely precipitated by the addition of an electrolyte, increases with the quantity of colloid in the sol. The maximum viscosity is dependent in a degree on the nature of the precipitating electrolyte. The viscosity is smaller with NO_3 and CNS anions than with sulphion and succinate ion. The maximal viscosity varies in concentrated sols on shaking. J. F. S.

Chemical Time Reactions with Colloids. DANIEL VORLÄNDER and REINHOLD HÄBERLE [with WALTER STRUBE] (*Ber.*, 1913, **46**, 1612—1628).—The authors have investigated the time reactions between colloidal solutions of Prussian-blue and arsenious sulphide respectively and alkalis. When sodium hydroxide is added to a dialysed solution of Prussian-blue, the colour does not disappear instantaneously but fades gradually; the rate of reaction increases with rise in temperature and with increase in concentration of the sodium hydroxide. The rate of reaction is, however, not proportional to the concentration of the hydroxide ions; it is quickest with barium hydroxide, and slowest with sodium and potassium hydroxides, strontium and calcium hydroxides falling in between. Tetramethylammonium hydroxide has a slower action than alkali hydroxide. The velocity does not depend on the solubilities of the respective ferrocyanides formed. Similar results hold when arsenious sulphide is used instead of Prussian-blue.

The observed time reactions thus depend on the nature of the cation and also on the concentration of the hydroxide ion. Before the actual chemical reaction occurs, adsorption of the hydroxides or of their ions takes place, and this adsorption may be the most rapid in the case of barium hydroxide.

It would be assumed that neutral salts would increase the particles of the hydrosol by adsorption and also surround them, and thus retard the action of alkalis; this is not the case, however, since sodium chloride greatly accelerates the action of sodium hydroxide. If the sodium chloride is added to the solution of, for example, Prussian-blue, before the sodium hydroxide, the acceleration is not so great as when it is added after the sodium hydroxide.

The action of neutral salts is very varied, not always being one of acceleration. A large number of examples are given, showing that the action is an individual one, depending on the salt.

The reaction also depends on the relative concentrations of the colloid, alkali, and neutral salt; for example, by varying the concentration of the Prussian-blue solution, a concentration can be found where the addition of barium chloride has no effect on the rate of reaction with barium hydroxide. Above this concentration the barium chloride has an accelerating, and below it a retarding, action. Also, Prussian-blue is decomposed more slowly by a large than by a small quantity of calcium hydroxide solution.

Contrary to the usual statement (compare Linder and Picton, T., 1892, **61**, 127; Billiter, A., 1905, ii, 305), the authors find that arsenious sulphide does not hydrolyse when suspended in water. They also find that very dilute solutions of arsenious acid and hydrogen sulphide can be mixed without giving a yellow solution of arsenious sulphide. If this solution contains a compound, it is very unstable, being partly hydrolysed into arsenious acid and hydrogen sulphide.

Arsenious acid gives no time reaction with alkalis. Time reactions in the formation of salts from bases and acids, including acid anhydrides and thio-acid anhydrides, are only known with

typical colloids, such as silicic acid, and the sulphides of arsenic, antimony, and tin. Carbon dioxide must also be included.

T. S. P.

The Kinetics of Ammonium Salts. EDGAR WEDEKIND (*Zeitsch. physikal. Chem.*, 1913, **83**, 370—372).—Polemical against Halban (see A., 1908, i, 723; 1909, ii, 722; 1911, i, 852; this vol., i, 354, 355).

J. F. S.

The Kinetics of Ammonium Salts. HANS VON HALBAN (*Zeitsch. physikal. Chem.*, 1913, **83**, 373).—Polemical. An answer to Wedekind and Paschke (see preceding abstract).

J. F. S.

Polymorphism. III. Equilibria in Binary Systems with a Polymorphic Substance. EFISIO MAMELI and ANNA MANNESSIER (*Chem. Zentr.*, 1913, i, 1665; from *Boll. Soc. Med. Chirurg. Pavia*, 1912, pp. 17. Compare this vol., ii, 19).—The melting-point curves of mixtures of the α- and β-forms of chloroacetic acid with naphthalene, piperonal, and acetic acid have been studied. The two modifications behave in the same way. While they act as dissolved substances, the curves fall together, and in the converse case the curves are parallel. Naphthalene shows two eutectic points, but the other substances give irregularities in the neighbourhood of the eutectic point, due to supersaturation and partial crystallisation.

J. C. W.

Equilibria in Ternary Systems. IV. and V. FRANS A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 1200—1213, 1213—1228).—Further theoretical discussion of the conditions of a liquid saturated with a solid and in equilibrium with the vapour.

T. S. P.

Equilibria in Quaternary Systems. VII. Lines of Solidification of Quaternary Mixtures from which Binary or Tertiary Mixed Crystals Separate. NICOLA PARRAVANO (*Gazzetta*, 1913, **43**, i, 454—469. Compare this vol., ii, 33, 140).—From a homogeneous, quaternary liquid, the following may separate on cooling: (1) the pure components; (2) binary mixed crystals; (3) ternary mixed crystals; (4) quaternary mixed crystals. Having already dealt with the first and last of these cases, in the present paper the author gives a mathematical analysis of the problems presented by the second and third in the case where there is complete miscibility both in the solid and in the liquid state.

R. V. S.

Equilibria in Quaternary Systems. VIII. Quaternary Systems with Binary Mixed Crystals with a Gap of Miscibility. NICOLA PARRAVANO (*Gazzetta*, 1913, **43**, i, 469—488. Compare preceding abstract).—In the present paper the author gives a mathematical discussion of two of the chief types of the systems

mentioned, namely, those with a binary diagram of Roozeboom's type V, and those with a binary diagram of Roozeboom's type IV.

R. V. S.

Velocities of Reaction and Equilibria. FRANS E. C. SCHEFFER (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 1109—1117).—The author extends the theory put forward by himself and Kohnstamm (*ibid.*, 1911, 789) with respect to the relation between the velocity of reaction and the thermodynamic potentials of the substances participating in the reaction (compare also A., 1912, ii, 328), and shows that the relation between the velocity constant and the temperature is given by the equations: $d \log k/dt = (\epsilon_t - \epsilon)RT^2$ and $\log k = (\epsilon - \epsilon_t)/RT - B$, where ϵ_t and ϵ represent the values of the energy of the intermediate transitional stage of the reaction and of the initial system respectively. The greater part of the known experimental data allows the substitution of a constant value for $\epsilon - \epsilon_t$.

T. S. P.

Limited Displacement of Monoethylamine by Ammonia Gas. FÉLIX BIDET (*Compt. rend.*, 1913, **156**, 1613—1615. Compare A., 1905, i, 686; 1912, ii, 915; this vol., ii, 197).—A study of the systems ammonia–ethylamine hydrochloride and ethylamine–ammonium chloride, the equilibrium pressures being measured at various temperatures. In both systems the equilibrium pressures rise with increase in temperature; the values in the two cases whilst in agreement at low temperatures differ considerably from 15° to 23·2°. In no case was any free ethylamine obtained at the end of the reaction. The system ammonia–ethylamine hydrochloride is similar in behaviour to the systems ammonia–amylamine hydrochloride and ammonia–ethylenediamine hydrochloride (*loc. cit.*), and fits in with the theory proposed admitting the existence of several basic salts formed by the action of the amine, displaced by the ammonia, on the initial neutral hydrochloride or on a basic hydrochloride already formed.

W. G.

Laws of "Concentrated" Solutions. V. Part I. Equilibrium between Arsenious Acid and Iodine in Aqueous Solution. Part II. General Law for Chemical Equilibrium in Solutions containing Ions. Part III. Energetics of the Reaction between Arsenious Acid and Iodine. EDWARD W. WASHBURN and EARLE K. STRACHAN (*J. Amer. Chem. Soc.*, 1913, **35**, 681—714).—The reaction between arsenious acid and iodine has been studied by Roebuck (A., 1903, ii, 14; 1906, ii, 76), but the value of the equilibrium constant calculated from his data is very uncertain owing to certain sources of error in his work. The reaction has now been re-investigated.

Determinations of the distribution ratio of iodine between carbon tetrachloride and water have given the value 85·0. Measurements of the equivalent conductivity of hydriodic acid solutions at 25° have furnished the following results, which are more than 2% higher than the values obtained by Ostwald: 0·15*N*, 389·5; 0·1*N*,

395·6; 0·08N, 398·5; 0·05N, 404·3. A study of the iodide–tri-iodide equilibrium in solution of hydriodic acid has been made by shaking solutions of iodine in hydriodic acid with carbon tetrachloride at 25° until equilibrium was established, and has yielded for the constant $[I_2][I^-]/[I_3^-]$ a value of $(1·30 \pm 0·015)10^{-3}$ for total ion concentrations between 0·05 and 0·15 equivalents per litre. In a mixture of HI and HI_3, both acids are ionised to the same extent. The value of Λ_0 for the $H_2AsO_4^-$ ion at 25° is 36 reciprocal ohms. The ionisation of arsenic acid at 25° is given by the relation $[H^+][H_2AsO_4^-]/[H_3AsO_4] = 10^{-3}(4·32 + 4C_i^{\frac{1}{2}})$, where C_i is the total ion concentration of the solution. The basic ionisation constant of arsenious acid at 25° is $[AsO^+][OH^-]/[H_3AsO_3] = 0·15 \times 10^{-14}$, in a solution with an ion concentration of 0·1 equivalent per litre. The value of the equilibrium expression

$$[H_3AsO_4][H^+]^2[I^-]^3/[H_3AsO_3][I^-]^3 = K_c$$

was determined by bringing a standard aqueous solution of arsenious acid in contact with a solution of iodine in carbon tetrachloride, and was found to be $5·5 \times 10^{-2}$.

The results show that the equilibrium $H_3AsO_3 + I_3^- + H_2O = H_3AsO_4 + 2H^+ + 3I^-$ obeys the law of mass action within the experimental error over a fairly wide range of concentrations. This is in marked contrast to the great deviation from the requirements of the law of mass action shown by the ionisation of a strong electrolyte. This behaviour is discussed from a thermodynamic point of view, and a general law is deduced for chemical equilibrium in solutions containing ions. On calculating K_c for the equilibrium between arsenious acid and iodine on the basis of this law, a result is obtained agreeing closely with the results of the experiments.

The heat of the reaction between arsenious acid and iodine is 1360 cal. The general expression for K_c is $\log_{10}K_c = -1·3495 + 0·00372t$. The free energy of the reaction is $-\Delta F^\circ = RT\log_e K_c = 5690 + 5·42T$ joules, in an aqueous solution having a constant ion concentration of 0·1 equivalent per litre. The potential of the normal arsenic electrode has been calculated, on the assumption that the potential of the normal iodine electrode is 0·256 volt when measured against the calomel electrode, and has been found to be 0·293 volt. E. G.

Stratified Disperse Systems RAPHAEL ED. LIESEGANG (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 269—273).—The author considers theoretically the reasons for the formation of layers in the structure of certain naturally occurring mineral deposits and of certain organic deposits. The theory advanced is that, given a solution which is very slowly evaporating in the absence of crystal centres, a supersaturation will take place and the solution become increasingly concentrated until the limit of the metastable region is reached; then there will be a deposit. If now the crystal centres are removed in some way, a further period of supersaturation will occur, and consequently later a second layer. It is possible this may be brought about by the supersaturation of a

second constituent of the solution crystallising over the first layer or by the adsorption of a colloidal substance, such as silica, which is known to greatly hinder further deposition of the same crystal sort. This theory is discussed in connexion with the layer formation of gallstones, urinary calculi, oolite formation, agate formation, layer crystals, and the layers of anhydrite in the Stassfurt deposits.

J. F. S.

The Combustion of Gaseous Mixtures and the Retardation of Ignition. J. TAFFANEL and LE FLOCH (*Compt. rend.*, 1913, **156**, 1544—1546).—A study of the retardation of ignition of mixtures of methane and air at various temperatures, the time of ignition being obtained by measuring the variations in pressure. Near to the ignition temperature the retardation is very marked, and reaches in some cases ten seconds. The intervals before ignition are much shorter with higher pressures. The retarding effect is just as marked when water vapour is introduced into the explosive mixture, the retardation not being due therefore to the gases being dry. A slow reaction goes on during the time before actual ignition occurs.

W. G.

Study of the Velocity of Reaction between Phenol and Formaldehyde. BENJAMIN JABLONOWER (*J. Amer. Chem. Soc.*, 1913, **35**, 811—820).—Although the reaction between phenols and formaldehyde has been made the subject of many investigations, it does not seem to have been studied from a physico-chemical standpoint.

It has been observed that when phenol is heated with formaldehyde solution in presence of a little ammonia as condensing agent, the liquid gradually increases in viscosity, and this suggested that the reaction might be studied by viscosity measurements. This was found impracticable, however, and an attempt was therefore made to investigate the velocity of the reaction by observing the density at regular intervals. The results indicate that under certain conditions the density increases regularly with the time of heating, but that in other cases the rate of increase in density decreases with the time of heating. The rate of increase of density rises with the temperature and with the quantity of ammonia present. The most regular results were obtained when the largest excess of formaldehyde was used. An equation is suggested for calculating the increase of density.

These results were obtained by comparatively crude experiments, and must not be regarded as strictly accurate.

E. G.

The Velocity of Substitutions in the Benzene Nucleus. FRANS E. C. SCHEFFER (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 1118—1128).—The theory given in the previous paper (this vol., ii, 572) is tested by application to the data obtained by Holleman and his co-workers on nitration and bromination of various aromatic compounds, and found to give satisfactory results. The conclusion is come to that the substitution entropies are identical for different positions in the nucleus.

T. S. P

Dynamic Researches Concerning the Reaction of Friedel and Crafts. SIMON C. J. OLIVIER and JAKOB BÖESEKEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 1069—1077).—The authors have measured the velocity of the action of *p*-bromobenzenesulphonyl chloride on an excess of benzene in the presence of aluminium chloride, the acid chloride being selected, since it is not decomposed by cold water, whereas it is rapidly decomposed on warming with aqueous silver nitrate, so that the unattacked sulphonyl chloride could be freed by means of cold water from aluminium chloride, and the hydrochloric acid formed and subsequently titrated with standard silver nitrate solution. Attempts to carry out experiments in carbon disulphide solution were unsuccessful, since reaction then proceeded in accordance with the scheme:

$$C_6H_4Br\cdot SO_2Cl + AlCl_3 + C_6H_6 = C_6H_4Br\cdot SO_2\cdot AlCl_2 + C_6H_5Cl + HCl.$$

The authors are led to the conclusion that the reaction takes place in two phases:

$$\text{(i)}\ C_6H_4Br\cdot SO_2Cl,AlCl_3 + C_6H_6 = C_6H_4Br\cdot SO_2Cl,AlCl_3,C_6H_6,$$

$$\text{(ii)}\ C_6H_4Br\cdot SO_2Cl,AlCl_3 + C_6H_6 = C_6H_4Br\cdot SO_2\cdot C_6H_5,AlCl_3 + HCl,$$

of which the first represents the real catalytic action resulting in the formation of a ternary compound, which proceeds slowly in regard to (ii). They consider, further, that the catalytic action of aluminium chloride is not attributable to its ability to combine with one of the molecules, since the free aluminium chloride is much more active than the combined portion, but is based on an influence, termed dislocation, which makes itself felt before the real compound has been formed. In harmony therewith it appeared that there was measured an additive action of the acid chloride with benzene, the first rendered active only so far as it is united with aluminium chloride, the second rendered active by the total aluminium chloride present.

Similar experiments have been made with toluene, chlorobenzene, bromobenzene, and nitrobenzene. H. W.

The Preservation of Hydrogen Peroxide. JAMES H. WALTON, jun., and ROY C. JUDD (*Zeitsch. physikal. Chem.*, 1913, **83**, 315—335). —The paper deals with the velocity of decomposition of 30% hydrogen peroxide at 80°. It is shown that the gasometric method of determining the rate of decomposition of hydrogen peroxide at this temperature leads to results which are inconcordant and not reproducible. It is surmised that the shaking of the solution introduces a factor into the decomposition of hydrogen peroxide which cannot be taken into reckoning. It is shown that the nature of the vessel in which the hydrogen peroxide is placed has a decided influence on the rate of decomposition, not on account of the nature of the surface of the glass, but rather on account of something dissolved out of the glass. Jena flasks which have been boiled with concentrated hydrochloric acid and then steamed for weeks give a minimum rate of decomposition. Such flasks allow of the determination of the velocity constant for a unimolecular reaction being obtained, and the same results can be

obtained when different flasks are employed. The rate of decomposition is much smaller in quartz flasks than in Jena glass flasks. Conductivity water which has been preserved in the steamed Jena glass flasks dissolves sufficient from the glass in a few hours to bring about an increased velocity of decomposition of hydrogen peroxide. Solutions of sodium silicate, sodium carbonate, and sodium hydroxide act catalytically on hydrogen peroxide, whereas calcium hydroxide does not affect the rate of decomposition. A solution of powdered glass decomposes hydrogen peroxide very readily; this is probably due to the presence of a metallic oxide dissolved out of the glass. Acetanilide acts towards hydrogen peroxide as a negative catalyst; it preserves hydrogen peroxide solutions even when they contain positive catalysts if it is present to the extent of 0·00148 mol. per litre, and in this respect it is superior to sulphuric acid. Concentrated solutions of sodium chloride preserve hydrogen peroxide, but when a positive catalyst, such as sodium hydroxide, is present, it has little action. Sulphuric acid is the most effective preservative for hydrogen peroxide; even when it is present to the extent of only 0·00066 gram per litre, it retards the decomposition in a marked degree. It retards the reaction more the more concentrated it is, but there is apparently no simple relationship between the amount of retardation and the concentration of the acid. J. F. S.

The Sensitiveness of Some Chemical Reactions. MARJAN GÓRSKI (*Zeitsch. anorg. Chem.*, 1913, **81**, 315—346. Compare Böttger, A., 1910, ii, 195).—The atomic sensitiveness is defined as the largest volume in litres in which at least one gram-atom or gram-molecule must be dissolved, in order that the reaction may be just visible. A beam of light from an arc is used as a means of detecting turbidity, and water repeatedly filtered through toughened paper is used.

The sensitiveness is found to increase with the concentration of the reagent used, and the precipitate in certain cases, such as that of barium sulphate, becomes more visible with time. The sensitiveness in this reaction is greater with an excess of potassium sulphate than with an excess of barium chloride, and similar conditions occur with calcium oxalate. Mercurous chloride is also obtained as a crystalline precipitate, whilst silver bromide and iodide are colloidal. As a colour reaction, that between cobalt salts, potassium thiocyanate, and alcohol has been studied. A comparison is made between this method of testing and the micro-chemical and spectroscopic methods, and the sensitiveness of a large number of qualitative reactions is tabulated. C. H. D.

Catalysis. XV. Reactions of Both the Ions and the Non-ionised Forms of Electrolytes. SOLOMON F. ACREE (*Amer. Chem. J.*, 1913, **49**, 345—368).—Evidence in favour of the view that both ions and non-ionised molecules may be concerned in all chemical reactions is adduced from a re-interpretation of the work of Arrhenius, Ostwald, Bredig, Goldschmidt, Stieglitz, and others,

as well as from the researches of the author and his co-workers. The latter investigations were made with concentrations varying from *N* to *N*/64, but experiments have now been undertaken to study the reversible addition of ethyl alcohol to *p*-bromobenzonitrile, and the catalytic effect of sodium, potassium, and lithium ethoxides in solutions as dilute as *N*/2048. The results so far obtained support the theory that both ions and non-ionised electrolytes are active in both concentrated and "ideal" solutions.

E. G.

Catalysis. XVI. Reactions of Both the Ions and the Non-ionised Forms of Electrolytes. Reversible Addition of Alcohols to Nitriles Catalysed by Sodium Ethoxide. ELI K. MARSHALL, jun., JULIA PEACHY HARRISON, and SOLOMON F. ACREE (*Amer. Chem. J.*, 1913, **49**, 369—405).—In an earlier paper (Marshall and Acree, this vol., i, 253), an account was given of a study of the addition of alcohols to nitriles in presence of ethoxides as catalysts. A further investigation of these reactions has been made as well as of the reversible change of ethyl iminoacetate and iminobenzoate into the corresponding nitrile and ethyl alcohol.

The results prove that the action of sodium ethoxide in these reactions is purely catalytic, and that the velocity of the non-catalysed reaction is so small as to be negligible. A comparison of the reaction-velocities and the conductivity data shows that the ethoxide ions have a definite effect on the velocity which can be expressed as a simple function of their concentration. The non-ionised sodium ethoxide also has an influence which can be expressed as a simple function of the concentration of the molecules. On referring all data to the *N*-solution and using K_i and K_m to express the effect of a gram-equivalent of the ethoxide ions and of the non-ionised sodium ethoxide respectively, constant values are obtained for K_i and K_m whatever the concentration of the ethoxide. For benzonitrile and ethyl iminobenzoate, $K_i : K_m = 0{\cdot}1172 : 0{\cdot}0976$, and for acetonitrile and ethyl iminoacetate $K_i : K_m = 0{\cdot}344 : 0{\cdot}228$.

The addition of sodium iodide in these reactions produces a "salt effect," which is due chiefly to a change in the concentrations of the ions and molecules as required by the theory of isohydric solutions.

The catalytic action of sodium ethoxide on the decomposition of imino-esters is analogous to the reactions of alkyl haloids with ethoxides and phenoxides and with sodium 1-phenyl-3-thiourazole. In all these cases, the velocity of the reaction can be expressed as a function of the concentration of the ions increased by a function of the concentration of the non-ionised molecules. E. G.

Representation of the Chemical Elements by means of Points in Ordinary Space. ARNALDO PIUTTI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 569—575).—The author describes a representation of the elements in three dimensions. He follows Borchers and Schmidt (compare Schmidt, A., 1911, ii, 198) in plotting on two rectangular co-ordinates atomic weights and equivalent volumes,

and in regarding the ordinates as positive or negative according as the elements are electropositive or electronegative, but he adds on a third axis the specific heats of the elements, chosen as far as possible between 0° and 100°. In view of the law of Dulong and Petit, the projection of the elements on the plane of the axes of atomic weights and specific heats satisfies the equation $xz = 6{\cdot}4$, that is, it is an equilateral hyperbola the asymptotes of which are the axes of x and z. Hence the points representing the elements lie on an equilateral hyperbolic cylinder. Further, since atomic weights and specific heats are essentially positive, all the points lie on one fold of the cylinder. The elements with atomic weights less than 6·4 lie on one side of the straight line forming the locus of the vertex of the hyperbola of the sections parallel to the plane xz, those with atomic weights greater than this (that is, all the elements except hydrogen and some extraterrestrial elements) on the other side. A plane representation of the space diagram is also given. R. V. S.

The Present Position of Mendeléev's Periodic System of the Elements. MAURICE CRABBÉ (*Bull. Soc. chim. Belg.*, 1913, **27**, 153—159).—A review especially of some of the more recent investigations on the relation between the atomic weights of the elements. D. F. T.

Some Consequences of Graham's Work: the Nature of Elements; the Diffusion of Liquids. HENRY E. ARMSTRONG (*Proc. Roy. Phil. Soc. Glasgow*, 1911-12, **43**, 67—96).—The Graham Lecture. A discussion of the periodic system; the chemical nature of the inactive gases; the process of diffusion; and the nature of hormones. C. H. D.

[The Nature of Auxiliary Valencies.] FRITZ EPHRAIM (*Zeitsch. physikal. Chem.*, 1913, **93**, 257—259).—Polemical. An answer to Friedrichs (this vol., ii, 497; see also this vol., ii, 129, 130; A., 1912, ii, 546). J. F. S.

Magnesia Apparatus. EDGAR WEDEKIND (*Zeitsch. angew. Chem.*, 1913, **26**, 303—304).—An extension of the applications of apparatus made of magnesia, or rather a mixture of magnesia and kaolin (compare A., 1912, ii, 382). The articles mentioned are spatulas, for flame tests; shallow troughs for containing sodium chloride, which, when heated in a Meker burner, give a constant source of sodium light; crucibles, and boats; test tubes. The articles will stand a temperature of 1300°. Tubes cannot be made to stand a vacuum, or for use with pure gases, since the material is porous. T. S. P.

A New Apparatus for Collecting Sediments from Turbid Liquids and for Extracting Liquids. EDUARD SPAETH (*Zeitsch. angew. Chem.*, 1913, **26**, 304).—The apparatus is an improvement on the author's sedimentation glass (A., 1897, ii, 281). It consists

essentially of an extraction funnel fitted with a special stop-cock. A small cavity is made in one part of the stop-cock; when put in connexion with the funnel it collects any sediment. The stop-cock is also bored in such a way that liquid contained in the funnel can be run out through the main body of the cock itself.

The funnel possesses a flat side, so that it will not roll about when laid down; it can also be placed on a water-bath and heated.

T. S. P.

Inorganic Chemistry.

Production of Hydrogen from Water and Coal from Cellulose at High Temperatures and Pressures. Friedrich Bergius (*J. Soc. Chem. Ind.*, 1913, **32**, 462—467).—According to Noyes, the dissociation of water increases nearly 2000-fold between the boiling and critical points. It should therefore be a fairly strong acid at high temperatures, if kept in the liquid condition, and in accordance with this the author has been able to obtain hydrogen in quantity by heating water and iron under pressure (not stated) at about 300°. The action is accelerated by the presence of ferrous chloride and copper. Ferroso-ferric oxide is the product of reaction.

In the decomposition of cellulose by heat, the reaction is strongly exothermic, and under ordinary experimental conditions it is impossible to maintain the temperature constant. This can be done, however, by making use of the high specific heat of water; the cellulose is heated with water under high pressures. At 340°, after about twelve hours, pure cellulose yields a black powder, which proves to be soft coal of about 84% C, 5% H, and 11% O, the reaction being probably: $4C_6H_{10}O_5 = C_{21}H_{16}O_2 + 3CO_2 + 12H_2O +$ 70,000 cal. The percentage of carbon rises with the length of heating and the temperature at which the reaction takes place, reaching a final value of 84% C. Peat gives similar results to cellulose. The reaction takes place much more quickly at 340° than at 310°, the temperature quotient being approximately 2.

The coal produced has the composition and all the qualitative reactions demanded by Donath for fossil coal, but it differs very much in its physical properties, as it is a very finely divided black powder. It may be converted into a substance with all the physical properties of natural coal by heating it above 300° under very high pressure (5000 atmospheres).

The author's experiments lead him to the conclusion that the formation of coal in nature takes place in two distinct reactions, namely, first the reaction of carbonisation, and secondly, the formation of anthracite under pressure. Without pressure, no formation of anthracite can occur. T. S. P.

Expulsion of Acids by Hydrogen Peroxide. JOACHIM SPERBER (*Chem. Zentr.*. 1913. i, 1490—1491; from *Schweiz. Woch. Chem. Pharm.*, 1913, **51**, 166—169).—A description in the terms of the theoretical views expressed in a former paper (this vol., ii, 400) of the action of hydrogen peroxide on some salts. The liberated hydroferrocyanic acid, in the case of its potassium salt, is frequently oxidised to Prussian-blue, which is then decomposed by the free alkali. J. C. W.

Optical Investigation of Solidified Gases. III. The Crystalline Properties of Chlorine and Bromine. WALTER WAHL (*Proc. Roy. Soc.*, 1913, *A*, **88**, 348—353).—Chlorine crystallises in the orthorhombic system, the crystals in sections both parallel and at right angles to the principal axis being strongly double-refracting; also the extinction between crossed nicols is parallel to the principal axis, as indicated by the cleavage. No polymorphic change was observed at temperatures between that of the melting point and that of liquid air. As the temperature falls to that of liquid air, the pale yellow colour of the crystals gradually decreases in intensity, until scarcely any colour is left. The crystals are slightly pleochroic.

Crystallised bromine is very similar to crystallised chlorine, except that all the properties appear more pronounced. The crystals, which belong to the orthorhombic system, are strongly pleochroic; the absorption is dark brownish-red in the direction of the prism axis, yellowish-red in the direction of a line bisecting the smaller prism angle, and pale yellowish-green in the direction of the line bisecting the larger prism angle. With decreasing temperature the intensity of the colour of the crystals gradually diminishes, becoming very pale yellow at the temperature of liquid air; this is due to the gradual disappearance of the strong trichroism.

A comparison of the crystalline properties of chlorine, bromine, and iodine is given. Pleochroism occurs with each element, its strength and character changing and increasing as the atomic weight increases. The three elements may be regarded as perfectly isomorphous. T. S. P.

The Dynamic Allotropy of Sulphur. HUGO R. KRUYT (*Proc. K. Akad. Wetensch. Amsterdam*, 1913. **15**, 1228—1236).—Mainly a criticism of Leeuw's paper on the relation between the modifications of sulphur (this vol., ii, 40), fresh experiments having been carried out in support of the criticism. The experiments show that the change in volume of strongly supercooled sulphur over the temperature range 70—95° is different from that observed by Leeuw, and that the phenomena occurring have no connexoin with the change $S_{rh} \rightleftarrows S_{mon}$. The author maintains the conclusions drawn from his previous work (compare this vol., ii, 132). T. S. P.

A New Modification of Sulphur. II. ADRIAAN H. W. ATEN (*Zeitsch. physikal. Chem.*, 1913, **83**. 442—458. Compare this vol., ii, 40).—A continuation of the work published in the previous

paper. The author shows that sulphur which has been heated to 170° and rapidly cooled contains just as much S_π as sulphur which has been heated to 445° and then rapidly cooled. It is shown that in sulphur chloride solution S_π changes fairly rapidly into S_μ. Experiments were then made in toluene solution, and it was shown that the solubility of sulphur which has been heated at 170° is greater than sulphur which has not been treated in this way; also it is shown that the solubility in the case of the treated sulphur is greater the larger the quantity of solid sulphur present. The increased solubility is studied in the light of a number of hypotheses, and it is shown that S_π must be present in the solid sulphur either as mixed crystals with S_λ or as a mixture; the experiments do not allow of an answer as to which form it is present. The solutions containing S_π are all strongly coloured yellow; this colour is shown to be due to sulphur and not to an impurity; in the case of a solution in carbon disulphide containing 18 atoms %, the colour was that of a strong aqueous solution of potassium chromate. On cooling a solution of $S_\pi + S_\lambda$ to $-80°$, the whole of the S_λ separated out, leaving only S_π in solution.

Experiments were made to obtain solid S_π by evaporating the solvent, but in the first experiments a white, amorphous powder, insoluble in carbon disulphide and toluene, was obtained, namely, S_μ. If the solvent was removed at $-80°$ by reduction of pressure, the residual sulphur was practically all soluble in toluene, with a small residue of S_μ; so that on distillation of a solution of S_π the dissolved substance is transformed into S_μ. It is shown to be extremely unlikely that the solutions of S_π are really solutions of S_μ. Two solutions of S_λ and $S_\lambda + S_\pi$ were submitted to a strong light; this caused an immediate precipitation of S_μ, less, however, in the case of $S_\lambda + S_\pi$ than in the other case, whereas if S_π is really S_μ, the greater precipitation should have come from the $S_\lambda + S_\pi$.

J. F. S.

Reactions Between Water and Sulphurous Acid at Different Temperatures. Formation of Hyposulphurous Acid. ÉMILE JUNGFLEISCH and LÉON BRUNEL (*Compt. rend.*, 1913, **156**, 1719—1724).—A study of the effect of heating aqueous solutions of sulphur dioxide, saturated at 0°, at different temperatures from 160° downwards. Water and sulphur dioxide will react at temperatures below 160°, and even at the ordinary temperature producing sulphur and sulphuric acid, but the reaction is much slower at the lower temperatures and with more dilute solutions. This production of sulphur and sulphuric acid really takes place in two stages, the first of which, resulting in the formation of hyposulphurous acid, is only noticeable at the lower temperatures:

$$(1)\ 3SO_2 + 2H_2O = H_2S_2O_4 + H_2SO_4.$$
$$(2)\ H_2S_2O_4 = S + H_2SO_4.$$

Certain secondary reactions of a minor character take place at the same time.

W. G.

Study of the Metallic Tellurites. VICTOR LENHER and EDWARD WOLESENSKY (*J. Amer. Chem. Soc.*, 1913, **35**, 718—733).—A study has been made of various metallic tellurites. In the case of the alkali metals, mono-, di-, and tetra-tellurites have been prepared, the first two by fusing tellurium dioxide with calculated quantities of the alkali carbonates, and the tetratellurites by decomposing the ditellurites with water. The tellurites of the other metals have been obtained by precipitation from a solution of a salt (usually the chloride) with sodium tellurite. The alkali tellurites are soluble in water, the alkali-earth salts slightly soluble, and those of the heavy metals are insoluble. Tellurites are unstable; at the ordinary temperature and in presence of moisture, tellurous acid is readily displaced by carbon dioxide. When heated in the air at 440—470°, the tellurites undergo oxidation, but neither the tetratellurites nor tellurium dioxide are oxidised under these conditions. In the case of potassium ditellurite, the oxidation results in the formation of the *compound*, K_2O,TeO_3,TeO_2. The precipitated tellurites are flocculent and amorphous, and, with the exception of the magnesium salt, do not show any tendency to crystallise.

The following salts have been prepared: Potassium tellurite, $K_2TeO_3,3H_2O$, ditellurite, and tetratellurite, $K_2Te_4O_9,4H_2O$; sodium tellurite, $Na_2TeO_3,5H_2O$, ditellurite, and tetratellurite, $Na_2Te_4O_9,4H_2O$. Ammonium tellurite probably exists in solution and also in the solid state when surrounded by a saturated solution of tellurous acid in ammonia, but on attempting to isolate it, it decomposes spontaneously at the ordinary temperature with formation of hydrated tellurium dioxide. Magnesium tellurite forms at least two definite hydrates, $5MgTeO_3,9H_2O$ and $10MgTeO_3,9H_2O$. Barium tellurite, precipitated from barium chloride solution, occludes large quantities of the chloride which cannot be completely removed by washing. Silver tellurite is anhydrous; it can be obtained in several varieties, differing from one another in colour. Manganous tellurite is very unstable, and is oxidised by the air at the ordinary temperature, the metal being converted into the tervalent state. Cadmium tellurite, $3CdTeO_3,2H_2O$; nickel tellurite, $NiTeO_3,2H_2O$; cobalt tellurite, $CoTeO_3,H_2O$; and lead tellurite, $3PbTeO_3,2H_2O$, are also described.

E. G.

Some Reactions of Hydrazine Nitrate. WILLIAM R. E. HODGKINSON (*J. Soc. Chem. Ind.*, 1913, **32**, 519—520).—Hydrazine nitrate, N_2H_4,HNO_3, has m. p. 70°, and may be kept at 100° for a long time without change. At 200° in a vacuum it decomposes in accordance with the scheme: $4N_2H_4,HNO_3 = 5N_2 + 2NO + 10H_2O$. When heated under pressure, it explodes violently; at ordinary pressures it burns rapidly. The aqueous solution has very little action on metals such as zinc, cadmium, and magnesium, which are strongly acted on by a solution of ammonium nitrate, but the fused salt acts more vigorously than fused ammonium nitrate. Zinc, copper, and most other metals, as well as oxides, sulphides,

nitrides, and carbides, cause a flaming decomposition at temperatures little above the melting point. Cobalt and nickel that have been thoroughly melted behaved like the other metals towards fused hydrazine nitrate, but commercial cube cobalt causes a very violent action, followed almost immediately by a severe explosion.

Nitrates of bases, such as aniline and toluidine, both in solution and when fused, behave towards most of the metals in a way analogous to ammonium nitrate. T. S. P.

Behaviour of the Hydronitrogens (Nitrogen Hydrides) and their Derivatives in Liquid Ammonia. IV. Pressure Concentration Isotherms in the System Ammonia, Ammonium Trinitride [Azoimide]. ARTHUR W. BROWNE and A. E. HOULEHAN (*J. Amer. Chem. Soc.*, 1913, **35**, 649—658. Compare Browne and Welsh, A., 1911, ii, 1084; Browne and Houlehan, A., 1911, ii, 1085).—An account is given of experiments on the two-component system, ammonia, ammonium azoimide, in which pressure-concentration isotherms were studied at 20°, 0°, and −33°. The results show that ammonium azoimide unites with ammonia to form a diammonate, $NH_4N_3,2NH_3$, which crystallises in colourless, transparent, elongated plates. This compound is stable at −33°, showing a dissociation pressure of about 22·8 cm. at this temperature, but is not stable at 0°; the inversion point is about −9°. One gram of liquid ammonia dissolves 0·7 gram of ammonium azoimide at −33°, and 1 gram at 0°. The vapour pressures of solutions saturated at these temperatures are 43·7 and 149 cm. respectively.

E. G.

Behaviour of the Hydronitrogens (Nitrogen Hydrides) and their Derivatives in Liquid Ammonia. V. Electrolysis of a Solution of Ammonium Azoimide in Liquid Ammonia. ARTHUR W. BROWNE and M. E. HOLMES (*J. Amer. Chem. Soc.*, 1913, **35**, 672—681).—Browne and Houlehan (A., **1911**, ii, 1085) have shown that when a solution of ammonium azoimide in liquid ammonia is treated with certain metals, the following reaction takes place: $M + NH_4N_3 = MN_3 + NH_3 + H$. It follows therefore that the solution is virtually a solution of free azoimide, and, as such, affords a convenient means of studying the properties of this substance in an anhydrous condition.

In the present paper an account is given of the behaviour of a solution of ammonium azoimide in liquid ammonia towards the electric current, the experiments being undertaken with a view to gaining information on the properties of the discharged N_3' ion.

It has been found that such solutions readily conduct the electric current, and that, when platinum electrodes are used, electrolysis takes place with liberation of hydrogen at the cathode and nitrogen at the anode. The ratio $H_2 : N_2$ varies from 1·65 to 2·15, with an average of 1·93, instead of the ratio 0·333, which would result if the discharged N_3' ions simply broke up into molecular nitrogen. These facts are best explained on the assumption that some of the discharged N_3' ions break up into molecular nitrogen, but that

most of them react with ammonia to regenerate ammonium azoimide and liberate nitrogen. When a graphite anode is employed, the ratio averages 0·334, indicating that the N_3' ions are converted quantitatively into molecular nitrogen. E. G.

Attempt to Prepare Nitro-Nitrogen Trichloride, an Electromeride of Ammono-Nitrogen Trichloride. WILLIAM A. NOYES (*J. Amer. Chem. Soc.*, 1913, **35**, 767—775).—Noyes and Lyon (A., 1901, ii, 601) have shown that the primary reaction between ammonia and chlorine yields nitrogen trichloride and nitrogen, and have suggested that in the course of the reaction the chlorine molecules may split up into Cl^+ and Cl^- ions, and that some of the N and H atoms are temporarily positive and others negative.

It has also been observed that when nitrogen trichloride is titrated with arsenious acid solution, one molecule of the trichloride is equivalent to six atoms of available chlorine. This indicates that the nitrogen of the compound is negative and the chlorine positive, and that it hydrolyses as a reversible reaction:

$$N^{---}Cl_3^{+++} + 3H^+O^{--}H^+ \rightleftharpoons N^{---}H_3^{+++} + 3Cl^+O^{--}H^+.$$

It then occurred to the author that there might be another nitrogen trichloride, in which the nitrogen would be positive and the chlorine negative, and which would hydrolyse normally, thus:

$$N^{+++}Cl_3^{---} + 3H^+O^{--}H^+ = H^+O^{--}N^{+++}O^{--} + H^+O^{--}H^+ + 3H^+Cl^-.$$

In this case, the two nitrogen trichlorides might be termed ammono-nitrogen trichloride and nitro-nitrogen trichloride respectively.

Attempts to prepare nitro-nitrogen trichloride have been made by passing a mixture of nitrosyl chloride and phosphorus pentachloride through a strongly heated porcelain tube. No appreciable amount of the trichloride was obtained, but evidence of its existence was secured, and an analysis of the products of the reaction showed that the compound indicated could not have been the ammono-nitrogen trichloride. E. G.

The Solid Hydrogen Phosphides. LOUIS HACKSPILL (*Compt. rend.*, 1913, **156**, 1466—1468).—The four alkali phosphides having the general formula M_2P_5 (compare Hackspill and Bossuet, A., 1912, ii, 252), when treated with very dilute acetic acid, give a hydrogen phosphide in the form of a yellow solid, the composition of which corresponds with H_2P_5. Further, the solid phosphide obtained by Stock, Böttcher, and Lenger (compare A., 1909, ii, 727), when heated in a vacuum at 80°, loses a considerable amount of gaseous phosphide, and after several hours the compound H_2P_5 is left behind. This substance is of an acid nature, since it furnishes metallic phosphides with corresponding formulæ, K_2P_5,Rb_2P_5, etc. W. G.

Crystallisation of Carbon Dioxide, Nitrous Oxide, and Ammonia. H. E. BEHNKEN (*Jahrb. Min.*, 1913, i, *Ref.* 182; from *Physical Review*, 1912, **35**, 66—73).—These substances were

crystallised on the stage of the microscope with the aid of liquid air. All of them belong to the cubic system, and carbon dioxide was obtained as good, clear, optically isotropic crystals, showing the cube and octahedron. L. J. S.

A Simple Method for the Preparation of Argon; Chemical Activation of Diatomic Gases in the Glow Discharge. JOHANNES STARK (*Physikal. Zeitsch.*, 1913, **14**, 497—498).—The author has observed that when oxygen from a cylinder (prepared by the fractionation of liquid air) is led into a tube through which canal rays are passing, and in which mercury vapour is also present, the oxygen rapidly disappears, the walls of the tube become coated with a deposit of mercuric oxide and mercuric nitrite, and argon, which was contained in the oxygen, is left behind. The spectrum shows the lines of mercury and argon; even the strongest lines of oxygen are very weak, whilst those of nitrogen are absent.

A ready method is thus given for obtaining small quantities of argon in a short time, and the author describes a simple piece of apparatus for carrying out such a process.

The ready combination of the mercury vapour with the oxygen and nitrogen is supposed to be due to the dissociation of the diatomic molecules into their atoms under the influence of the discharge; the atoms are then very active chemically. It is further shown that when submitted to the glow discharge, oxygen readily combines with aluminium, and hydrogen reduces mercuric oxide below 100°, etc. T. S. P.

Reduction of Some Volatile Halogen Compounds with Potassium Powder. ALEXANDER C. VOURNASOS (*Zeitsch. anorg. Chem.*, 1913, **81**, 364—368).—Pure phosphorus trichloride and similar compounds do not react with massive potassium when cold, but reaction is readily brought about by dissolving the halogen compound in toluene, and using the potassium in the form of dust, obtained by shaking vigorously in hot toluene. The potassium must be freshly prepared in the required quantity for each experiment. Phosphorus trichloride is thus completely reduced, according to the equation $PCl_3 + 6K = 3KCl + K_3P$, and by adding a little glacial acetic acid to the product, gaseous, non-inflammable hydrogen phosphide may be obtained. Phosphorus bromide and iodide behave similarly.

Arsenic trichloride yields metallic arsenic, but no arsenide, and this is also the behaviour of antimony and bismuth. The chlorides of carbon and silicon are not acted on at the temperature of boiling toluene. Tin tetrachloride yields finely divided metallic tin. Boron trichloride is only slowly reduced, yielding amorphous boron; the bromide somewhat more readily. Titanium tetrachloride yields partly the dichloride and partly titanium.

Potassium amalgam is much less active than the powdered metal. C. H. D.

Alcoholic Potassium Hydroxide. RUDOLF GAZE (*Chem. Zentr.*, 1913, i, 1361; from *Apoth. Zeit.*, 1913, **28**, 174).—The author claims that alcoholic potassium hydroxide made by his method (A., 1911, ii, 225) will keep colourless much longer than the solution prepared according to Malfatti (A., 1911, ii, 979).

J. C. W.

Temperature-Concentration Diagrams of Potassium Sulphate with the Sulphates of the Alkaline Earths and of Lead, with Reference to the Dimorphism of Anhydrite, Celestine, Barytes, and Anglesite. WERNER GRAHMANN (*Zeitsch. anorg. Chem.*, 1913, **81**, 257—314).—Calcium sulphate may be melted in an electric furnace without decomposition, and gives the freezing point 1450°, and transformation point 1193°. The following transformation points are also observed: strontium sulphate, 1152°; barium sulphate, 1149°; lead sulphate, 852°.

A special form of heating microscope is described for the optical determination of transformation temperatures. Anhydrite, celestine, barytes, and anglesite pass into α-modifications, probably monoclinic, at the transition temperature.

Potassium and glucinum sulphates form a single compound, $K_2SO_4,2GlSO_4$, with a maximum m. p. about 910°. Solid solutions are not formed. The compound is tetragonal, and the eutectic with potassium sulphate is fine-grained and sometimes radiating. The system potassium sulphate–magnesium sulphate has been examined by Nacken (A., 1908, ii, 692), whose results are confirmed. Solid solutions are formed to a limited extent at the potassium end of the series. The diagram of the system potassium sulphate–calcium sulphate differs in several respects from that given by Müller (A., 1910, ii, 776). α-Potassium sulphate retains up to 18 mol. % $CaSO_4$ in solid solution at high temperatures, but the solubility diminishes with falling temperature, and disappears at the transformation temperature. The compound $K_2SO_4,2CaSO_4$ decomposes into β-calcium sulphate and liquid at 1004°, and undergoes a polymorphic change at 938°. There are thus three breaks in the ascending branch of the freezing-point curve. The diagram of the system potassium sulphate–strontium sulphate is entirely similar. The limits of solid solution at the eutectic temperature are 0—22 mol. % $SrSO_4$, and the compound $K_2SO_4,2SrSO_4$ is resolved into liquid and β-$SrSO_4$ at 980°, and undergoes a transformation at 775°. The system potassium sulphate–barium sulphate is so far different that no evidence of a compound is formed. The first branch of the freezing-point curve, representing the solidification of solid solutions, passes through a maximum at 1087°. The limit of saturation is 24 mol. % $BaSO_4$, and, as before, the β-modification does not form solid solutions.

In the system potassium sulphate–lead sulphate, solid solutions are formed up to 27 mol. % $PbSO_4$, diminishing with falling temperature. The compound $K_2SO_4,2PbSO_4$ has a maximum m. p. 948°, and is dimorphous, with a transformation point at 544°. In addition to this, a compound, $K_2SO_4,PbSO_4$, is formed at 619° by a

reaction in the solid state. A number of regularities among the systems considered are pointed out. C. H. D.

Reciprocal Behaviour of Alkali Sulphates, Chromates, Molybdates, and Tungstates at Low and at High Temperatures. III. MARIO AMADORI (*Atti. R. Accad. Lincei*, 1913, [v], **22**, i, 609—616. Compare this vol., ii, 512).—The curve of crystallisation of the system K_2SO_4–K_2WO_4 is continuous; there is a slight minimum 10° below m. p. of the tungstate. The transformation point of the tungstate is not visible in mixtures containing more than 15 mol. % of sulphate. The transformation point of the sulphate followed a curve descending to 482° for mixtures containing 50 mol. %, below which point it is no longer visible.

In the system K_2CrO_4–K_2WO_4 the curve is also continuous, and it is intermediate between the m. p. of the two salts. The transformation points follow curves rising to the transformation points of the pure salts, but were not observable for the mixtures between 15% and 40% of chromate.

The curve of the system K_2MoO_4–K_2WO_4 is almost a straight line intermediate between the m. p. of the two salts. Here also the transformation points are only observable in mixtures rich in one or other constituent.

The author has also made experiments with potassium dichromate, potassium dimolybdate, and potassium ditungstate. Potassium dimolybdate has m. p. 484°, potassium ditungstate has m. p. 555°. Neither salt shows any transformation point. The curves of the three systems formed by taking pairs of these salts are continuous, and are very similar to those of the corresponding normal salts.

R. V. S.

Potassium and Sodium Chromates; Mixed Crystals and Double Salt; Relation to the Corresponding Sulphates. E. FLACH (*Jahrb. Min.*, 1913, i, *Ref.* 212; from *Inaug. Diss. Leipzig*, 1912).—Solubility determinations and thermal curves indicate the existence of the double salt $3K_2CrO_4,Na_2CrO_4$ ("chromglaserite," corresponding with the sulphate glaserite). This rhombohedral double salt is capable of forming mixed crystals to a limited extent with sodium chromate. Fused mixtures on cooling give at first hexagonal mixed crystals, which during the transformation interval of 669—371° mostly split into the simple chromates and mixed crystals of chromglaserite and sodium chromate. The topic axes of the isomorphous simple chromates and sulphates and of the double salts are compared. L. J. S.

The Error Due to Salts in the Colorimetric Measurement of Hydrogen Ion Concentration in Sea-water. SÖREN P. L. SÖRENSEN and SVEN PALITZSCH (*Biochem. Zeitsch.*, 1913, **51**, 307—313. Compare A., 1910, ii, 404).—The necessary corrections, plotted in the form of curves, are given for borate mixtures and phenolphthalein, borate mixtures, and naphtholphthalein, and phosphate mixtures and naphtholphthalein. S. B. S.

Complex Citrophosphate Salts. ALFREDO QUARTAROLI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 511—512).—Polemical. The author considers not only that his work has not been recognised by Pratolongo in the publications of this author, but also that the existence of complex ions in citrophosphate solutions (Quartaroli, A., 1911, ii, 489) is demonstrated by the experiments of Pratolongo himself (this vol., ii, 282, 467). R. V. S.

Binary Systems of Lithium Chloride with the Chlorides of the Alkali Earth Metals. CARLO SANDONNINI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 629—636. Compare this vol., ii, 137).—Lithium chloride and magnesium chloride form in all proportions solid solutions, which are also stable at low temperatures. The curve shows a minimum corresponding with 40 mol. % of $MgCl_2$ and 570°.

Lithium chloride and calcium chloride give a continuous series of solid solutions, which crystallise along a curve having a very acute minimum corresponding with 36·4 mol. % of $CaCl_2$ and 492°. Mixtures between 10 mol. % and 60 mol. % of $CaCl_2$ show an evolution of heat after solidification, and the curve indicates that the solid solutions break up at a temperature very near that of crystallisation, yielding a mechanical mixture of two solid solutions containing the components in very limited proportions.

With strontium chloride and with barium chloride, lithium chloride yields simple eutectics. The eutectic in the case of strontium chloride corresponds with 48 mol. % of $SrCl_2$ and 492°, whilst in the case of barium chloride the eutectic lies at about 33 mol. % of $BaCl_2$ and 510°. R. V. S.

Anhydrous Condition and Stability of Fused Lithium Perchlorate and Their Bearing on the Atomic Weight of Silver. THEODORE W. RICHARDS and MARSHALL W. COX (*Chem. News*, 1913, **107**, 267—268).—In their work on the atomic weights of silver and lithium Richards and Willard (A., 1910, ii, 292) weighed lithium perchlorate, which had been fused and dried at 300°. This procedure involved two possible sources of error: (1) the retention of traces of moisture by the salt, (2) slight decomposition of the salt. The chlorate or chloride resulting from (2) could easily be detected, but the investigation of (1) is difficult. It is now shown that lithium perchlorate treated as described loses no appreciable trace of water when heated to 400° (when slight decomposition occurs) or to 430° (when much oxygen is given off). It is possible, however, that traces of water may be held by the salt in the form of lithium hydroxide, and this point is still under investigation. T. A. H.

The Behaviour of Ammonium and Alkali Nitrates and Nitrites, and also of the Corresponding Salts of Some Substituted Ammonium Compounds Towards Reducing Agents. WILHELM VAUBEL (*Chem. Zeit.*, 1913, **37**, 637—638. Compare Kaufmann, A., 1901, ii, 554).—In order to accelerate the expulsion

of nitric acid from solutions before precipitation with hydrogen sulphide, the author's students added ammonia, and then heated. It was found that in spite of long heating considerable quantities of combined nitric acid remained behind; in spite of this, however, after acidifying with hydrochloric acid no precipitate of sulphur was produced with hydrogen sulphide. Further experiments showed that mixtures of ammonium chloride and nitric acid, and of ammonium nitrate and nitric acid were reduced by hydrogen sulphide, whereas one of ammonium nitrate and hydrochloric acid was not, unless the acid was concentrated. This is apparently not in agreement with the law of mass action.

The above observations led to further experiments on the action of other reducing agents on ammonium nitrate and nitrite. The ordinary metals, with the exception of iron, reduce ammonium nitrate to nitrite. With iron the reduction generally gives ammonia without the intermediate formation of nitrite, although in some cases nitrite was detected; at the same time a small portion of the iron dissolves, giving a complex compound in which the iron may be in the ferrous, ferroso-ferric, or ferric condition.

The intermediate formation of nitrite occurs in the action of iron on aniline and *p*-toluidine nitrates, alkali nitrates, and calcium nitrate.

Neutral solutions of ammonium, potassium, and sodium nitrites, have no action on iron in the cold; the latter also have no action, or only a very slow one, when hot. T. S. P.

Modifications of Silver. III. Silver from Solid Compounds. VOLKMAR KOHLSCHÜTTER and E. EYDMANN (*Annalen*, 1913, **398**, 1—48. Compare A., 1912, ii, 253, 845).—A substance changing by molecular decomposition to a more highly condensed state appears to be in a condition of molecular plasticity, since the appearance of the final product is markedly affected by material and physical factors operating during its formation. Silver is a substance in which the property is particularly pronounced. The hair and mirror modifications of silver have already been described (*loc. cit.*). The present communication deals with the appearance and properties of silver produced from its solid compounds either by direct decomposition or by interaction with another substance. External factors, such as the temperature and so forth, and, as far as possible, the course of the reactions have been studied, since without a knowledge of these conditions the production of different modifications is not intelligible. The preparation and the decomposition of silver oxide, carbonate, oxalate, azoimide, hyponitrite, and nitrite are described. Many interesting facts are stated, but in a form unsuitable for abstraction. Mention may be made, however, of the facts that the decomposition of the carbonate is endothermic and of the oxalate exothermic; also that a certain amount of silver nitrate is produced during the decomposition of the nitrite and hyponitrite. Since amorphous silver becomes crystalline by heating under fused silver nitrate, the production of this salt during the last two decompositions accounts for the presence of a little crystallised silver in

the products of these decompositions; in all other cases the silver is amorphous.

A remarkable fact has been observed in connexion with the decomposition of silver carbonate. Silver oxide, heated in a vacuum, decomposes most favourably at 320°. Silver carbonate decomposes rapidly in a vacuum at 216°. If the gas (carbon dioxide) is pumped off, the product can be heated to 320° without any further evolution of gas. When, however, the product is allowed to cool and is then reheated, a rapid evolution of gas occurs at 235° and the decomposition of the oxide then proceeds normally. The reduction of silver oxide by hydrogen at about 70° and finally at 100—120° is described, as also its reduction by partly dried carbon monoxide at the ordinary temperature; the reduction of silver oxide by dry carbon monoxide only commences at about 100°. Finely divided silver has also been prepared from silver chloride by Wislicenus's method of reduction with zinc and dilute sulphuric acid, by Stas' method with aqueous potassium hydroxide and lactose, and by Vanino's method with sodium hydroxide and formaldehyde. Aqueous silver nitrate has also been reduced by sulphur dioxide. This silver is crystalline; silvers obtained by the other methods are amorphous, and differ from one another distinctly in colour, lustre, friability, and size of the particles.

The isolation of silver in such different forms is the reason for the frequently expressed view that the metal occurs in allotropic modifications. Now, the essential difference between allotrcpes is the difference in the energy-content. This difference has been measured by various observers by different methods, the results of which lead to the inference that silver does exist in allotropic modifications. The authors, however, are of opinion that the quantitative differences in the energy-content of various modifications of silver are due, not to allotropy, but to the difference in the size of the particles, being conditioned by surface-energy. Employing the various modifications of silver mentioned above, they have examined the reduction of ferric alum in dilute sulphuric acid by silver, and find that the equilibrium constant between the ferric, ferrous, and silver ions is, for the different modifications, not sufficiently different to justify the inference that the modifications are allotropic. This conclusion is supported by measurements of the potential between the silver and the silver ions in the cell,

$$Ag\,|\,0{\cdot}1N\text{-}AgNO_3\,|\,KNO_3\,|\,N\text{-}KCl,HgCl\,|\,Hg,$$

and by determinations of the density of the different modifications of silver in a Muthmann pyknometer containing benzene.

Since Bredig and Teletov have shown that the velocity of the catalytic decomposition of hydrogen peroxide by platinum is proportional to the active surface of the metal, the authors have attempted to verify their opinion that the differences in the energy-content of the various modifications of silver are due to differences in the surface energy by measuring the velocity of the decomposition of hydrogen peroxide in the presence of silver, either by the diminution of the potassium permanganate titre, or, better, by measuring the volume of oxygen evolved. The various modifications of silver

exhibit quantitative differences in their catalytic activity; silvers obtained by the formaldehyde reduction or from the oxide by means of carbon monoxide or hydrogen are the most, and about equally, active.

A description is given of experiments in the sintering or shrinking of silver by heating. For a given modification the shrinking is the same whether the silver is heated slowly or suddenly, but the shrinking of the various modifications of silver is very different; silver powder prepared by wet processes begins to sinter noticeably at 200°, whilst powders prepared by dry processes only begin to shrink appreciably at 300°. C. S.

Electrolytic Preparation of Calcium and Calcium Alloys. WILHELM MOLDENHAUER and J. ANDERSEN (*Zeitsch. Elektrochem.*, 1913, **19**, 444—447).—Starting from the fact that at high temperatures potassium is more electropositive than calcium (Daneel and Stockem, A., 1905, ii, 388), the authors have carried out experiments with the object of preparing metallic calcium from molten mixtures of calcium and potassium chlorides. They first determined the melting-point curve of mixtures of the two chlorides, and find a maximum at 740° which lies between two minima both at 630°. The maximum melting point occurs for a mixture of equal molecules of the two chlorides, and is stated to represent the melting point of $KCaCl_3$, whilst the minima occur at the compositions 85% $CaCl_2$ and 40% $CaCl_2$; the former is the eutectic point for $CaCl_2$ and $KCaCl_3$, whilst the latter is the eutectic point for KCl and $KCaCl_3$.

The first electrolyses were for the purpose of preparing calcium alloys which should contain no potassium. A mixture of 85% $CaCl_2$ and 15% KCl was placed in an iron crucible which served as the cathode, a graphite rod being used as anode. The mass was melted by the current and a quantity of zinc added; this melted, and formed eventually the cathode. In this way calcium zinc alloys were obtained containing up to 67% calcium which were absolutely free from potassium. In a similar manner lead calcium alloys were obtained up to 81·9% calcium. Pure calcium itself was prepared from a mixture of 85% $CaCl_2$ and 15% KCl, using the Rathenau method, the current density being 60—110 amperes per sq. cm. The metal was practically free from potassium, and the current efficiency varied between 75% and 90% of the theoretical. Experiments with 40% $CaCl_2$ and 60% KCl did not give a coherent stick of calcium as in the other cases, probably due to separation of potassium and the high melting point of the alloy. J. F. S.

Action of Silver Salts and Colloidal Metals on Luminophores. IV. LUDWIG VANINO and PAULA SACHS (*J. pr. Chem.*, 1913, [ii], **87**, 508—512. Compare A., 1909, ii, 731; 1910, ii, 847; 1911, ii, 885).—The authors have investigated the effect of the addition of traces of silver nitrate on the luminosity of the phosphorescent sulphide mixtures previously described, and find that although in some instances the addition produces an increased

luminosity, this is not universally the case, the silver nitrate often having little or a deleterious effect.

In the preparation of the phosphorescent stones, colloidal metals may be used with advantage in the place of the nitrates hitherto employed; thus the replacement of silver and bismuth nitrates by colloidal solutions of the metals is accompanied in many instances by an increase in the luminosity. F. B.

Calcium Boride. EDGAR WEDEKIND (*Ber.*, 1913, **46**, 1885—1889).—Calcium metaborate (30 grams), when reduced by means of calcium (50 grams) in the author's apparatus (this vol., ii, 225), gives rise to the theoretical quantity of calcium boride, CaB_6, which has been obtained previously by Moissan in an impure condition. The reaction product is extracted with dilute acetic acid and then dilute hydrochloric acid, and finally washed with hot water. It forms a fine, light brown, microcrystalline powder, $D^{18} = 2 \cdot 11$, and is a conductor of electricity. If two electrodes are made by compressing the powder, and an arc struck between them, the chief mass sinters together, giving a product which cuts glass. On heating in the air, superficial oxidation to borate takes place. Other chemical properties are as given by Moissan.

Experiments to obtain barium boride from barium borate and calcium were not successful, the product always containing calcium. T. S. P.

Pozzuolana. GIOVANNI GIORGIS and GINO GALLO (*Gazzetta*, 1913, **43**, i, 353—361. Compare Gallo, A., 1908, ii, 844).—It was observed (*loc. cit.*) that when lime-water acts on pozzuolana the substance swells up into a flocculent mass, which is the object of chemical investigation in this paper. The experiments were carried out with material from S. Paolo and Pratolungo (which are typical Roman pozzuolane) and from Bacoli. The mucilaginous substance was obtained by treating the pozzuolana with lime-water for six months with frequent stirring, and the results of its analysis are given in two tables. The behaviour of the two first-named materials was similar, but the Bacoli product gave a greater residue insoluble in hydrochloric acid and in potassium hydroxide, and this agrees with the fact that this pozzuolana sets more slowly. The results indicate a tendency to the formation of definite compounds in the reaction, but the small amount of calcium found in the gummy product as compared with the quantity of silicon and aluminium, indicates that the action is far from complete after the period of the experiment. The residue insoluble in hydrochloric acid and in potassium hydroxide differs in composition from the original pozzuolana.

The authors reply to criticisms by Manzella (A., 1912, ii, 352). R. V. S.

Technical Preparation of Baryta. I. LUIGI MARINO (*Gazzetta*, 1913, **43**, i, 416—422).—This paper forms the introduction to a series of researches undertaken with the object of simplifying the

technical preparation of baryta, so as to reduce its cost and make it more available for the treatment of molasses. The author finds that the reduction of barium sulphate to barium sulphide is effected by reducing gases better than by coal, which is generally employed at present. The reduction with hydrogen, methane, water gas, illuminating gas, etc., occurs at about the same temperature, as these gases inflame with oxygen, and the temperature of reduction can be lowered by the aid of suitable catalysts, just as combination with oxygen can be favoured by the same means. For commercial purposes the best results are obtained with water-gas, the reduction occurring at 525—540°. In practice a temperature of 600—625° is employed. R. V. S.

Technical Preparation of Baryta. II. Reduction of the Sulphates of the Alkaline Earths with Different Gases. LUIGI MARINO and D. DANESI (*Gazzetta*, 1913, **43**, i, 423—434. Compare preceding abstract).—The authors have investigated the reduction of the sulphates of barium, calcium, and strontium with each of the gases: hydrogen, methane, carbon monoxide, water gas, and illuminating gas. The reduction was effected by passing the gas over the sulphate contained in a boat placed in a porcelain tube. The tube could be heated electrically. The temperature was measured with a platinum, platinum-rhodium couple, and the beginning of the reduction was taken to be indicated by the first appearance of traces of hydrogen sulphide or of carbon dioxide in the issuing gas; at a somewhat higher temperature the formation of water is visible. In all cases the reduction is complete at temperatures a little above those at which the water makes its appearance. In the case of barium sulphate the product of reduction is always the sulphide; strontium sulphate yields sulphide with traces of oxide and thiosulphate, whilst from calcium sulphate, sulphide and small quantities of oxide and thiosulphate are also obtained. The temperature of reduction is different for the different gases, and has intermediate values for mixtures of gases; it is lowest for barium sulphate, higher for strontium sulphate, and highest for calcium sulphate.
R. V. S.

Technical Preparation of Baryta. III. Rotatory Furnace for the Continuous Production of Barium Sulphide by Reduction of the Sulphate with Gaseous Substances. LUIGI MARINO and D. DANESI (*Gazzetta*, 1913, **43**, i, 434—439. Compare two preceding abstracts).—The essential part of the furnace consists of an iron tube covered externally by a porcelain tube, which is provided with a nickel spiral for electrical heating, the whole being jacketed with magnesia. The tube and its covering are rotated at any desired speed, and are also inclinable to any desired, fixed angle. The barium sulphate is fed into the tube from a hopper at the upper end, and the sulphide falls into a receptacle connected with the other end, the inclination and speed of the tube being so adjusted that the sulphate stays in the tube long enough to be reduced completely (about one hour at 600—650°). The

reduction is effected with water-gas, which is passed into the tube from the lower end. The yield of sulphide is 95—98%. R. V. S.

Metallic Glucinum. FRITZ FICHTER and KASIMIR JABLCZYNSKI (*Ber.*, 1913, **46**, 1604—1611).—Glucinum is best obtained by the electrolysis of a fusion containing 1 mol. of sodium fluoride to 2 mols. of glucinum fluoride (compare Lebeau, A., 1898, ii, 511), using a nickel crucible as cathode, a carbon rod anode, and a current strength of 7—10 amperes at 15 volts. The temperature must not rise too high, otherwise an alloy of glucinum and nickel is formed. The metal is isolated from the fusion by dissolving the salts in water, the solution being prevented from becoming acid by the addition of ammonia and by repeated renewal of the water. The crystals of glucinum so obtained are freed from admixed oxide by centrifugalisation in a mixture of ethylene dibromide and alcohol (D 1·95); they have D=1·842. The small crystals so obtained cannot be melted together under ordinary conditions, owing to the coating of oxide formed preventing coalescence; it is necessary to form cylinders by compression, and then heat them up in an electric vacuum furnace, or in one containing hydrogen at 11—15 mm.

The m. p. is $1280° \pm 20°$. The regulus of metal has hardness between 6 and 7, and scratches glass; the freshly-filed metal is steel-grey in colour. At the ordinary temperature it is brittle, but at higher temperatures ductile. The specific electrical conductivity is $5·41 \times 10^4$ reciprocal ohms.

The resistance to the action of water is caused by a surface film of oxide. As anode in a solution of sodium ammonium phosphate it acts as a rectifier, similarly to aluminium. It is not so readily attacked by alkalis as is usually stated to be the case. T. S. P.

Compounds of Arsenious Acid with Glucinum. BENNO BLEYER and BR. MÜLLER (*Arch. Pharm.*, 1913, **251**, 304—319. Compare A., 1912, ii, 644; this vol., ii, 137).—It was found to be impossible to prepare definite compounds of arsenious acid with glucinum, and consequently the behaviour of a colloidal precipitate (gel) of glucinum hydroxide with solutions of arsenious anhydride in water was investigated. It was found that when using even freshly prepared glucinum hydroxide (10 grams of precipitate=0·6349 gram GlO) only very small amounts of the arsenious anhydride were absorbed, due probably to the rapidity with which the precipitated hydroxide loses its colloidal character. With glucinum hydroxide precipitated by ammonia and ammonium chloride in the arsenious solution larger quantities of the anhydride were absorbed at the ordinary temperature, and these were absorbed in accordance with the adsorption law. At the temperature of boiling water the quantities absorbed were less than at the ordinary temperature, and followed Henry's law, that is, the relation between the quantity of arsenious anhydride absorbed and that remaining in the solution was constant. T. A. H.

Electrometallurgy of Zinc. Gino Gallo (*Gazzetta*, 1913, **43**, i, 361—385).—Reviewing the methods employed in the metallurgy of zinc, the author points out that electrolysis is not successful because, when zinc chloride is employed, it is necessary either to obtain the absolutely anhydrous salt or to electrolyse for a long period before the separation of metallic zinc begins. He finds, however, that these difficulties can be overcome by employing zinc fluoride instead of the chloride. Anhydrous zinc fluoride is readily prepared by heating for two hours at 125° either the hydrated fluoride or the silicofluoride. When the anhydrous salt is heated, it reacts with the water vapour of the flame below its m. p. (734°), yielding hydrogen fluoride and zinc oxide. If, however, it is previously mixed with an equal amount of sodium chloride, or even with half that quantity, the m. p. is lowered to about 500° and fusion is readily effected. When the fused mixture is electrolysed, a very small current is sufficient to cause the immediate separation of shining globules of metallic zinc, whilst if zinc oxide is added to the fused mass from time to time, only oxygen is evolved at the positive pole, a tension of 3 volts being employed. Details are given of a large-scale process founded on this method, using blende or calamine. The previous removal of the iron of the ores is desirable, for if this is not done the iron accumulates in the electrolysing vessel. The removal can be effected by magnetic selection, or by a new method here described, which consists in treating roasted blende or natural calamine with hydrofluosilicic acid. A pure solution of zinc silicofluoride is thus obtained, whilst all the iron is precipitated as ferric hydroxide. If the solution is evaporated and the residue heated at 150°, the zinc salt decomposes, leaving zinc fluoride. The silicon fluoride evolved is collected and used again. R. V. S.

Zincoso-zincic Chloride. Rasik Lal Datta and Haridas Sen (*J. Amer. Chem. Soc.*, 1913, **35**, 779—780).—*Zincoso-zincic chloride*, Zn_3Cl_5 or $ZnCl,2ZnCl_2$, obtained by the gradual addition of zinc to fused zinc chloride until it ceases to be dissolved, is a bluish-white, hygroscopic solid, and is rapidly hydrolysed by water. The study of this compound is being continued, and attempts are being made to prepare zincous chloride, ZnCl. E. G.

Etched Figures of Crystals of Zinc Ammonium Sulphate. N. I. Surgunov (*Bull. Acad. Sci. St. Pétersbourg*, 1913, 405—406).—The etched figures of crystals of zinc ammonium sulphate, $Zn(NH_4)_2(SO_4)_2,6H_2O$, show the symmetry to be expected from holohedral forms of the monoclinic system (compare Tutton, T., 1905, 1140). T. H. P.

Arsenic Compounds of Cadmium. Sergei F. Schemtschuschny (*Intern. Zeitsch. Metallographie*, 1913, **4**, 228—247).—The freezing-point curve of the alloys of cadmium and arsenic, which has been determined as far as 70 atomic % As, has two maxima, corresponding with the compounds Cd_3As_2, m. p. 721°, and

$CdAs_2$, m. p. 621°, respectively. The formation of the latter compound is readily suppressed by undercooling, so that the descending branch of the Cd_3As_2 curve may be followed as far as a metastable eutectic point at 526°. The compound Cd_3As_2 has a polymorphic transformation point at 578°. The normal eutectic points are at 319°, close to the freezing point of cadmium and at 610°. Solid solutions are not formed to an appreciable extent, and there is no indication of the formation of a compound, CdAs, even after prolonged heating of the solid alloys. The structure of alloys rich in arsenic varies greatly with the presence or absence of inoculation.

The compound Cd_3As_2 is grey with a red shade, whilst $CdAs_2$ is very dark grey with a blue shade.

The atomic-volume curve consists of three straight lines, with well-marked breaks at the composition of the two compounds. Both compounds are formed from their components with considerable expansion. Cd_3As_2 has D 6·25 and $CdAs_2$ D 5·86. The latter compound is harder than either component. C. H. D.

Solid Solutions of Compounds of Calcium, Strontium, Barium, and Lead with those of the Rare Earths. I. FERRUCCIO ZAMBONINI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 519—524).—The author proposes to ascertain the existence of solid solutions of the types mentioned, because it is assumed in the explanation of the composition of some important minerals containing the rare earths. The present paper gives the results obtained by the method of thermal analysis in the case of the system $PbWO_4$–$Ce_2(WO_4)_3$. The m. p. of cerium tungstate is 1089°, that of lead tungstate 1125°. The two substances are miscible in all proportions, both in the liquid and in the solid state, and the curve shows no thermal effect at any point. R. V. S.

Metallurgy of Copper as Carried Out in Ancient Times in the Lands which are Populated by Rumanians at the Present Time. C. NICOLESCU-OTIN (*Bull. Sci. Acad. Roumaine*, 1912-3, **1**, 297—302).—The author has analysed various prehistoric articles made of copper, or of copper and tin, and also various Roman articles made respectively of copper, lead, and zinc; copper, lead, and tin; and copper, lead, tin, and zinc. Comparison of the impurities present in these articles with the impurities present in the Rumanian ores of the present day, lead him to the conclusion that the metals used were obtained from the local ores. Apparently the prehistoric metallurgists could smelt copper almost as well as the Romans, since their products contained at times as much as 99% copper. T. S. P.

Cupric Iodate. JAMES F. SPENCER (*Zeitsch. physikal. Chem.*, 1913, **83**, 290—296).—The preparation of cupric iodate is described, and the action of heat and its solubility in water and solutions of potassium iodate and copper sulphate of varying concentrations determined. The solubility is determined by measuring the ionic

concentration of both ions by means of electrodes of the second and third types. The electrode for measuring the iodate ion is described (A., 1912, ii, 1129). An electrode of the third type is described for the measurement of cupric ions; it has the form $Hg|Hg_2(IO_3)_2|Cu(IO_3)_2|Cu^{\cdot\cdot}$ and the value $\epsilon = 0{\cdot}6060 + 0{\cdot}0297 \log Cu^{\cdot\cdot}$ at 25°. The solubility of $Cu(IO_3)_2,H_2O$ at 25° is $3{\cdot}30 \times 10^{-3}$ gram mols. per litre, and it is depressed normally by the addition of either copper sulphate or potassium iodate to the solution, without the formation of complexes. Cupric iodate loses its water of crystallisation at 240°, but only takes it up again very slowly even when placed in water. J. F. S.

New Method for the Preparation of Ammoniacal Copper Salts. KSHITIBHUSHAN BHADURI (*Zeitsch. anorg. Chem.*, 1913, **81**, 406—408. Compare this vol., ii, 53).—Powdered cupric oxide is rubbed with concentrated ammonia until dissolved; the ammonium salt of the required acid is then added, and the rubbing continued until solid salt separates.

Ammonical cupric thiocyanate, $Cu(CNS)_2,4NH_3$, forms blue crystals, which lose first 2 and then $3NH_3$. Ammoniacal cupric ferricyanide, $Cu_3[Fe(CN)_6]_2,5NH_3$, prepared from ammoniacal cupric hydroxide and potassium ferricyanide, forms black crystals, and is very stable. $Cu(NO_3)_2,3NH_3,2H_2O$ is stable in air. $CuI_2,6NH_3$ is blue and unstable. C. H. D.

The Sulphate-tensions and Affinity of the Rare Earths. LOTHAR WÖHLER and M. GRÜNZWEIG (*Ber.*, 1913, **46**, 1726—1732).—The sulphate-tensions of the rare earths have been measured (compare A., 1908, ii, 290) over a range of temperatures varying from 800 to 1020°, in order to obtain a measure of their affinity, that is, of their basic character. The following table shows the order in which the earths arrange themselves according to the value of the partial pressure (in mm. of mercury) of sulphur trioxide (P^{SO_3}) over their sulphates at 900°, and also the heat of dissociation (Q), calculated according to Nernst's theorem:

Metal...	Sc.	Sa.	Gd.	Nd.	Pr.	Er.	Yb.	Lu.	Yt.	La.
P_{SO_3}	11	8	7	6	5·5	5	4	3·5	3	2
Q (Cal.) ...	54·5	56·6	56·9	57·2	57·4	57·6	58·2	58·5	58·9	59·8

These figures show that the rare earths belong to the strongest bases; the heats of dissociation are the greatest hitherto observed for tervalent sulphates. The above order is, however, different from that which has hitherto been assumed, namely, Sc, Yb, Er, Gd, Sa, Y, Ce^{III}, Nd, Pr, La.

The basic sulphates of the above elements are readily obtained by heating the sulphates in the air at 800—850°; *basic neodymium* and *praseodymium sulphates* both conform to the general formula: R_2O_3,SO_3.

The tension curves run almost parallel and very close to each other, the horizontal difference between them, measured in degrees centigrade, being small. This means that it would be more or less difficult to separate two sulphates from each other by heating them

to a constant, intermediate temperature at which one gives the basic sulphate and the other remains undecomposed and soluble in water. An example is given, however, of the separation of an artificial mixture of neodymium and praseodymium sulphates by this means.

T. S. P.

Copper–Aluminium Alloys with 84 to 90% of Copper. H. HANEMANN and P. MERICA (*Intern. Zeitsch. Metallographie*, 1913, **4**, 209—227).—A close analogy is observed between the structure of these alloys and that of steel. Quenching from above the eutectoid point gives a martensitic structure in the case of hypoeutectoid alloys. Hypereutectoid alloys, like high carbon steels, yield a homogeneous solid solution when quenched from a sufficiently high temperature, the β-phase in copper-aluminium alloys taking the place of austenite in steels, whilst the γ-phase resembles cementite. The microscopic structures are discussed in detail. C. H. D.

The β-Constituent of Aluminium Bronzes. A. PORTEVIN (*Intern. Zeitsch. Metallographie*, 1913, **4**, 257—260. Compare preceding abstract).—The β-constituent in alloys of copper and aluminium may occur in a cellular or lamellar form, the cellular type predominating in the neighbourhood of primary crystals.

C. H. D.

Crystallographic Investigation of Hydrated Aluminium and Ferric Nitrates. N. I. SURGUNOV (*Bull. Acad. Sci. St. Pétersbourg*, 1913, 407—412).—Nonahydrated aluminium and ferric nitrates deliquesce rapidly in the air at the ordinary temperature. For monoclinic crystals of the aluminium salt, $Al(NO_3)_3,9H_2O$, which show several faces not observed by Soret (*Arch. Sci. phys. nat.*, 1886, [iii], **16**, 460), the author finds $a:b:c=$ $1·1321:1:1·9174$, $\beta=131°32'$; Soret gave $a:b:c=$

$$1·13398:1:1·91913,\ \beta=131°36'.$$

The ferric salt, $Fe(NO_3)_3,9H_2O$, forms pale red, monoclinic crystals, $a:b:c=1·1296:1:1·9180$, $\beta=131°34'$. T. H. P.

The System Manganese–Silver. G. ARRIVAUT (*Compt. rend.*, 1913, **156**, 1539—1541).—The author has made a thermal study of the system manganese–silver, and the results indicate the existence of a definite *compound*, $MnAg_2$. A microscopic examination of the solidified mixtures of various concentrations in manganese, and a study of the *E.M.F.* of such mixtures against an electrode of silver support this view in opposition to Hindrichs (A., 1908, ii, 856). This compound forms a continuous series of mixed crystals with silver, and its limit of miscibility, in the liquid state, with manganese is about 30% of manganese. W. G.

A Basic Salt of Manganese Iodide. PETR. KUSNEZTOV (*Chem. Zentr.*, 1913, i, 1659; from *Izvesta Don. Polytech. Inst. Novotscherkask*, 1913, **2**, ii, 1—7).—When air is passed through a concentrated solution of manganese iodide or when the solution is repeatedly

evaporated, a *basic manganese iodide*, $MnI_2,MnO,6H_2O$, is formed in colourless, microscopic, doubly-refractive needles, which gradually give up iodine at 115—120°. J. C. W.

Tervalent Manganese. I. JULIUS MEYER (*Zeitsch. anorg. Chem.*, 1913, **81**, 385—405).—Potassium manganicyanide is more easily prepared than other manganic salts. For its preparation 400 grams of crystallised potassium cyanide are dissolved in the smallest possible quantity of water, and 100 grams of powdered manganous carbonate are added. Air is then drawn through. At first a blue mass of the manganocyanide, $K_4Mn(CN)_6$, is formed, and this oxidises, becoming orange-red. If gently warmed on the water-bath, about a day is necessary for the reaction. The precipitate is collected, washed with alcohol and ether, and dried in air. The reaction is: $2K_4Mn(CN)_6 + O + H_2O = 2K_3Mn(CN)_6 + 2KOH$. The salt may be recrystallised from 10% potassium cyanide solution. Boiling with water precipitates manganic hydroxide:

$$K_3Mn(CN)_6 + 3H_2O = 3KCN + 3HCN + Mn(OH)_3.$$

The hydrolytic constant at 18° is $K = 2 \times 10^{-10}$. Concentrated solutions are reddish-yellow, probably owing to the presence of small quantities of manganic cyanide.

Precipitated manganic hydroxide closely resembles ferric hydroxide. It is not altered by shaking with water and air, and is therefore not to be regarded as a mixture of manganous hydroxide and the peroxide. It dissolves in cold concentrated hydrochloric, sulphuric, phosphoric, and hydrofluoric acids, the last three solutions being fairly stable. The double fluoride, K_2MnF_5, may be isolated in the solid state. Heating converts the hydroxide into the oxide, with partial oxidation. C. H. D.

Allotropy in General and that of Iron in Particular. CARL BENEDICKS (*J. Iron Steel Inst.*, 1912, **86**, 242—294. Compare Smits, A., 1912, ii, 165, 769, 1058, 1176).—The expansion of silver iodide has been determined in a small apparatus in which the rod of substance is held between two silica rods. From $-180°$ silver iodide has a positive coefficient of expansion, which at $-100°$ is $1{\cdot}8 \times 10^{-6}$, but becomes imperceptible at 0°. From 40° to 140° a gradual contraction occurs, followed by a sudden and very large contraction at about 147°. There is a much larger positive coefficient of expansion above 147°. With rapid heating the contraction from 140° onwards is more gradual, and is only complete at 165°. These results indicate a solubility of the one modification in the other below 147°.

The allotropy of iron is discussed from this standpoint. The point Ar_2 is regarded as the mere termination of the Ar_1 change. β-Iron is then a solid solution of γ-iron in α-iron, the quantity of the former increasing with the temperature. C. H. D.

Metallography of Some Ancient Iron Objects. H. HANEMANN (*Intern. Zeitsch. Metallographie*, 1913, **4**, 248—256).—An ancient Celtic tool from Steinsburg, near Römhild, consists mainly

of ferrite and pearlite with slag inclusions, and has been prepared by fusion. The point, however, consists of martensite, and has been hardened in water without subsequent tempering. This is evidence of the great stability of martensite at the ordinary temperature. An axe from the same neighbourhood consists of soft, almost carbonless iron. A Greek faun, dating from the beginning of the Christian era, consists of cast iron containing phosphorus. A Roman discus consists of wrought iron. C. H. D.

Electrolytic Method for the Prevention of the Corrosion of Iron and Steel. JOHN K. CLEMENT and L. V. WALKER (*J. Ind. Eng. Chem.*, 1913, **5**, 361—366).—Results of experiments carried out by the authors show that the corrosion of iron immersed in sulphuric acid may be prevented by the application of a counter *E.M.F.*; the density of the current required depends on various factors, the more important being acid concentration, amount of dissolved oxygen, and degree of circulation of the electrolyte. The influence of these factors has been investigated, and curves are given showing the current density necessary under various conditions. The current density required can be calculated approximately from the loss in weight of the unprotected metal under given conditions. W. P. S.

A New Chemical Cause for the Rusting of Iron. WILHELM VAUBEL (*Chem. Zeit.*, 1913, **37**, 693—694).—Although nitrates are known to accelerate the action of water on iron, the phenomenon does not appear to have been systematically examined.

Ammonium nitrate is the most effective of this class of salt in attacking iron, and it is very generally present in common water in contact with iron, for this metal will reduce a portion of the dissolved nitrates to ammonia; the same process, namely, the reduction of the nitrate radicle to ammonia, occurs in the action of ammonium nitrate on iron, the latter undergoing oxidation. The rusting is assisted by the increased activity of oxygen at the attacked spot, and also by the action of the water itself, which, it is stated, in the presence of ammonium nitrate will act on iron, forming iron oxide and hydrogen, especially if the temperature is slightly raised. Under ordinary conditions the reduction of nitrate to ammonia by iron occurs without any appreciable formation of nitrite (compare Droste, *Chem. Zeit.*, 1912, **36**, 678).

As has already been shown (Bonnema, *Chem. Zeit.*, 1903, **27**, 148, 825), ferrous oxide and hydroxide in contact with air give rise to a certain amount of nitrite. If, as is quite possible, nitrate is produced in the same manner, it is clear that for the rusting of iron only a minimal quantity of an ammonium salt need be present, for the ammonium nitrate could then be easily formed.

Ammonium nitrite and nitrites of the alkali metals are almost without any action on iron, as also is ammonium nitrate in alkaline solution. Nitrates of the alkali metals are not nearly so active as ammonium nitrate. The action of the last salt gives rise to ferrous and ferric hydroxides, and also to a certain amount of dissolved

iron, apparently in the form of a complex ion, as the usual reagents do not affect the solution. D. F. T.

Copper in Steel. The Influence on Corrosion. D. M. BUCK (*J. Ind. Eng. Chem.*, 1913, 5, 447—452).—The steels used were two basic open hearth steels, containing respectively: C, 0·10; Mn, 0·34; S, 0·034; P, 0·019; and C, 0·13; Mn, 0·45; S, 0·036; P, 0·042; and one Bessemer steel containing C, 0·08; Mn, 0·46; S, 0·070; P, 0·092. The amount of copper added was sufficient to give a copper content of either about 0·15 or 0·25%. The steels with and without copper were put through the same mill operations, and were finally obtained as corrugated strips, which were tested for atmospheric corrosion at three different stations: (1) in the Pennsylvania Coke regions, where the air contains notable amounts of sulphurous and sulphuric acids, etc.; (2) on the sea coast; (3) in the country. The strips were put on open sheds and exposed to the atmosphere on all sides, the time of the test lasting for several months; observations were made from time to time.

Full details are given with respect to each test piece. As a general result it may be considered as proved that copper has a very beneficial effect in retarding corrosion; the copper-containing steels resist the atmosphere from one and a-half to two times as well as normal steels without copper, and there is little or no difference in the average between a copper content of 0·15 and 0·30. Accelerated acid tests gave similar results, but it should be pointed out that in some cases the results of the acid tests are directly opposite to the results of the atmospheric tests. T. S. P.

Influence of Various Elements on the Corrodibility of Iron. CHARLES F. BURGESS and JAMES ASTON (*J. Ind. Eng. Chem.*, 1913, 5, 458—462).—Electrolytic iron, alloyed with various other elements, was used; the test samples were submitted both to acid (20% sulphuric acid for one hour) and atmospheric corrosion, in the latter case for a period of 162 days.

Electrolytic iron showed no special resistance to corrosion, in contradiction to the commonly accepted view that a close approach to purity would indicate a high resistance to acid attack. The other alloys behaved as follows, the added metal being printed in italics: *Aluminium*, 0·067—1·33%. No particular effect. *Arsenic*, 0·29—3·56%. Fair resistance to acid attack, which resistance falls off appreciably with increase in arsenic content. Atmospheric corrosion about the same as for electrolytic iron. *Cobalt*, 1·04—5·05%. Resistance to acid not particularly striking, but falls off appreciably with increasing cobalt content; the same general effect occurs in the atmospheric tests. Effect is not nearly so good as with nickel. *Copper*, 0·089—7·05%. A marked decrease in corrosion (compare preceding abstract). *Lead*, 0·061%. Atmospheric corrosion decreased by one-half, but acid corrosion the same. *Manganese*, 0·50—10·42%. No particular effect, and results inconsistent. *Nickel*, 0·27—75·06%. Good effect, there being a general tendency for increased resistance with increasing content of nickel.

Selenium, 0·017%. Acid resistance very low, and atmospheric corrosion high. *Silicon*, 0·23—2·82%. Corrosion generally high. *Silver*, 0·28—0·69%. Behaviour similar to electrolytic iron. *Tin*, 0·28—1·56%. Resistance to acid is good with small tin content, but diminishes as percentage of tin increases. Atmospheric tests give no particular result. *Tungsten*, 0·40—23·86%. Tests are very good, but irregular. Markedly decreased corrosion is obtained only after high tungsten addition.

There does not seem to be any quantitative relation between acid and atmospheric corrosion. T. S. P.

Iron and Nitrogen. JOHN H. ANDREW (*J. Iron Steel Inst.*, 1912, **86**, 210—235).—A special form of carbon tube electric furnace is used, in which pressures up to 1000 atmospheres may be obtained. Iron is melted in magnesia crucibles, the temperature being determined by means of an optical pyrometer, sighted through a glass window. The iron absorbs small quantities of nitrogen when melted under a high pressure of the gas. The absorption of 0·3% of nitrogen entirely suppresses the critical points of pure iron, and this nitrogen is only removed by prolonged heating in a vacuum. With steel containing 0·6% of carbon, the absorption of 0·25% of nitrogen lowers the Ar_1 point. Hydrogen has no effect on the critical points of steel when introduced into the liquid metal under pressure. C. H. D.

The Separation of Graphite in Alloys of Iron and Silicon. GEORGES CHARPY and ANDRÉ CORNU (*Compt. rend.*, 1913, **156**, 1616—1618).—In alloys of iron and silicon containing but little carbon, the carbon is entirely precipitated as graphite by annealing, provided that the silicon content is above 3·5% and that the annealing is carried out at a temperature above 750° and below a certain limit temperature, which is a function of the total carbon in the alloy. The bottom limit of this temperature range is lowered and the top limit raised as the percentage of silicon increases, and the top limit is raised when the percentage of carbon increases. W. G.

The Gases Evolved on Heating Steel to its Melting Point in a Vacuum. G. WESLEY AUSTIN (*J. Iron Steel Inst.*, 1912, **86**, 236—241).—The iron or steel is used in the form of a cylindrical test-bar, and is enclosed in a gas-tight insulated steel tube and heated by means of an alternating current. The gas is pumped off and analysed. In steels the quantity of gas evolved increases with the carbon content. Cast iron contains a smaller quantity of gas, and the proportion of carbon monoxide is smaller. C. H. D.

New Method of Revealing Segregation in Steel Ingots. SIR ROBERT HADFIELD (*J. Iron Steel Inst.*, 1912, **86** 40—47).—Segregation in trial ingots of steel may be recognised by adding some molten copper when partial solidification has taken place. The copper remaining liquid longer than the steel is drawn into any cavities which are formed, and is detected by its colour when the solid ingot is cut through. C. H. D.

The Transformation Points and the Structure of Nickel-chrome Steels. LÉON GUILLET (*Compt. rend.*, 1913, **156**, 1774—1776. Compare A., 1903, ii, 650; 1904, ii, 739).—A study of the influence of chromium on the transformation points of nickel steels. The metallographic examination of various alloys shows that for the same content in carbon and chromium a perlitic steel containing nickel possesses a marked tendency for the eutectoid structure; thus a steel containing 0·25% C, 2·40% Ni, and 0·66% Cr has the appearance of an ordinary steel containing 0·75% C, whilst one containing 0·30% C and 0·78% Cr corresponds to an ordinary steel containing 0·35% C. The addition of chromium to a nickel steel acts differently according to the nickel and carbon content of the alloy. Whilst 0·6% Cr does not lower the transformation points of steels containing 2·5 to 3·4% Ni and 0·08 to 0·25% C, an addition of 1·2% Cr produces a marked effect on steels containing 4 to 6·25% Ni, increasing the hysteresis very considerably. W. G.

Ammonium Ferrous Sulphate and its Alkali-metal Isomorphs. ALFRED E. H. TUTTON (*Proc. Roy. Soc.*, 1913, *A*, **88**, 361—387).—A full crystallographic investigation of ammonium ferrous sulphate. The principal conclusion arrived at, which further confirms the deductions from the previous investigations of the zinc and magnesium groups of double sulphates and selenates, and those from the study of the magnesium group of double chromates, is the following: The ammonium salts are truly isomorphous with the potassium, rubidium, and cæsium salts of the large monoclinic series of salts having the general formula $R_2M\{(S,Se,Cr)O_4\}_2,6H_2O$, but not eutropic with them, the three latter salts alone being eutropic. It is a singular fact that scarcely any change in structural dimensions occurs when ammonium and rubidium are interchanged for each other, that is, when ten atoms ($2NH_4$) replace two atoms (Rb_2), for they do so without appreciably altering the dimensions of the unit cell of the space-lattice.

T. S. P.

The Instability of Ferric Silicofluoride and its Spontaneous Transformation into Another Double Fluoride of Silicon and Iron. ALBERT RECOURA (*Compt. rend.*, 1913, **156**, 1618—1620).—In further confirmation of the behaviour of ferric fluoride in solution (compare A., 1912, ii, 353), the author finds that normal ferric silicofluoride cannot exist when it is prepared in solution either by saturating hydrofluosilicic acid with ferric hydroxide, or by double decomposition, since it decomposes immediately according to the equation:

$$Fe_2F_6,3SiF_4 = SiF_4 + Fe_2F_6,2SiF_4,$$

the silicon fluoride liberated being decomposed by the water. On leaving this solution of the ferric silicofluoride to evaporate in the air a colourless syrup is obtained, corresponding in composition with $Fe_2F_6,2SiF_4,Aq$. On pushing the evaporation further in a desiccator, the syrup slowly evolves silicon fluoride, and tends to become transformed into hydrated ferric fluoride.

Chromium silicofluoride undergoes a similar decomposition in aqueous solution. W. G.

Univalent Nickel Compounds. I. ITALO BELLUCCI and R. CORELLI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 603—608).—The present paper deals chiefly with the work of Moore (A., 1894, i, 102; 1895, ii, 168), who by reducing potassium nickelocyanide obtained a red solution, which, he considered, contained a nickel compound of the type Ni_3X_2. The authors find that Moore's method of analysis (depending on the reduction of ammoniacal silver nitrate) is not sufficiently accurate to support his conclusions. R. V. S.

Chromous Compounds which are Stable in the Air. WILHELM TRAUBE and W. PASSARGE (*Ber.*, 1913, **46**, 1505—1508).—The authors have found that chromous salts form stable double compounds with hydrazine or hydrazine salts. They may be exposed to the air for days without changing their properties; in fact, some of them are stable when suspended in water and exposed to the air. Their stability depends probably on their slight solubility in water and also on the reducing properties of the hydrazine; if they are dissolved in acids or in ammonia, the solutions possess the ordinary properties of solutions of chromous salts.

The salts are of the type $MCl_2,2N_2H_4$ and $MSO_4(N_2H_4)_2H_2SO_4$, where M is a bivalent metal; numerous salts of this type, containing metals other than chromium, are already known (compare Curtius and Schrader, A., 1895, ii, 10; Ferratini, A., 1912, ii, 345).

The general method of preparation is from chromous acetate, which is suspended in air-free water covered with a layer of light petroleum. The acetate is dissolved by the addition of exactly the necessary quantity of dilute acid, and then a solution of hydrazine hydrate or sulphate added. The desired salt precipitates readily, and after being collected it is washed with water, alcohol, and ether and dried over sulphuric acid.

Chromous dihydrazine chloride, $CrCl_2,2N_2H_4$, is a lilac-coloured powder, as also is the corresponding *bromide*, $CrBr_2,2N_2H_4$. The *iodide*, $CrI_2,2N_2H_4$, is greyish-blue. The *double salt* of chromous and hydrazine sulphates, $CrSO_4,(N_2H_4)_2H_2SO_4$, is a sky-blue, crystalline powder, which is sparingly soluble in water. T. S. P.

A Simple Method for the Preparation of Molybdenum and Tungsten Carbides. SIEGFRIED HILPERT and M. ORNSTEIN (*Ber.*, 1913, **46**, 1669—1675).—Molybdenum and tungsten carbides can be obtained by heating the finely powdered metals in carbon monoxide or in a mixture of methane and hydrogen. Experiments made at different temperatures show that the limiting amount of carbon taken up corresponds with simple stoicheiometric proportions. These limits, when molybdenum is treated with carbon monoxide, correspond with the carbide, Mo_2C, at 600° and 1000°. At 800° the composition varied between MoC and Mo_2C_3, the relations being

made more complex by the effect of temperature on the equilibrium $2CO \rightleftarrows C + CO_2$, and on the velocity of reaction.

At 1000° tungsten gives the carbide W_3C_4 in carbon monoxide, and the carbide WC in a mixture of methane and hydrogen (1 : 1) at 800°. The hydrogen is admixed with the methane in order to suppress the dissociation: $CH_4 \rightleftarrows C + 2H_2$.

The carbides are also formed when the trioxides of the metals are used instead of the metals. T. S. P.

The Constitution of the Paramolybdates and the Paratungstates. HIPPOLYTE COPAUX (*Compt. rend.*, 1913, **156**, 1771—1774).—The author suggests that the constitution of the paramolybdates should be represented by the formula

$$M^I_6[Mo(Mo_2O_7)_3O_3],$$

where M^I is a univalent metal, and that they are thus derived from an orthomolybdic acid, H_6MoO_6, by the substitution of Mo_2O_7 for each of three oxygen atoms. Similarly, complex salts, such as sodium molybdoaluminate and molybdoperiodate, would be represented by $Na_3Al(Mo_2O_7)_3$ and $Na_5I(Mo_2O_7)_3O_3$, corresponding with the orthoaluminate, Na_3AlO_3, and the periodate, Na_5IO_6.

The paratungstates he considers as hydrotungstates, and represents them by $M_5^I[H(W_2O_7)_3]$.

In support of these formulæ he instances their behaviour with respect to the absorption of ultraviolet light and dehydration on heat; thus the paratungstates absorb less than the metatungstates, but much more than the simple tungstates. Similarly, the paramolybdates absorb less than the silicomolybdates, but more than the simple molybdates or the molybdoperiodates, which are obviously of a complex nature. W. G.

Crystallisation of Fusions of Tin Chloride with Potassium and Sodium Chlorides. G. RACK (*Centr. Min.*, 1913, 373—379).—Mixtures of tin chloride (m. p. 239°) and potassium chloride (m. p. 777°) in various proportions were fused, and the concentration-temperature diagram given. There are double salts, $3SnCl_2,KCl$ (m. p. 208°) and $SnCl_2,KCl$ (m. p. 224°), and eutectics with 17 mol. % KCl and 38 mol. % KCl at 201° and 180° respectively. The pair tin chloride and sodium chloride (m. p. 800°) yields no double salt, but a eutectic with 32 mol. % NaCl at 183°. L. J. S.

New Method for the Preparation of Vanadium Tetrachloride. A. T. MERTES (*J. Amer. Chem. Soc.*, 1913, **35**, 671—672).—Vanadium tetrachloride can be prepared by passing dry chlorine over ferro-vanadium contained in a hard glass tube and heated by means of a combustion furnace. The reaction takes place thus: $FeV + 7Cl = FeCl_3 + VCl_4$. The vanadium chloride distils over, whilst the ferric chloride remains in the tube. This method is considered superior to any recorded previously. Vanadium tetrachloride is best preserved by dissolving it in carbon tetrachloride. Ferric chloride is insoluble in this solvent, and hence vanadium chloride can be easily freed from it. E. G.

The Synthetic Silicates of Bismuth. C. NICOLESCU OTIN (*Bull. Sci. Acad Roumaine*, 1912–13, **1**, 189—196).—Various mixtures of bismuth oxide and silica were melted in an electric furnace, and cooling curves of the fusions taken. The products were also investigated microscopically. Mixtures of bismuth oxide and silica in the following molecular proportions gave rise to compounds: 1:8, 1:3, 1:2, 2:3, 1:1, 3:2, 2:1, 3:1, and 10:1. The respective freezing points (points at which crystallisation commenced), and densities at 20°, of these compounds were as follows: 992°±7°, 6·623 847°±1°, 8·109; 873°±4°, 8·657; 877—736°, 8·984; 890—772°, 8·924; 791°, 8·388; 803—843°, 9·138; 822°±4°, 8·897; 832°±1°, 9·136. Pure bismuth oxide melted at 825°±1° and had D^{20} 8·559. T. S. P.

Action of Hypophosphite Solutions on Platinum Salts. ADOLF SIEVERTS [and, in part, ERNST PETERS] (*Zeitsch. Chem. Ind. Kolloide*, 1913, **12**, 263—268).—The paper deals with the investigation of the action of sodium hypophosphite on very dilute solutions of potassium platinochloride. It is shown that the course of the reaction varies with the molecular ratio of the reacting substances. If the hypophosphite is added in great excess ($120NaH_2PO_2 : 1K_2PtCl_4$), then on warming light brown or yellow stable solutions are formed, which may be evaporated to dryness without decomposition, and do not show the usual platinum reactions. These solutions are shown by ultra-microscopic examination to be solutions of crystalloids. On warming, the yellow solutions give rise to a vigorous evolution of hydrogen, and it is probable that the solution contains a complex compound of platinous chloride and sodium hypophosphite. The smaller the molecular relationship between the reacting substances the darker the solution on warming; if the ratio lies between 20:1 and 40:1 a dark brown solution is obtained, which is not sensitive to the addition of electrolytes, and slowly deposits a precipitate and becomes colourless. This solution also gives a vigorous evolution of hydrogen on warming. Similar dark brown solutions can be obtained by substituting sodium phosphite for the hypophosphite. These solutions liberated hydrogen on warming, but much more slowly than solutions containing hypophosphite. The reddish-brown solutions can be rendered stable by the addition of gelatin or gum arabic, and then show similarities, particularly in respect of their absorption spectra, to the "red platinum" obtained by L. Wöhler (A., 1910, ii, 1075). The evolution of hydrogen is to be represented by the reaction $Na_2HPO_2 + H_2O = Na_2HPO_3 + H_2$, which is catalysed by the bivalent platinum compound. If the molecular ratio of the reacting substances is made 1:1, then even in extremely dilute solutions greyish-brown to brown liquids are obtained, which are of themselves stable but very sensitive to the addition of electrolytes which produce very rapidly dark-coloured precipitates. These solutions are similar to the black solutions of platinum sols produced by Bredig's method. They act catalytically on hydrogen peroxide and on electrolytic gas at the ordinary temperature with fair rapidity. They are shown by

optical means to be platinum sols of high dispersity. On the addition of an electrolyte the Tyndall cone becomes visible, and particles are visible in the ultra-microscope showing rapid movement. Chloroplatinic acid and potassium platinichloride are not suitable for the preparation of platinum sols, because at an equal dilution they either do not react at all or only very slowly with sodium hypophosphite. J. F. S.

The Anhydrous Platinum Haloids, $PtCl_4$ and $PtBr_4$. ALEXANDER GUTBIER and FR. HEINRICH (*Zeitsch. anorg. Chem.*, 1913, **81**, 278—384). [With L. von MÜLLER and J. LIEBERS.]—Anhydrous platinic chloride is most conveniently prepared by heating hydrogen platinichloride in a stream of dry chlorine in an apparatus containing diphenylamine. The product is irregularly crystalline, and not very hygroscopic, but absorbs water slowly.

[With M. BLUMER.]—Platinic bromide has not been obtained in a pure condition. Hydrogen platinibromide is obtained by heating platinum sponge with bromine and concentrated hydrobromic acid in a sealed tube at 180°, but dissociation into platinous bromide and bromine always takes place during drying to an extent which depends on the temperature. C. H. D.

The Stability Regions of the Four Anhydrous Platinum Chlorides; the Volatility of the Metal in Gaseous Chlorine and the Preparation of Oxygen-free Chlorine. LOTHAR WÖHLER and S STREICHER (*Ber.*, 1913, **46**, 1591—1597).—The temperatures of decomposition or formation, in an atmosphere of chlorine under normal pressure, were found to be as follows: For platinum tetrachloride, 370°; at 374° it lost some chlorine, to absorb it again at 364°. The three corresponding temperatures for the trichloride were 435°, 440°, and 430°. The decomposition temperature of platinum dichloride is 582°.

Evidence was obtained for the existence of a yellowish-green *platinum monochloride*, PtCl, which, however, is stable only over 1—2° between 581° and 583°.

The molecular heats of formation in Calories of the chlorides from chlorine and the next lower chloride are calculated to be: PtCl, 16·10; $PtCl_2$, 16·08; $PtCl_3$, 13·1; and $PtCl_4$, 11·77. The valency isobars of the chlorides of both iridium and platinum do not show any regularities in their relations with each other.

Investigation of the volatility of both iridium and platinum in a current of chlorine showed the formation and volatilisation of exothermic chlorides in the gaseous phase at temperatures above those in which the solid phase could exist.

Oxygen-free chlorine cannot be obtained from potassium permanganate and hydrochloric acid (Wedekind, P., 1909, **25**, 59); it is necessary to use hydrated manganese dioxide in place of the permanganate. T. S. P.

The Action of Complex-forming Acids or their Salts on Platinum Ammonia Compounds I. Reactions with Potassium Xanthate. LUDWIG RAMBERG (*Ber.*, 1913, **46**, 1696—1700).—Certain acids, especially those containing sulphur, react with

platinum ammonias, ammonium salts being eliminated and salts formed which must be classed as internal complex salts. The reaction takes place according to the scheme: $Pt(NH_3)_2X_2 + 2HA = PtA_2 + 2NH_4X$, and goes especially readily with the *cis*-platinous ammonias.

By the action of potassium xanthate (2 mols.) on *cis*-dinitratodiammineplatinum, platinous xanthate, $Pt(S{\cdot}CS{\cdot}OEt)_2$ (compare A., 1906, i, 791), results, together with considerable quantities of a brown, amorphous powder containing nitrogen. If the ammonia which is eliminated during the reaction is fixed with acetic acid, the yield of platinous xanthate is considerably increased. A similar reaction takes place with *cis*-dichlorodiammineplatinum in the presence of acetic acid; if the molecular proportions used are 1 : 1, only half the dichloro-compound enters into reaction. When *trans*-dinitratodiammineplatinum is used, an almost quantitative yield of *dixanthodiammineplatinum*, $Pt(NH_3)_2(S{\cdot}CS{\cdot}OEt)_2$, is obtained as an almost colourless, microcrystalline powder, which is not soluble in the ordinary solvents without decomposition. The fact that ammonia is not eliminated during the reaction affords fresh support to the idea that ammonia is more firmly bound in the *trans*- than in the *cis*-position. The compound loses ammonia slowly in a desiccator over concentrated sulphuric acid, and all the ammonia is eliminated on solution in glacial acetic acid, giving in this latter case platinous xanthate, two isomeric forms of which do not exist (compare A., 1910, i, 218). T. S. P.

The Behaviour of Hydrogen towards Palladium. ALEXANDER GUTBIER, HEINRICH GEBHARDT, and BERTA OTTENSTEIN (*Ber.*, 1913, **46**, 1453—1457).—The authors have investigated the absorption of hydrogen by palladium at temperatures varying between −50° and +105°. The palladium was used in the form of sponge, which was obtained by heating ammonium palladiochloride in an oxygen-free stream of carbon dioxide, the temperature used being as low as was consistent with the expulsion of all the ammonium chloride. The method of measuring the absorption of hydrogen was similar to that used by Paal and Amberger (A., 1905, ii, 397).

The results obtained are in agreement with those of Paal and Amberger, namely, that with decrease in the temperature there is a considerable increase in the absorption; they contradict the results of Hemptinne (A., 1899, ii, 228) and of Baerwald (*Compt. rend.*, 1907, ii, 202). The absorption is a minimum at 20°.

The palladium hydride obtained was pyrophoric. T. S. P.

The Anhydrous Chlorides of Iridium Corresponding with its Four Stages of Valency. LOTHAR WÖHLER and S. STREICHER (*Ber.*, 1913, **46**, 1577—1586).—Anhydrous iridium tetrachloride can be obtained from the trichloride and chlorine only at temperatures under 100° and under high pressures. At 60° and a pressure of less than 20 atmospheres it is formed within five days, using liquid chlorine; at 15° the chlorine pressure is less than 5 atmospheres. The pure substance could not be prepared. The complex H_2IrCl_6

loses hydrogen chloride only at temperatures above 100°, where the pressure of the chlorine is already greater than one atmosphere.

The best method for the preparation of iridium trichloride is by chlorination of the metal at 600—620°; the reaction is complete in a few minutes. Investigation of the chlorine pressure shows that the trichloride can exist under a chlorine pressure of one atmosphere between 763° and <100°.

The investigation of the chlorine tension of the trichloride led to the discovery of the conditions necessary for the isolation of *iridium dichloride*, $IrCl_2$, and *iridium monochloride*, IrCl. The former is a brown, crystalline substance which exists between 763° and 773° under a chlorine pressure of one atmosphere; the latter exists under the same conditions between 773° and 798°, and forms copper-red crystals; D = 10·18. Both the dichloride and monochloride are insoluble in bases or acids, even in concentrated sulphuric acid.

The molecular heats of formation of the mono-, di-, and tri-chlorides from chlorine and iridium, iridium monochloride and dichloride respectively are calculated to be 20·55, 20·05, and 19·87 Cals. respectively. T. S. P.

Measurement of the Relative Surface Energy of Iridium Trichloride. LOTHAR WÖHLER and S. STREICHER (*Ber.*, 1913, **46**, 1720—1725).—Strongly sintered iridium metal powder, which has been heated to 900°, gives the brown trichloride at 600° (compare preceding abstract). If this is reduced in hydrogen at low temperatures, and again chlorinated at 600°, the yellow trichloride is obtained. On further reduction and chlorination the dark green trichloride results. During these alternating processes the metal produced at the various stages becomes more and more finely divided, that is, more and more rich in surface energy; the same holds for the oxide obtained from the metal. The various trichlorides should therefore owe their colours to the varying stages of fineness of the particles, that is, they should be simply surface modifications; this was shown to be the case by measurements of their absorptive power towards methylene-blue, and of their velocity of sedimentation.

Measurements of their chlorine tension showed that in comparison with the sintered trichloride the surface energy is unexpectedly great, being greater than the difference between the three valency stages of the chlorides. T. S. P.

Activation of Chlorate Solutions by Osmium. II. KARL A. HOFMANN, OSKAR EHRHART, and OTTO SCHNEIDER (*Ber.*, 1913, **46**, **46**, 1657—1668).—It has been shown previously (this vol., ii, 62) that feebly acid or neutral solutions of the alkali chlorates readily act as oxidising agents in the presence of traces of osmium tetroxide. Further experiments have shown that the process, in all probability, consists in the formation of an additive compound between the chlorate and the osmium tetroxide, which compound then acts as

the oxidising agent. It cannot be due to the formation of some higher osmium oxide, since osmium tetroxide does not take up oxygen from chlorate solutions, and the lower oxides of osmium take only as much oxygen from the chlorate as to give the tetroxide. Neither is it due to catalytic decomposition of the chlorate, since osmium tetroxide does not appreciably increase the velocity of evolution of oxygen from either solid chlorate or chlorate solutions.

The formation of an additive compound is evidenced by the following: (1) the solubility of potassium chlorate is increased in a solution of osmium tetroxide; (2) the addition of osmium tetroxide to a solution of potassium chlorate raises the oxidation potential to a point which is higher than that of either of the components; (3) the velocity with which iodine is liberated from a solution of potassium iodide indicates that the concentration of the active substance is proportional to the product of the concentrations of the osmium and chlorate.

Chlorate is reduced directly to chloride without the intermediate formation of hypochlorite or chlorite; according to the authors, this is due to the fact that the lower oxide of osmium formed during the process from the additive compound is Os_2O_5 or OsO_2,OsO_3, and this requires three oxygen atoms for the regeneration of osmium tetroxide.

Comparison of the effects produced by osmium tetroxide and ruthenium hydroxide shows that the former is generally more active; also, owing to the fact that it is soluble in water and therefore has an unlimited surface, it does not show the poisoning phenomena which are generally observed with suspended particles.

Numerous further examples of oxidations brought about by the presence of osmium tetroxide are given. Substances with the ethylene linking, which readily add on halogens or ozone, are attacked, but not so vigorously, in a way similar to that in which permanganate acts. The strongly adsorbing, amorphous charcoal is oxidised vigorously, whilst the chemically more active, but weakly adsorbing, amorphous silicon is not acted on. T. S. P.

Mineralogical Chemistry.

Helium in Blue Rock-salt. SIEGFRIED VALENTINER (*Jahrb. Min.*, 1913, i, *Ref.* 195; from *Kali*, 1912, 6, 1—3).—In 1200 grams of the blue rock-salt from Wilhelmshall at Anderbeck was found 1·5 c.c. helium, or 0·13 c.c. per 100 grams, whilst Strutt in 1908 found only 0·0233 c.c. per 100 grams in the ordinary rock-salt from Stassfurt. This much greater amount of helium suggests a radioactive origin for the blue coloration. L. J. S.

Hetærolite from Leadville, Colorado. WILLIAM E. FORD and WALTER M. BRADLEY (*Amer. J. Sci.*, 1913, [iv], **35**, 600—604).—A dark brown to black mineral with radiating, mamillary structure, found in vugs with hemimorphite and smithsonite at a contact of limestone and quartzite in the Wolftone mine, is identified with hetærolite, a species previously known only from Franklin, New Jersey. The lustre is submetallic, and the streak dark chocolate-brown. Fragments under the microscope are transparent and dark brown, and the fibres are birefringent with straight extinction. H $5\frac{1}{2}$—6, D 4·6. The mineral is infusible before the blowpipe; when heated, water, but no oxygen, is expelled. It is easily soluble in hydrochloric acid, with evolution of chlorine. Analysis gave:

ZnO.	MnO.	O.	CaO.	H_2O.	SiO_2.	Total.	Mn_2O_3.
37·56	50·34	5·99	trace	4·36	2·69	100·94	56·00

Neglecting silica, these results agree with $4ZnO,3Mn_2O_3,2H_2O$. The soluble silica is, however, probably present as admixed hemimorphite, and deducting this, the formula becomes $2ZnO,2Mn_2O_3,1H_2O$. Schaller's analysis (A., 1910, ii, 220) of the New Jersey mineral gives the same formula when the water is taken into account. L. J. S.

The "Hydromagnesite" from Sasbach, Kaiserstuhl, Baden. WILHELM MEIGEN (*Jahrb. Min.*, 1913, i, *Ref.* 202; from *Ber. oberrhein. geol. Ver.*, 1910, **43**, 79—80).—The mineral forms hard, nodular, white masses in cavities in lava. Analysis gave: MgO, 47·89; CO_2, 51·88%, proving it to be pure magnesite. The water shown in earlier determinations is referred to admixed zeolites. L. J. S.

The So-called Hydrodolomite of Marino (Vulcano Laziale). FEDERICO MILLOSEVICH (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 642—647).—Microscopical and chemical examination of this mineral shows that it is not a distinct species, but an aggregate of calcite and hydromagnesite. R. V. S.

Contact Minerals from the Crystalline Limestones of the Kaiserstuhl, Baden. RICHARD DAUB (*Jahrb. Min.*, 1913, i, *Ref.* 214—217; from *Inaug. Diss. Freiburg i. Br.*, 1912, 45 pp.).—An average sample of 3000 grams of the koppite-bearing limestone from Schelingen was dissolved in dilute acetic acid, leaving a residue of 440 grams, containing: Magnoferrite, 5%; apatite, 5%; koppite, 2%; mica + serpentine, 2·8%; forsterite, 0·2% = 15%. These minerals are each described. The green mica is barytbiotite, and occurs as distinct crystals. It is a mica of the second class, and almost optically uniaxial. The refractive indices (for sodium light, $\gamma = \beta = 1·6053$, $\alpha = 1·5749$) differ but little from those of other biotites, so that barium has little influence on the optical constants. Analysis by M. Dittrich gave I. Forsterite, D 3·18—3·25, gave

analysis II by Dittrich, corresponding with $25Mg_2SiO_4 + 1(Fe,Mn)_2SiO_4$:

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	BaO.	SrO.	K_2O.	Na_2O.	H_2O.	Total.
I.*	29·80	18·43	2·41	0·53	—	8·17	25·02	5·11	trace	5·04	0·29	4·96	99·80
II.	38·74	1·23	1·42	2·25	1·33	1·75	50·54	—	—	0·39	0·15	0·37	98·17

* H_2O below 110°, 0·46 ; H_2O over 110°, 1·19 ; H_2O ignition 3·31 = 4·96. TiO_2 nil.

A monticellite-bearing limestone also occurs; this contains also perovskite (dysanalyte) and more rarely diopside, apatite, magnetite, and mica. In a third type of limestone, gehlenite occurs.

L. J. S.

Magnetite from the Kaiserstuhl, Baden. ERNST HUGEL (*Jahrb. Min.*, 1913, i, *Ref.* 200; from *Inaug. Diss. Freiburg i. Br.*, 1912, 47—49).—Indistinct crystals isolated from the crystalline limestone containing dysanalyte, from Vogtsburg, gave:

SiO_2.	TiO_2.	Fe_2O_3.	FeO.	Al_2O_3.	MgO.	Total.
0·34	4·70	62·39	23·24	6·80	2·59	100·06

Deducting some magnesia and alumina as present in admixed mica, this analysis corresponds with:

$$4Fe_3O_4 + MgAl_2O_4 + FeTiO_3 + 2Fe_2O_3.$$

L. J. S.

Magnoferrite from Kaiserstuhl, Baden. ERNST HUGEL (*Jahrb. Min.*, 1913, i, *Ref.* 200; from *Inaug. Diss. Freiburg i. Br.*, 1912, 50—53).—Analysis of material separated from the limestone of Schelingen gave:

TiO_2.	Fe_2O_3.	FeO.	Al_2O_3.	MgO.	MnO.	Insol.	Total.
1·31	61·95	18·72	6·57	6·74	3·40	1·10	99·79

corresponding with:

$$15Fe_3O_4 + 6MgFe_2O_4 + 4MgAl_2O_4 + 3MnFe_2O_4 + FeTiO_3.$$

L. J. S.

Dysanalyte from Kaiserstuhl, Baden. ERNST HUGEL (*Jahrb. Min.*, 1913, i, *Ref.* 208—209; from *Inaug. Diss. Freiburg i. Br.*, 1912, 1—46).—Analyses (I, mean of three; II, mean of two) of two samples of dysanalyte from Vogtsburg gave:

	SiO_2.	TiO_2.	Cb_2O_5.	CaO.	Ce_2O_3.	FeO.	Al_2O_3.	K_2O.	Na_2O.	MnO.	MgO.	Total.
I.	0·29	48·31	16·12	21·63	3·32	5·35	1·25	0·39	4·20	0·02	trace	100·88
II.	0·33	38·70	25·99	23·51	3·08	5·69	0·82	0·44	1·72	—	—	100·28

The corresponding formulæ ($R = Ca,Fe,Na_2,(CeO)_2,(AlO)_2$) are:

I. $RCb_2O_6 + 6RTiO_3 + 1\frac{1}{2}RTi_2O_5$.

II. $RCb_2O_6 + 4RTiO_3 + \frac{1}{2}RTi_2O_5$.

Uranium is present in traces, and the mineral is slightly radioactive. In one sample, $Ce_2O_3 : La_2O_3 = 2 : 1$. The large, although variable, amount of columbium indicates that dysanalyte must be regarded as a distinct species (compare O. Hauser, A., 1908, ii, 60).

L. J. S.

Minerals Hitherto Found in the Granulites of Cala Francese on the Island della Maddalena [Sardinia]. DOMENICO LOVISATO (*Mem. R. Accad. Lincei*, 1913, [v], **9**, 404—436).—The author enumerates the minerals, thirty-two in number, which he has found in the granulite of this locality in addition to its essential components (quartz, monoclinic and triclinic felspar and mica biotite). Analyses have been made by Rimatori and by Manis of fourteen of these. R. V. S.

The Melting Point of Silicates. Influence of Size of Grain on Melting Point. Determination of the Melting Point of Some Silicates by Slow Heating. HANS LEITMEIER (*Zeitsch. anorg. Chem.*, 1913, **81**, 209—232).—Two specimens of the same mineral, differing only in size of grain, are heated in a platinum boat divided into two compartments, and examined from time to time. The commencement of melting may be affected to the extent of 60—70°, whilst the temperatures of complete liquefaction do not differ more than 20—40°, except in the case of augite.

Finely levigated material is tested in the same manner, heating very slowly, thirty-six to forty-eight hours being taken to reach the melting point. The following results have been obtained, the first temperature in each case being the beginning of melting, the second that of liquefaction: Adularite (St. Gothard), 1145°; augite (Bohemia), 1145—1150°; ægirite (Langesundfjord), 940—950°; labradorite (Kamenybrod), 1245—1250°; diopside (green, from Zillertal), 1260—1290°; diopside (colourless, Rotenkopf in Zillertal), 1295—1320°; diopside (artificial), 1305—1320°. The exact determination of the melting point of natural silicates is almost impracticable, and the meaning of the preliminary sintering is uncertain, although the experiments with adularite suggest that a mineral could be completely melted at the sintering temperature if sufficient time were allowed. C. H. D.

Melting Phenomena of the Plagioclase Felspars. N. L. BOWEN (*Amer. J. Sci.*, 1913, [iv], **35**, 577—599).—The following determinations of the melting intervals were made by the method of quenching. A charge, after being kept at a definite temperature for one hour, was suddenly chilled in mercury, and the material then examined under the microscope for the presence of glass or crystals. The pure artificially prepared materials previously examined by Day

Composition.	Temp. of beginning of melting. Solidus.	Temp. of completion of melting. Liquidus.
An	1550°±2°	1550°±2°
Ab_1An_5	1465 ±4	1521 ±2
Ab_1An_2	1372 ±4	1490 ±2
Ab_1An_1	1287 ±4	1450 ±2
Ab_2An_1	1205 ±5	1394 ±2
Ab_3An_1	1175 ±8	1362 ±2
$Ab_{77\cdot5}An_{22\cdot5}$	1158 ±5	—
Ab_4An_1	—	1334 ±2
Ab_8An_1	—	1265 ±3
$Ab_{98}An_2$	1100 ±10	—

and Allen (A., 1906, ii, 177) were used. Mixtures richer in albite than Ab_2An_1 could not be completely crystallised, and were therefore of no use for fixing the solidus point; in this case the natural crystallised felspars were employed—oligoclase, $Ab_{77\cdot5}An_{22\cdot5}$, from Bakersville, North Carolina, and albite, $Ab_{98}An_2$, from Amelia Co., Virginia.

These results are plotted on a temperature-concentration diagram, and are confirmed by determining the composition of the liquid phase (the quenched glass) by means of the refractive indices. This diagram demonstrates the great difference in composition of the liquid and solid phases at any temperature, and explains why the composition of the crystals (zoned crystals in igneous rocks) continuously changes with falling temperature, becoming progressively more acid. From theoretical considerations on the lines suggested by van Laar (A., 1906, ii, 422), the latent heats of melting are calculated as 104·2 cal. per gram for anorthite, and 48·5 for albite. L. J. S.

Talc of "Grangie Subiaschi" in Val Pellice (Alpi Cozie) and the Minerals Associated with it. ALESSANDRO ROCCATI (*Atti R. Accad. Sci. Torino*, 1912–13, **48**, 630—642).—In this locality three varieties of talc can be distinguished: (1) a compact, white substance without included minerals, giving on analysis numbers pointing to the formula $H_2Mg_3Si_4O_{12}$; (2) a greenish-white, laminated talc of the formula $H_4Mg_6Si_7O_{22}$; (3) minute laminæ of talc in a calcareous matrix; this variety has a composition corresponding with the formula $H_4Mg_5Si_6O_{19}$. The associated minerals include an actinolite, sp. gr. 3·01, having a composition corresponding with the formula $3(Mg,Fe)SiO_3,CaSiO_3$, pyrites, limonite, and a garnet having a composition required by the formula $3CaO,(Al,Fe)_2O_3,3SiO_2$. Nodules (sometimes of large size), consisting chiefly of hyaline quartz, are also found included in the talc. R. V. S.

The Acidulo-alkaline Water of Uliveto. New Analyses and Physico-chemical Researches. RAFFAELE NASINI, LUIGI MARINO, FERNANDO AGENO and C. PORLEZZA (*Gazzetta*, 1913, **43**, i, 321—353).—This paper gives a detailed account of the composition and properties of this water. The gases dissolved in 1 litre at 27·6° comprise carbon dioxide, 769·12 c.c.; oxygen, 0·33 c.c.; nitrogen and rare gases, 16·81 c.c. The total solids of 1 litre of the water amount to 2·4400 grams (dried at 105°) or 2·3800 grams (dried at 180°). The composition of the residue (expressed as metallic and acid radicles) is Na 0·35331, Li 0·00066, Ca 0·43436, Mg 0·03900, Cl 0·36075, SO_4 0·44868, CO_3 0·62475, (P_2O_5,Fe_2O_3,Al_2O_3) 0·00466, SiO_2 0·02036; total, 2·28653. The waters are notably radioactive, the activity being chiefly due to radium emanation. The gas obtainable from the water contains much helium. R. V. S.

Analytical Chemistry

A Compact, Accurate Burette for Use in Nitrogen Work or Whenever Many Measurements of Standard are Necessary. FRANK C. GEPHART (*J. Ind. Eng. Chem.*, 1913, **5**, 490).—The burette consists of three bulbs of such capacity that the marks on the narrow portion of the burette beneath them read, respectively, 25, 15, and 10 c.c., reading from the top. It is connected to the stock of standard solution by a side-tube opening beneath the lowest graduation. T. S. P.

Extraction Apparatus. WALTHER FRIESE (*Pharm. Zentr.-h.*, 1913, **54**, 541—542).—The substance to be extracted is placed in a cylindrical vessel supported in a wider tube; the top of the latter is connected with a reflux apparatus, whilst its lower end is contracted so as to form a tube which passes through the cork of the extraction flask. The solvent falls from the condenser into a small funnel tube which reaches to the bottom of the cylindrical vessel; the solvent continuously rises in the latter, flows over the upper edge, and returns to the extraction flask. W. P. S.

Juice of the Blueberry as an Indicator. G. N. WATSON (*Amer. J. Pharm.*, 1913, **85**, 246—247).—Blueberry juice when carefully neutralised imparts an olive-green colour to alkaline and a rose colour to acid solutions. The author states it may be used in volumetric analysis instead of cochineal or litmus. Like the latter, it is sensitive to carbon dioxide, which, if present, should therefore be removed by boiling. L. DE K.

An Electric Desiccator for the Analysis of India Rubber and Other Organic Compounds. L. J. D. HEALY (*J. Ind. Eng. Chem.*, 1913, **5**, 489—490).—The desiccator possesses a side-tube connecting with a manometer and vacuum pump, and also an opening in the top, through which passes a thermometer. A resistance is inside the desiccator, and is connected with a lamp rheostat, so arranged that any temperature from 45—175° can be obtained. The procedure in drying rubber is as follows: After being placed in the desiccator the latter is exhausted and heated to about 60°, the current being left on for an hour. If the pressure at any time rises to more than 75 mm. the desiccator is again exhausted. At the end of the hour the desiccator is allowed to cool and air admitted. This procedure is repeated until the weight of the rubber is constant. The process takes four to five hours as compared with about two hundred hours by the ordinary method. T. S. P.

Assay of Bleaching-powder or Hypochlorites. F. DUCELLIEZ (*Bull. Soc. chim.*, 1913, [iv], **13**, 494—497).—The method proposed by Hanriot and subsequently investigated by Blattner for the assay of

bleaching agents yielding chlorine has been re-examined. The method depends on the measurement of the oxygen liberated when nickel or cobalt oxide is placed in contact with a hypochlorite. The liberation of oxygen is very slow at 20°, but becomes rapid at 45°. The author suggests the use of cobalt chloride in presence of alkali as a catalyst, and describes an apparatus for carrying out the estimation. The results quoted indicate that the process is rapid and accurate. T. A. H.

Colour Reactions of Chlorates. M. EMMANUEL POZZI-ESCOT (*Bull. Soc. chim.*, 1913, [iv], **13**, 498—499).—In connexion with the colour reaction for chlorates described by Pieraerts (this vol., ii, 238) the author points out that the sensibility is greatly increased by using sulphuric acid in place of hydrochloric acid, and that the substitution of benzidine for aniline results in the production of an orange-yellow coloration, which forms a still more sensitive test. Further, in presence of sulphuric acid aniline gives a blue coloration with chlorates and reddish-brown with nitrates or iodates. Benzidine, however, gives the same coloration with all three kinds of salts. Directions for applying the test are given. T. A. H.

Fluorine in Reagents. P. CARLES (*Bull. Soc. chim.*, 1913, [iv], **13**, 553—556).—Methods of detecting fluorine in, and of eliminating it from, a number of common reagents are described. Sulphuric and hydrochloric acids are usually free from fluorine, but nitric acid almost always contains it, as does also potassium nitrate. Barium hydroxide of commerce always contains insoluble fluorides, so that clear solutions are generally free from fluorine, and this is also the case with barium acetate. Sodium hydrogen carbonate and the corresponding potassium salt are rarely free from fluorine, and ammonium carbonate always contains it. Crystallised acetic acid carefully freed from the mother liquor is free from fluorine. T. A. H.

Use of Sodium Potassium Tartrate in the Estimation of Oxygen in Water. J. J. VAN ECK (*Chem. Weekblad*, 1913, **10**, 455—464).—A summary of previous work on the use of sodium potassium tartrate in the estimation of oxygen in water, and a discussion of the cause of the low values obtained with certain types of salt solution, and of the lack of definiteness in the end-point of the reaction. A. J. W.

Estimation of Sulphur in Illuminating Gas. R. S. MCBRIDE and E. R. WEAVER (*J. Ind. Eng. Chem.*, 1913, **5**, 474—476).—A comparison of the referee's, Hinman-Jenkins, and Elliott apparatus for the estimation of sulphur in gas showed that any one of these apparatus is capable of giving satisfactory results when due precautions are taken.

The referee's apparatus is the ordinary one used in such tests. The Elliott apparatus is essentially the same, the principal difference being the use of two condensing cylinders through which the

gases pass successively. The Hinman-Jenkins apparatus differs from the referee's greatly in form, but in principle only in the use of concentrated ammonium hydroxide instead of ammonium carbonate as a source of ammonia. T. S. P.

Rapid Estimation of Sulphur in Pyrites Cinder. A. B. CONNER (*J. Ind. Eng. Chem.*, 1913, 5, 399—401).—The method described by Nitchie (A., 1912, ii, 682) was found to be trustworthy. W. P. S.

Apparatus for the Precipitation of Barium Sulphate under Varying Conditions. H. G. SMITH (*J. Ind. Eng. Chem.*, 1913, 5, 416—417).—The solution containing the sulphate is heated to boiling in a beaker, and a bent test-tube containing barium chloride is placed in the beaker during this period. The test-tube has a capillary opening in its side near the upper end, and when the solution boils, the test-tube is placed across the top of the beaker so that the hot barium chloride solution flows slowly through the capillary into the solution in the beaker. W. P. S.

Estimation of Sulphate in Ammonium Sulphate Solution, with Special Reference to the Testing of Illuminating Gas. R. S. MCBRIDE and E. R. WEAVER (*J. Ind. Eng. Chem.*, 1913, 5, 469—474).—The authors have tested the various methods for the estimation of sulphate in solutions such as are obtained in the estimation of sulphur in coal gas, that is, which may contain ammonium carbonate and silica (dissolved from the glass). For ordinary purposes an accuracy of 2—3% is ample.

For accurate work the gravimetric methods, using the precautions usually taken, are to be preferred. For rapid work the volumetric and nephelometric methods are useful. The volumetric method tested was very similar to that of Holliger (A., 1910, ii, 239), and is as follows: 300 c.c. of the sample are acidified with 10 c.c. of hydrochloric acid (1 : 1), the solution is heated to boiling, and then 15 c.c. of barium chloride solution (50 grams per litre) added. After boiling for five minutes 15 c.c. of potassium dichromate solution (30·5 grams per litre) and a few drops of a dilute solution of ferric chloride are added, after which precipitation is brought about by excess of ammonium hydroxide. After boiling for five minutes, the precipitate is collected, well washed, and the chromate in the filtrate estimated iodometrically. A blank estimation is necessary.

In the turbidimetric method the neutralised solution of the sulphate is precipitated at 25—30° with barium chloride, and the turbid liquid poured into a graduated glass cylinder until the filament of an electric lamp placed below just cannot be seen. By comparison with results obtained with solutions of known strength, the percentage of sulphate can then be estimated. T. S. P.

Estimation of Polythionate in Presence of Thiosulphate and Free Sulphur Dioxide. WALTHER FELD (*Zeitsch. angew. Chem.*, 1913, **26**, 286—288).—The process is as follows: The sulphur

dioxide and thiosulphate are titrated with iodine. The resulting free acid is titrated with sodium hydroxide after adding ammonium chloride and methyl orange. Half of the alkali consumed equals the iodine taken up by sulphur dioxide; the remaining iodine represents the thiosulphate. Another part of the solution is now shaken for half an hour with an emulsion of manganous sulphide, made up to a definite bulk and filtered. An aliquot part of the filtrate is boiled with excess of mercuric chloride solution, ammonium chloride is added, and the acidity liberated is titrated with sodium hydroxide and methyl-orange. The acidity which represents the sulphur dioxide and thiosulphate is deducted from the total acid; the balance represents the S_4O_6 (polythionate).

The emulsion is prepared as follows: 600 c.c. of a normal solution of manganous sulphate are heated to 60°, and a rapid stream of hydrogen sulphide is passed; a few drops of aqueous potassium hydroxide are added, and the liquid is filtered. After again heating at 60° a rapid stream of the gas is passed while adding drop by drop a solution of potassium hydroxide (about 50 grams) so as to precipitate about 80—85% of the manganese present. After expelling the excess of hydrogen sulphide by heating in a water-bath at 80°, the mixture is ready for use. L. DE K.

Estimation of Ammonia by the Formaldehyde Method and of Formaldehyde by means of Ammonia. M. EMMANUEL POZZI-ESCOT (*Ann. Chim. anal.*, 1913, **18**, 193—194).—The author points out that the formaldehyde method described by Gaillot (this vol., ii, 240) for the estimation of ammonia is not new, and that it is, moreover, less trustworthy than the ordinary distillation method. The converse reaction may, however, be used for the estimation of formaldehyde if the influence of the ammonium salts is taken into consideration (compare A., 1908, ii, 320). W. P. S.

The Application of Folin's Method for the Estimation of Ammonia to Fertilisers. OTTO FOLIN and ALFRED W. BOSWORTH (*J. Ind. Eng. Chem.*, 1913, **5**, 485).—Two grams of the fertiliser are placed in a 100 c.c. graduated flask, about 50 c.c. of water added, and then 25 c.c. of approximately normal hydrochloric acid. After making up to 100 c.c. the contents of the flask are well shaken, and again after a few minutes. When the heaviest undissolved particles have settled, 5 c.c. of the supernatant liquid are transferred to the tube of the Folin apparatus (compare A., 1903, ii, 239), and the ammonia estimated according to Folin's method (compare Folin and Farmer, A., 1912, ii, 702). T. S. P.

Estimation of Hydroxylamine. ERWIN RUPP and H. MÄDER (*Arch. Pharm.*, 1913, **251**, 295—300).—Meyeringh's method for the estimation of hydroxylamine, which involves oxidation by iodine in presence of magnesia or sodium phosphate and titration of the excess of iodine, is shown to be subject to two errors: (1) that the sodium phosphate or magnesia used may convert some of the iodine into iodide or hypoiodite, and (2) that the nitrous oxide formed may be in part oxidised by the iodine, and thus use up some of

the reagent. Actual trials showed that very different quantities of iodine are needed, depending (*a*) on the nature and quantity of the material employed to absorb the hydriodic acid formed in the reaction, and (*b*) on the time during which the reaction mixture is allowed to stand.

Titration by means of sodium hypobromite is suggested. Ten grams of sodium hydroxide are dissolved in water, 15 grams of bromine added, and the solution made up to 1000 c.c. The strength of this solution is then determined by diluting 20 c.c. with 50 c.c. of water, adding 1 gram of potassium iodide and 20 c.c. of dilute hydrochloric acid, and titrating with $N/10$-sodium thiosulphate. For estimating hydroxylamine, 20 c.c. of the sodium hypobromite solution is mixed with 75 c.c. of water, and hydrochloric acid added drop by drop until the colour changes from yellow to the brown of bromine. Not more than 0·01 gram of hydroxylamine is then added, and the mixture, after standing five minutes, titrated with sodium thiosulphate solution, after the addition of potassium iodide and hydrochloric acid. T. A. H.

Gas Analytical Estimation of Nitric Oxide and Oxygen, Depending on the Smooth Formation of Nitrous Acid Anhydride from these Gases. GABRIEL KLINGER (*Ber.*, 1913, **46**, 1744—1748).—The method for the estimation of nitric oxide has been given previously (this vol., ii, 74); that for oxygen is simply the reverse, and follows as a matter of course. It should be noted especially that the gases and stick potassium hydroxide used must be dry, otherwise nitrous acid is formed, which is oxidised by the excess of nitrogen trioxide to nitric acid.

The nitric oxide used should be dried by passing it through concentrated sulphuric acid. Mercury is used as the liquid in the burette and potassium hydroxide pipette. T. S. P.

Effect of Sulphates on the Estimation of Nitrates. WALTER P. KELLEY (*J. Amer. Chem. Soc.*, 1913, **35**, 775—779).—In connexion with a study of the estimation of nitrates in soil extracts by the phenoldisulphonic acid method, Lipman and Sharp (*Univ. Cal. Publ.* in *Agric. Sci.*, 1912, **1**, 21) have stated that on evaporating a nitrate solution containing sodium sulphate considerable loss of nitrate takes place.

It has now been found that in presence of the sulphate of sodium, potassium, or ammonium, loss of nitrate occurs, but that the sulphates of calcium and magnesium do not occasion any loss. It is shown that the loss is due to the presence of small quantities of the hydrogen sulphate, either contained in the sulphate or produced by slight hydrolysis. If sodium carbonate is added to the solution before evaporation, the loss is entirely prevented.
E. G.

Detection of White Phosphorus in Matches, etc. F. SCHRÖDER (*Arb. K. Gesundheit*, 1913, **44**. Reprint, 29 pp.).—The material is treated with a little benzene, and a strip of filter paper 10 cm. long

and 3 cm. in diameter is soaked in it. This is then suspended in a glass tube connected to a Victor Meyer's heating apparatus, and exposed to a current of air at 40—50°. Even when the benzene solution contains no more than 0·01 milligram of white phosphorus per c.c. the paper will soon become luminescent. The test must, of course, be carried out in a perfectly dark room. Other varieties of phosphorus do not give the reaction. L. DE K.

Estimation of Phosphorus in Steels Containing Vanadium. JOHN R. CAIN and F. H. TUTTLE (*J. Washington Acad. Sci.*, 1913, **3**, [9], 249).—In order to ensure a complete precipitation of the phosphorus in presence of vanadium by the molybdate process and the formation of a pure "yellow precipitate," a slight excess of ferrous sulphate should be added, and the following conditions should be observed: The precipitation should take place at 15—20°, so as to prevent rapid oxidising action on the vanadium or the ferrous sulphate by the nitric acid; the partial neutralisation with ammonia must be made before adding the iron sulphate; otherwise the liquid might get too warm. If oxides of nitrogen are formed, these interfere with the complete precipitation of the phosphorus owing to re-oxidation of the vanadyl salt. A good shaking apparatus should be used. L. DE K.

Volumetric Estimation of Hypophosphorous Acid and Hypophosphites. LUIGI MARINO and A. PELLEGRINI (*Gazzetta*, 1913, **43**, i, 494—497).—The methods which have been proposed for titrating hypophosphite solutions are not entirely satisfactory. Rapid and accurate estimation is, however, possible, if the oxidation of the hypophosphorous acid is effected by the $N/5$-alkaline permanganate prepared as described for the estimation of selenious acid (Marino, A., 1910, ii, 155). The alkaline permanganate is added to the dilute hypophosphite solution until a permanent pink coloration is obtained; the liquid is then acidified with sulphuric acid, and the excess of permanganate is titrated in the usual way.

R. V. S.

Estimation of Phosphoric Acid. LUDWIG MOESER and G. FRANK (*Zeitsch. anal. Chem.*, 1913, **52**, 346—349).—About 0·5 gram of native phosphate is heated to boiling with 4—6 c.c. of strong sulphuric acid in a round-bottomed flask for ten to fifty minutes; care must be taken that the mass shall not get dry. When cold the mass is extracted with 30—40 c.c. of 95% alcohol, which completely dissolves the phosphoric acid. In order to render the solution more filterable, 2 c.c. of 10% alcoholic potassium hydroxide are added, which causes a precipitate of potassium sulphate.

From the filtrate (after diluting this with an equal volume of water) the phosphoric acid is precipitated by adding slight excess of ammonia, and then, after heating to boiling, magnesium mixture.

Manganese, if present in more than traces, interferes with the process. In such cases a precipitation of the phosphoric acid as the ammonium manganese compound is proposed. L. DE K.

Estimation of Water-soluble Phosphoric Acid in Ammonium Superphosphates. (Influence of Temperature.) ERNST BÜTTNER (*Chem. Zeit.*, 1913, **37**, 662).—The author finds that about 0·5% more water-soluble phosphoric acid is found when ammonium superphosphate is shaken for thirty minutes with water at a temperature of 18—20° than when the temperature is allowed to fall to 16° during the shaking operation. The solubility of the phosphate also increases with the fineness of the superphosphate. W. P. S.

Preparation of Petermann's Solution. F. ZÖHREN (*Chem. Zeit.*, 1913, **37**, 611—612).—To prevent loss of ammonia during the preparation of Petermann's solution for the estimation of citrate soluble phosphoric acid, it is recommended that the citric acid solution be placed in a flask provided with a side-tube connected with a small flask containing a portion of the citric acid solution. The larger flask is closed with a rubber stopper, and the ammonia is added gradually through a tube passing through the stopper and extending beneath the surface of the solution in the flask; the latter is provided with a stirring apparatus, and may be cooled during the addition of the ammonia. When all the ammonia has been introduced, the contents of the smaller flask are added.

W. P. S.

Effect of Ignition on the Solubility of Soil Phosphates. GEORGE S. FRAPS (*J. Ind. Eng. Chem.*, 1913, **5**, 416).—When soil is ignited the quantity of phosphoric acid soluble in dilute hydrochloric acid is increased, although it may, or may not, be rendered more soluble in hot nitric acid. It may be concluded that a portion of the phosphoric acid, rendered soluble by ignition, is probably of inorganic origin. W. P. S.

Estimation of Active Oxygen in Perborates and in Washing Powders Containing the Same. FRANZ M. LITTERSCHEID and P. B. GUGGIARI (*Chem. Zeit.*, 1913, **37**, 690—691).—The available oxygen in perborates may be conveniently found from the loss in weight when 2 grams of the sample are treated with dilute (25%) sulphuric acid and about 2 grams of purified manganese dioxide in a Geissler carbon dioxide apparatus. One-half of the loss in weight = available oxygen.

In applying the process to washing mediums, 20 grams of the sample are treated with 120 c.c. of water at 70°; dilute (25%) sulphuric acid is slowly added to expel carbon dioxide, and the whole is made up to 200 c.c. One gram of kieselguhr is added, and the mixture well shaken and filtered. An aliquot part of the solution is then tested as described in the Geissler apparatus.

L. DE K.

New Rapid Method for the Estimation of Carbon in Iron and its Alloys. ERNST SZÁSZ (*Zeitsch. angew. Chem.*, 1913, **26**, 281—284).—A rather complicated apparatus is described and

figured for the combustion of iron and its alloys in a small volume of absolutely pure oxygen; the resulting carbon dioxide is then measured in the usual manner in a gas burette; it may also be collected in a weighed absorption apparatus.

The combustion of alloys liable to cake should be carried out with addition of alumina; for ferromolybdenum, addition of heavy magnesium oxide is recommended so as to prevent volatilisation of molybdenum trioxide, which otherwise might cause an obstruction.

L. DE K.

A Vitrified Clay Combustion Tube with Tapered Outlet for the Estimation of Carbon in Steels, Ferro-alloys, and Graphite. CHARLES MORRIS JOHNSON (*J. Ind. Eng. Chem.*, 1913, **5**, 488).—The author has found a vitrified clay combustion tube to be a more than satisfactory substitute for a silica tube, since it is not so readily affected by basic material. T. S. P.

Estimation of Total Carbon in Soils. M. EMMANUEL POZZI-ESCOT (*Bull. Assoc. chim. Sucr. Dist.*, 1913, **30**, 618—621).—A quantity of the soil, containing not more than 0·3 gram of organic matter, is mixed in a nickel boat with 0·1 gram of fused potassium dichromate and 1 gram of lead chromate, and the combustion is then carried out in the usual way. A large excess of oxygen must be employed, but the rate at which this gas is passed through the combustion tube must be slow. The tube should be packed with copper oxide (in the form of threads) for a length of at least 350 mm., and the usual piece of copper foil may be replaced by silvered pumice. The carbon dioxide formed is absorbed in a suitable apparatus and weighed. The author criticises a method described recently by Grégoire (this vol., ii, 243), in which a large quantity of soil is heated with a relatively small quantity of copper oxide, and the resulting carbon dioxide absorbed in barium hydroxide solution, the latter being then decomposed and the volume of the liberated gas measured. W. P. S.

Gravimetric Estimation of Carbon Dioxide. A. DEJEANNE (*Bull. Soc. chim.*, 1913, [iv], **13**, 556—560 *).—The method depends on the absorption of the carbon dioxide in an excess of a standard solution of barium, calcium, or strontium hydroxide. To this liquid, which now contains the carbonate in suspension, a known quantity of magnesium chloride is added. In these conditions the magnesium hydroxide formed is precipitated completely, carrying the carbonate (in suspension) with it. The quantity of barium, calcium, or strontium in an aliquot part of the clear mother liquor is then estimated as the sulphate, oxalate, or carbonate respectively.

T. A. H.

The Application of the Fontactoscope in the Estimation of the Emanation Content of Spring Waters. W. HAMMER and FR. VOHSEN (*Physikal. Zeitsch.*, 1913, **14**, 451—454).—When radioactive water is shaken with air in a closed fontactoscope, and

* and *Ann. Falsif.*, 1913, **6**, 335—339.

the saturation current measured after different intervals of time, it is found that in the early stages the decay curve which is obtained deviates considerably from the theoretical curve. This has been found to be due to the liberation of the solid disintegration products in the process of shaking. The fine spray containing the dissolved solids settles after a time, and the later portion of the decay curve agrees with that obtained for pure radium emanation.

For exact measurements, it is recommended that observations should not be made until three hours have elapsed since the active water was shaken up with the air enclosed in the apparatus. The disturbance is, however, quite small at the end of fifteen minutes, and for many purposes observations may be commenced after this shorter time interval. H. M. D.

Estimation of the Soluble Salts in Soils by Electric Methods. A. FLODERER-MAGYARÓVAR (*Bied. Zentr.*, 1913, **42**, 228—230; from *Mitt deut. landw. Ges.*, **42**, 579).—In estimating the soluble salts in soils it is necessary to take into account the amount of moisture in the soil, the temperature, the specific conductivity of the salts in different concentrations, and the structure of the soil.

N. H. J. M.

Control of the Purification of Boiler Feed-Water. C. BLACHER (*Zeitsch. angew. Chem.*, 1913, **26**, 288).—A reply to Weissenberger (this vol., ii, 338). The author states that his improved dropping flasks are correct to 0·25 German degree. L. DE K.

Differentiation of the Magnesium Hardness in Water, Especially with Regard to the Hardening of River Water by the Waste Liquors from Potassium Chloride Factories. HERMANN NOLL (*Zeitsch. angew. Chem.*, 1913, **26**, 320—327).—The author gives further details of his method of differentiation of the magnesium hardness into carbonate and non-carbonate hardness (compare A., 1912, ii, 997). He has also investigated the applicability of Precht's method (A., 1879, 1053) of determining the magnesium chloride content of potassium salts to the investigation of waters. For this purpose a known volume of water is evaporated to dryness, the residue dried at 110° during half an hour, cooled and extracted with 96% alcohol, the magnesium chloride being determined gravimetrically in the extract. This method differs from that devised by the author, in that only the magnesium chloride is determined in the former, whilst the total non-carbonate hardness due to magnesium salts is estimated in the latter.

The author is led to the conclusion that neither method yields strictly accurate results, but that the figures obtained by his own method are the more closely in accord with the actual state of equilibrium of the dissolved salts. Determinations of alkalinity and magnesia in the concentrated water readily give results which are of comparative value, whilst a combination of the two methods allows an approximate differentiation of the non-carbonate hardness due to magnesia. H. W.

The Presence of Strontium Compounds in Blende. EDGAR BEYNE (*Bull. Soc. chim. Belg.*, 1913, **27**, 159—164).—The author finds that zinc blende may contain strontium in quantities up to 4·8% (expressed as SrO), the strontium being present probably in the form of carbonate. In the ordinary course of analysis the strontium would be precipitated with the barium and included with this in the final statement, thus introducing the possibility of a considerable error in the calculation of the sulphur which should not be removable by roasting. It is suggested that the mixed precipitate of barium and strontium sulphates should be treated with fusion mixture, and the barium precipitated from the acetic acid solution as chromate, then reprecipitated and weighed as sulphate; the strontium in the filtrate and washings is then collected as carbonate, being afterwards also reprecipitated and weighed as sulphate. D. F. T.

Spelter Analysis. ERIC J. ERICSON (*J. Ind. Eng. Chem.*, 1913, **5**, 401—402).—Methods are described for the estimation of lead, iron, and cadmium; copper, tin, and antimony may also be separated when present in the spelter, and the amount of zinc is found by difference. The sample is treated with dilute hydrochloric acid for fifteen hours, and the insoluble portion separated by filtration: this insoluble portion is then dissolved in nitric acid, tin and antimony oxides are removed, and the lead is estimated in the filtrate by the volumetric method described previously by the author (A., 1904, ii, 780). Cadmium is estimated in the ammoniacal filtrate from the lead dioxide, by double precipitation as sulphide, trichloroacetic acid being employed in separating traces of zinc in the second precipitation (T., 1907, **91**, 964). Iron is estimated in another portion of the sample by titration with permanganate. W. P. S.

Rapid Technical Estimation of Lead Dioxide in Red Leads. CESARE FINZI and ERNESTO RAPUZZI (*Zeitsch. anal. Chem.*, 1913, **52**, 358—367).—The apparatus consists of a 200—250 c.c. flask fitted with a doubly perforated cork, through which pass a stop-cock funnel and an exit tube, which is connected by means of a rubber tube (fitted with a pinch-cock) with a nitrometer. Fully 1 gram of the sample is introduced into the flask, also 30—40 c.c. of water, and the air is expelled by boiling; a little more water is introduced through the funnel, and the boiling continued for a while. The rubber tube is then temporarily closed with the pinch-cock, and the flame again removed. When cooled somewhat, 20 c.c. of hydrazine reagent are introduced, a slight heat is applied, and the nitrogen evolved is collected and measured with the ordinary precautions. One atom of nitrogen = 1 mol. of lead dioxide. The reagent is prepared as follows. Sufficient hydrazine sulphate to yield a 12% solution of hydrazine acetate is decomposed by means of barium acetate. The liquid is filtered, and 10% of acetic acid added. L. DE K.

Some Sensitive Copper Reactions. Detection of Copper by means of Dextrose. DANIEL SCHENK (*Chem. Zentr.*, 1913, i, 1233; from *Apoth.-Zeit.*, 1913, **28**, 137).—The reversed Fehling's reaction will detect 1/20,000 gram-mol. crystallised copper sulphate in a litre. J. C. W.

The Analysis of Copper Tin Alloys. WILLIAM GEMMELL (*J. Soc. Chem. Ind.*, 1913, **32**, 581—584).—In the estimation of tin in a copper tin alloy by treating with nitric acid, and obtaining the tin directly as stannic oxide, the last-named substance is always yellow, due to the presence of copper and iron oxides. To avoid this source of error, the author dissolves two grams of the alloy in a mixture of 10 c.c. of nitric acid (D 1·42) with 10 c.c. of sulphuric acid (D 1·84) and 30 c.c. of distilled water; both copper and tin dissolve completely, and after expelling oxides of nitrogen and diluting with an equal bulk of water, the copper is estimated by deposition on a rotating platinum electrode. The tin in the remaining solution can be precipitated as stannic oxide by diluting and boiling, or more conveniently by pouring into a cold 2% solution of sulphuric acid saturated with hydrogen sulphide; it is then dissolved in ammonium sulphide and the tin estimated electrolytically.

For the estimation of lead 5—10 grams of the alloy are dissolved in the above acid mixture, and the solution evaporated until the sulphuric acid fumes; the liquid is then diluted, and the lead sulphate collected and weighed. Iron, nickel, and zinc can be successively estimated in the usual manner in the solution from which copper and tin have been removed; the iron is precipitated with ammonium hydroxide, the nickel with dimethylglyoxime, and the zinc then calculated by difference or estimated electrolytically; as an alternative the iron and nickel can be precipitated together by sodium hydroxide and separated afterwards. D. F. T.

Analysis of a Mixture of Sodium Carbonate and Copper Sulphate. HENRI J. F. DE VRIES (*Zeitsch. anal. Chem.*, 1913, **52**, 350—357).—Two grams of the mixture (an insecticide used in agriculture) are dissolved in a known volume of *N*/5-sulphuric acid, the carbon dioxide is boiled off, and the liquid, when cold, diluted to 100 c.c. Of the filtrate, 25 c.c. are now titrated with *N*/10-sodium hydroxide, the end-point being shown by a slight separation of basic copper sulphate. This gives the sodium carbonate. Solution of phenolphthalein is now added, and the titration continued with continuous shaking until the colour of the precipitate formed turns ultramarine or violet-blue. This gives the copper sulphate. The relation between the alkali and copper sulphate must be determined by a practical experiment. The analysis should be controlled by a determination of the carbon dioxide, say, by means of Scheibler's apparatus. If this, calculated to sodium carbonate, should exceed the titration result, sodium hydrogen carbonate is present, which may be found by an easy calculation and then allowed for. L. DE K.

Estimation of Manganese in Soils. MILAN J. STRITA (*Zeitsch. anal. Chem.*, 1913, **52**, 337—345).—The process is intended for soils moderately rich in calcium. Fifty c.c. of a 25% hydrochloric acid extract (=10 grams of sample) are evaporated in a 200 c.c. flask, with addition of 25 c.c. of fuming nitric acid, to a small bulk, and then further evaporated in a porcelain dish to a syrupy consistency; evaporation three times in succession with 10—20 c.c. of strong nitric acid is then recommended. Finally, the mass is taken up with dilute nitric acid and rinsed into a 100 c.c. flask, when heat is applied to effect complete solution. When cold, two drops of $N/10$-thiocyanate and, if necessary, 1 c.c. of $N/10$-iron-alum are added, and the red colour produced is removed by addition of $N/10$-silver nitrate. After again adding a little thiocyanate, the liquid is made up to the mark, shaken, and filtered.

Twenty-five c.c. of the solution are now mixed with 17 c.c. of strong nitric acid, cooled to 18°, and shaken for fifteen minutes with 1—1·25 grams of bismuth peroxide. After cooling for a few minutes by a stream of cold water, the liquid is filtered through a tube, the bottom of which is a perforated porcelain plate covered with asbestos, and the residue is well washed. The permanganate formed is now estimated in the usual manner by means of standardised solution of hydrogen dioxide, the excess of which is titrated with standard permanganate. L. DE K.

Estimation of Iron in Water. OTTO MAYER (*Mon. Sci.*, 1913, **3**, I, 81).—A detailed description of two modifications of a method for the colorimetric estimation of iron in water, based on the action of potassium thiocyanate on ferric salts, the intensity of the colour obtained being compared with those of standard solutions of ferric thiocyanate. F. M. G. M.

The Quantitative Separation of Iron and Chromium. FRANCOIS BOURION and A. DESHAYES (*Compt. rend.*, 1913, **156**, 1769—1771).—By submitting a mixture of chromic and ferric oxides, heated gradually from 200—650°, to the action of a slow current of chlorine charged with sulphur dichloride vapour, a mixture of the chlorides is obtained, from which the ferric chloride alone is extracted by cold water. This method is applicable to mixtures not containing more than 30% of chromic oxide. With more than this percentage, an equal volume of powdered ammonium sulphate must be added to the mixed oxides before chlorination, which is then conducted at first at a low temperature, finally heating the mixture gradually up to 650°. This method gives very accurate results up to 80% of chromic oxide. W. G.

Iodometric Estimation of Free and Combined Chromic Oxide. MAX GRÖGER (*Zeitsch. anorg. Chem.*, 1913, **81**, 233—242).—Chromites may be brought into solution by Storer's method of treatment with concentrated nitric acid and potassium chlorate (*Zeitsch. anal. Chem.*, 1870, **9**, 71). The subsequent precipitation as barium chromate is unsatisfactory, and the good results obtained

by **Pearson** (*ibid.*, 108) are due to a compensation of errors, the solubility of barium chromate in ammonium acetate solution being balanced by the retention of barium chloride by the precipitate.

The substance containing not more than 0·3 gram of chromium oxide is warmed on the water-bath with 10 c.c. of nitric acid, D 1·4, adding one gram of potassium chlorate gradually in the course of an hour. The solution is then boiled for an hour to expel chlorine, cooled, and diluted to 250 c.c., of which 50 c.c. are titrated immediately, and a further 50 c.c. evaporated to dryness and re-dissolved before titration, as a check on the complete expulsion of chlorine.

For the titration, 50 c.c. of dilute sulphuric acid (4%) and 10 c.c. of potassium iodide solution (10%) are added, diluting with 100 c.c. of water after five minutes. The final colour change, in presence of starch, is from pure blue to bluish-green, and is very sharp. Copper and iron must be removed by boiling with potassium hydroxide and filtering before titration. Manganese must be absent, and the method fails to dissolve natural chromite.

C. H. D.

Separation of Chromium and Manganese. W. CORNELIUS (*Pharm. Zeit.*, 1913, **58**, 427).—The metals should be first converted into alkali permanganate and dichromate. On warming the dilute solution on the water-bath with sodium nitrite the manganese is completely precipitated as hydrated peroxide, which is then, after thorough washing with boiling water, converted by ignition over the blowpipe into mangano-manganic oxide.

The filtrate containing the chromate is then acidified with hydrochloric acid, when the liberated nitrous acid causes instant reduction of the chromate. The chromium is then precipitated with ammonia as hydroxide, and ignited to oxide. L. DE K.

Separation of Chromium and Manganese. W. DEDERICHS (*Pharm. Zeit.*, 1913, **58**, 446).—The metals present are converted into sulphates by evaporation with sulphuric acid and fused with sodium hydroxide and a little sodium peroxide. The mass is then treated with hot water, and the solution heated with more sodium peroxide until the green colour has disappeared and the liquid is of a pure yellow colour. The precipitated hydrated manganese dioxide is well washed with hot water, and finally converted by ignition into manganomanganic oxide.

The chromate is estimated iodometrically as usual after acidifying the filtrate with hydrochloric acid, or may be precipitated by neutralising the solution with nitric acid and adding mercurous nitrate; on ignition the precipitate yields chromic oxide.

L. DE K.

The Simultaneous Estimation of Small Quantities of Titanium and Vanadium Colorimetrically. JOSEPH W. MELLOR (*Trans. Engl. Cer. Soc.*, 1913, **12**, 33—35).—When dilute acidified solutions of titanium and of vanadium sulphates, coloured by the

addition of hydrogen peroxide, are measured in a Lovibond's tintometer, making use of the red rays, a straight line curve is obtained for the relation between the concentration of the titanium or vanadium and the tintometer scale. A like relation is found to hold for titanium solutions to which dihydroxymaleic acid (Fenton, T., 1908, **93**, 1064) has been added, and, moreover, the colour is not affected by the presence of vanadium. Knowing the above three relations, which must be determined for the particular observation trough used, it is easy to estimate the amounts of titanium and vanadium present in a solution. In part of the solution the amount of titanium is estimated after the addition of dihydroxymaleic acid; this amount is then allowed for in the measurements on the other part of the solution after the addition of hydrogen peroxide.

In the analysis of a silicate the vanadium and titanium oxides are found with the iron and aluminium oxides in the ammonia precipitate. After washing, calcining, and weighing, the mass is fused with eight times its weight of sodium pyrophosphate, and the resulting cake, when cold, is treated by Gooch's process or by the ether process to remove the iron. The solution is acidified with sulphuric acid, and the titanium and vanadium estimated as given above. T. S. P.

Volumetric Estimation of Gold. VICTOR LENHER (*J. Amer. Chem. Soc.*, 1913, **35**, 733—736).—Lenher (this vol., ii, 514) and Diemer (this vol., ii, 515) have found that sulphurous acid is capable of reducing auric chloride to the aurous state in presence of certain other salts. It is now shown that gold can be estimated volumetrically with ease and accuracy by any of the following methods.

(1) Auric chloride is treated with excess of potassium iodide and the iodine liberated in accordance with the equation:

$$AuCl_3 + 2KI = AuCl + 2KCl + I_2$$

is titrated with standard sulphurous acid. (2) Auric chloride is treated with excess of a strong solution of magnesium chloride and then with potassium iodide, and the iodine is titrated with sulphurous acid. (3) Auric chloride is treated with potassium bromide, and the bromine liberated according to the equation $AuCl_3 + 2KBr = AuCl + 2KCl + Br_2$ is titrated with sulphurous acid. (4) Auric chloride is treated with magnesium chloride and potassium bromide, and the bromine is titrated with sulphurous acid (5 and 6). Auric chloride is treated with magnesium chloride or sodium chloride, and the resulting yellow solution is titrated with sulphurous acid until it becomes colourless. E. G.

Chemistry Applied to Coal Mining. JOHN HARGER (*J. Soc. Chem. Ind.*, 1913, **32**, 460—462).—The Home Office method for the estimation of the composition of fire-damps gives correct results only when the inflammable gas present is pure methane. In some fire-damps there appears to be no other inflammable gas, but in many cases the author has found large quantities of heavy hydrocarbons.

By the following method, using the Haldane apparatus, it is possible to estimate the actual volume of inflammable gas without making any assumption as to its composition: (1) In one portion of the sample the carbon dioxide and oxygen are estimated and the volume of residual inflammable gas plus nitrogen noted. (2) In a fresh portion the carbon dioxide is estimated; the inflammable gas is burned, the carbon dioxide formed is absorbed, and then the residual oxygen and the volume of residual nitrogen noted. From (1) the inflammable gas plus nitrogen, and (2) the nitrogen, the volume of inflammable gas is ascertained. This method also gives the amount of oxygen used, which is very important as a check on the other figures.

An improved method for estimating the inflammable gas is as follows: The carbon dioxide and oxygen are first estimated, and the residual mixture of nitrogen and inflammable gas is driven into the combustion pipette, which contains, instead of the simple platinum spiral, one covered with copper oxide. The spiral is heated by an electric current in the usual way, and the inflammable gas converted into carbon dioxide and water. The remainder of the procedure is as usual.

Bog iron ore acts as a very strong catalyst for the preparation of inert gas free from carbon monoxide. In the presence of a small quantity of oxygen the combustion of the last traces of carbon monoxide is affected at 200° or over. A mixture of hydrogen and air burns at 100° when passed over bog iron ore. This ore can be used instead of palladium preparations in gas analysis.

In the absence of air, carbon monoxide is burnt by copper oxide at temperatures below 100°; hydrogen at one or two degrees above 100° and rapidly at 150°, whilst methane is apparently untouched at these temperatures. The use of copper oxide at 150° is suggested for removing hydrogen from methane when the latter is required pure, and also for estimating hydrogen in the presence of methane.

The presence of carbon dioxide in moderate amount does not appear to influence the combustion of liquid, gaseous, or solid combustibles, but in certain cases, for example, with coal dust, it does seem to exercise a profound influence on the starting of such combustions. T. S. P.

Analytical Methods for Petroleum. P. S. Sadtler (*J. Ind. Eng. Chem.*, 1913, **5**, 393—394).—The quantity of oxygen in petroleum and asphalts may be estimated by burning the substance in an atmosphere of hydrogen and collecting and weighing the water produced. A silica tube is used for the combustion, the further end of the tube being packed with iron-wool; at the beginning of the operation this is heated to bright redness, and hydrogen is passed through the tube until the calcium chloride tube attains a constant weight. The portion of the combustion tube containing the sample is then heated whilst the current of hydrogen is maintained. A U-tube packed with glass-wool is placed between the combustion tube and the calcium chloride tube, and serves to condense vapours other than that of water. A blown petroleum residuum, or so-called

artificial asphalt, was found to contain 3·88% of oxygen when analysed by this method. W. P. S.

Distinction Between Light Petroleum and So-called "Pine-Benzines" (Turpentine Substitutes) by means of Distillation and Solubility Tests. DAVID HOLDE (*Chem. Zeit.*, 1913, **37**, 610—611).—When light petroleum is distilled in an Engler flask the difference in temperature at the beginning of the distillation, as shown by two thermometers, the bulb of one of which is immersed in the boiling liquid whilst the bulb of the other is opposite the exit tube, is usually from 30° to 40°; in the case of turpentine substitutes this difference is generally from 5° to 14°, and in a few instances amounts to 18°. A mixture of 1 vol. of light petroleum with 3 vols. of 96% alcohol always yields a turbid fluid, whilst in the case of turpentine substitutes the mixture is clear.
W. P. S.

Quantitative Estimation of Light Petroleum in Turpentine. (Miss) C. BAKKER (*Chem. Weekblad*, 1913, **10**, 420—425).—The adulterated sample is agitated with concentrated sulphuric acid, and after keeping for twenty-four hours the upper layer is agitated with fuming nitric acid. It is then distilled with steam, and the volume of the light petroleum is measured directly. A. J. W.

The Maumène Number of Turpentine Oil. CARLO GRIMALDI and L. PRUSSIA (*Chem. Zeit.*, 1913, **37**, 657).—When 20 c.c. of turpentine oil are mixed in a vacuum jacketed vessel with 10 c.c. of a freshly prepared mixture of 1 vol. of sulphuric acid, D 1·84, with 7·5 vols. of *iso*amyl alcohol, a rise in temperature of from 77° to 85·7° is observed; the fraction of the oil boiling between 155° and 156° gives a similar Maumène number. Substitutes for turpentine oil (pine oils, etc.) yield numbers which lie below 47°, whilst petroleum oils show practically no rise in temperature with the test.
W. P. S.

Estimation of Caoutchouc by Bromination. WILHELM VAUBEL (*Gummi Zeit.*, 1912, **26**, 1879—1880. Compare Esch, A., 1911, ii, 946).—A description of a rapid method for the estimation of caoutchouc by direct bromination according to the equation:

$$C_{10}H_{16} + 6Br = C_{10}H_{14}Br_4 + 2HBr.$$

The caoutchouc (2 grams) is dissolved in carbon tetrachloride, the solution treated with potassium bromide (5 grams) and 200 c.c. of dilute hydrochloric acid (1:10), followed by 40 c.c. of a standard solution of 2% potassium bromate; a particle of potassium iodide is added, and the iodine set free titrated in the usual manner.
F. M. G. M.

Direct Estimation of Caoutchouc by Titration of Bromine. FRANZ KIRCHHOF (*Gummi Zeit.*, 1913, **27**. 9).—The author discusses Vaubel's method (preceding abstract) of analysing caoutchouc by estimating the excess of free bromine after bromination, and does not consider it satisfactory. F. M. G. M.

New Method for the Direct Estimation of Caoutchouc. L. G. WESSON (*J. Ind. Eng. Chem.*, 1913, **5**, 398).—The method depends on the conversion of the caoutchouc into its nitrosite derivative and the estimation of the carbon in the latter, the quantity of caoutchouc being calculated from the amount of carbon found. The sample is extracted with acetone, and then dissolved or allowed to swell up in carbon tetrachloride; nitrous gases are passed through the solution to saturation, and the nitrosite formed is dissolved in acetone, from which it is separated by precipitation or evaporation. The quantity of carbon is then estimated in the nitrosite by combustion. W. P. S.

Adapted Wiley Extractor for Caoutchouc Extractions. CHARLES P. FOX (*J. Ind. Eng. Chem.*, 1913, **5**, 417).—In place of the usual reservoir, a large glass tube may be substituted; large charges of thin sheet caoutchouc rolled on fabric may be inserted in this tube, which is fitted below the condenser within range of the drip of the condensed solvent. W. P. S.

Estimation of Nitrogen in Caoutchouc. WALTER SCHMITZ (*Gummi Zeit.*, 1912, **26**, 1877—1879).—The author considers the Kjeldahl method to be the most satisfactory for the estimation of nitrogen in caoutchouc. The caoutchouc (2—3 grams) is heated in a 300 c.c. Kjeldahl flask with 45—50 c.c. of concentrated sulphuric acid, with the subsequent addition of copper oxide and potassium sulphate. The distillation of the ammonia can be carried out by (1) direct heating, (2) by the help of a current of steam, or (3) with the aid of a current of air, whilst for the final estimation of ammonium sulphate, potassium iodate and potassium iodide with subsequent titration of the freed iodine is suggested; or sodium oxalate or carbonate can be employed.
F. M. G. M.

Estimation of Nitrogenous By-products in Raw Caoutchouc. ALEXANDER TSCHIRCH and WALTER SCHMITZ (*Gummi Zeit.*, 1912, **26**, 2079—2080. Compare Utz, A., 1912, ii, 1002).—A preliminary account of a method by which crude Para caoutchouc is prepared for the estimation of nitrogen. The caoutchouc (2·5 grams) is neither washed nor freed from resin, but after drying in a vacuum desiccator is heated at 80° with 40—60 c.c. of pentachloroethane, cooled, diluted with chloroform, and the solution filtered; the nitrogen estimations are carried out on the residue, and the contents of the filtrate by the Kjeldahl method. F. M. G. M.

[Examination of Drinks and Animal Organs Suspected to Contain Wood Spirit.] FRANCESCO OLIVARI (*Chem. Zentr.*, 1913, i, 1780; from *Arch. Farmacol. sperim.*, 1913, **15**, 83—96).—See this vol., i, 797.

Estimation of Methyl and Ethyl Alcohols in Mixtures Containing Both. JULIUS MEYERFELD (*Chem. Zeit.*, 1913, **37**, 649—651. Compare A., 1912, ii, 1103).—The dichromate

method for the estimation of methyl and ethyl alcohols yields trustworthy results in the case of the alcohols themselves, and also in mixtures of the same provided that the difference in density of the two alcohols is taken into account in calculating the respective quantities of the alcohols from the amount of dichromate consumed. W. P. S.

Estimation of Glycerol in Fermented Liquids. M. EMMANUEL POZZI-ESCOT (*Bull. Assoc. Chim. Sucr. Dist.*, 1913, **30**, 743—749).—One hundred c.c. of the liquid are treated with about 2 grams of lead hydroxide, heated to remove alcohol and other volatile substances, then neutralised with potassium hydroxide, and filtered; the filtrate and washings together should have a volume of 50 c.c. The filtrate is now distilled under reduced pressure at a temperature of 60°, a current of steam being passed through the distillation flask towards the end of the distillation. The distillate containing the glycerol is then concentrated to a volume of about 40 c.c., and the glycerol is estimated by the well-known dichromate method. W. P. S.

Identification of Phenol by Bromine Water. OTTO ANSELMINO and A. MANDKE (*Chem. Zentr.*, 1913, i, 1543—1544; from *Apoth.-Zeit.*, 1913, **28**, 214).—Bromine water produces a white turbidity with phenol in the extreme dilution of 1 to 38,000. J. C. W.

Effect of Temperature, Acid Concentration, and Time on the Bromination of Phenol for Quantitative Estimations. L. V. REDMAN, A. J. WEITH, and F. P. BROCK (*J. Ind. Eng. Chem.*, 1913, **5**, 389—393).—Having investigated the bromination method for the estimation of phenol, the authors recommend the following procedure: Fifty c.c. of water, 5 c.c. of hydrochloric acid, D 1·2, and 15 c.c. of the phenol solution under examination (this solution should not be stronger than $N/10$) are placed in a stoppered bottle, and $N/10$-bromide-bromate solution (2·76 grams of potassium bromate and 15 grams of potassium bromide per litre) is added with continuous shaking until the contents of the bottle exhibit a slight yellow colour; the temperature of the liquid should be about 22°. After shaking for one minute, 0·5 c.c. of a 20% potassium iodide solution is added, the mixture is shaken for another minute, and the iodine then titrated with $N/10$-thiosulphate solution. Each c.c. of $N/10$-bromide-bromate solution corresponds with 0·0015675 gram of phenol. W. P. S.

Estimation of Phenol in the Presence of Organic Matter. E. MOORE MUMFORD (*Chem. News*, 1913, **107**, 253).—A method for the estimation of phenol in such substances as the media used in bacteriology consists in sulphonating the phenol, nitrating the phenolsulphonic acid, and converting the resulting product into ammonium picrate, the quantity of the latter being then estimated colorimetrically. A quantity of the solution under examination is heated to 90° with a few c.c. of sulphuric acid; 10% potassium

nitrate solution is then added, and the mixture is boiled until all organic matter has been destroyed. After cooling, the solution is rendered alkaline with ammonia, and the coloration obtained compared with that yielded by a known amount of phenolsulphonic acid which has been nitrated and treated with ammonia.

W. P. S.

Estimation of Quercetin in Wine. THEODORE VON FELLENBERG (*Chem. Zentr.*, 1913, i, 1366; from *Mitt. Lebensmitt. Hyg.*, **4**, 1—14).—The foliage of the vine contains quercetin, 1 kilo. of the fresh shoots yielding 0·17 gram (compare Neubauer, A., 1873, 933). Wine, however, contains the substance in the form of its methylpentosan, quercitrin. The yellow dye in wine can be estimated by dyeing-out on mordanted wool and matching against standards. The brownish-red dye in red wine is first removed by unmordanted wool. The dye is developed by fermentation, especially of the grape husks, and can be increased by boiling the husks or the wine with dilute sulphuric acid. Any parts of the vine which are, or have been, green will furnish the dye on warming with dilute sulphuric acid, so that it seems to consist of quercetrin, quercetin, and a decomposition product of a substance allied to chlorophyll.

J. C. W.

Estimation of the Bromine Absorption of Wine. THEODORE VON FELLENBERG (*Chem. Zentr.*, 1913, 1367—1368; from *Mitt. Lebensmitt. Hyg.*, **4**, 14—41).—A standard solution containing potassium bromate and bromide has been applied to the estimation of three "bromine numbers": *A*, the bromine absorbed by the original wine; *B*, that required by the residue after distilling off the alcohol and precipitating with lead acetate; and *C*, the bromine required after shaking the concentrate with basic lead acetate. *A*—*B* gives a measure of the true tanning materials, such as tannin, and also of the dyes (see preceding abstract); *B*—*C* represents those chlorophyll-like substances which absorb bromine; and *C* is accounted for by those substances which give a colour reaction with vanillin and hydrochloric acid (this vol., ii, 78). The author hopes to be able to apply the process to the detection of sophistication.

J. C. W.

Convenient Quantitative Method of Estimation of Pentoses in Presence of Other Sugars by means of Spectral Observations. ERW. PINOFF and K. GUDE (*Chem. Zeit.*, 1913, **37**, 621).—The method is based on Tollens's reaction for the pentoses, the reaction being carried out in alcoholic solution. The coloured solution is then diluted with alcohol until the red and yellow absorption bands are just on the point of disappearing when 20 c.c. of the alcoholic solution is submitted to examination in a cylindrical tube of 3 cm. internal diameter.

Twenty-five c.c. of the pentose solution, containing not more than 3% of pentoses, are mixed with 25 c.c. of hydrochloric acid (D 1·19), 50 c.c. of 96% alcohol, and 0·6 gram of phloroglucinol.

The solution is heated to boiling on a water-bath in a flask provided with a reflux condenser, the boiling continued for half an hour, after which the solution is rapidly cooled. If n volumes of alcohol are required for the dilution of one volume of the resulting solution in order to reduce the intensity of the absorption bands so that they can just be recognised under the above conditions, then the percentage of pentose in the solution submitted to examination is given by $4(n+1)\,0{\cdot}0237$. If $n=0$, this represents 0·0948%, and this is the smallest quantity which gives rise to recognisable absorption bands.

Experiments with solutions containing dextrose, lævulose, and sucrose, together with pentose, have shown that these substances do not interfere with the estimation. H. M. D.

Volumetric Application of Titanium Chloride to the Estimation of Invert Sugar. LEOPOLD RADLBERGER and WILHELM SIEGMUND (*Chem. Zentr.*, 1913, i, 1307—1308; from *Österr.-ung. Zeitsch. Zucker-Ind. Landw.*, 1913, **42**, 34—44).—The method resolves itself into an estimation of the unreduced copper left in a known volume of Fehling solution. The solution is filtered, made up to 500 c.c., and aliquot parts are acidified, treated with potassium thiocyanate and a little ferric chloride, and titrated in the cold in a carbon dioxide atmosphere with titanium chloride, made by boiling 100 c.c. of the 15% solution with 100 c.c. of concentrated hydrochloric acid and diluting to two litres with air-free water. The reduction of the red ferric thiocyanate does not occur until all the cupric thiocyanate is reduced, according to the equations:

$$CuSO_4 + 2KCNS = Cu(CNS)_2 + K_2SO_4,$$
$$Cu(CNS)_2 + TiCl_3 + HCl = CuCNS + TiCl_4 + HCNS.$$

The standardisation of the titanium chloride is effected as follows. The copper sulphate solution is estimated electrolytically, and then 25 c.c. are mixed with 25 c.c. of the Rochelle salt solution, and made up to 500 c.c. Twenty-five, 50, and 100 c.c. are mixed with 2, 4, and 8 c.c. sulphuric acid (D 1·16), 10, 20, and 40 c.c. 10% potassium thiocyanate, and 0·5 c.c. ferric chloride (equivalent to 0·1 c.c. titanium solution), and titrated until the red colour disappears. These conditions are observed for all titrations. The end-point is very sharp, and the method is rapidly carried out and gives good results. J. C. W.

Aluminium Hydroxide as a Protein Precipitating Reagent in the Estimation of Lactose in Milk. WILLIAM H. WELKER and HOWARD L. MARSH (*J. Amer. Chem. Soc.*, 1913, **35**, 823—824).—Experiments are described which indicate that moist aluminium hydroxide can be employed with advantage for the removal of proteins from milk in the process of estimating lactose (compare Marshall and Welker, this vol., ii, 568). The results are not affected by the use of an excess of the reagent, and filtration takes place more rapidly than in the case of the copper-alkali method.

E. G.

Estimation of Milk Sugar in Milk by Precipitation with Ammonium Sulphate. ERICH KRETSCHMER (*Zeitsch. physiol. Chem.*, 1913, **85**, 286—291. Compare Salkowski, A., 1912, ii, 610).—Salkowski's method of estimating milk sugar in milk with the polarimeter after precipitation of the proteins with ammonium sulphate has been compared with a number of other processes. It gives accurate results, and is very suited for rapid working.

E. F. A.

Polarimetric Estimation of Sucrose in Honey by the Lehmann-Stadlinger Method. E. J. SARIN (*Zeitsch. anal. Chem.*, 1913, **52**, 367—371).—The author has found the above process to be quite suitable for the technical assay of honey. The process is based on the difference in rotation before and after inversion of the honey. Using a 10% solution, and observing the rotations at 20° in a Schmidt-Haensch apparatus, the difference in the observations is multiplied by 0·5725; result = sucrose. L. DE K.

The Polarimetric Estimation of Starch in Barley. E. SCHWARCZ (*Zeitsch. ges. Brauwesen*, 1913, **36**, 85—88, 97—102).—The author discusses the work of Lintner (A., 1908, ii, 1077), and describes numerous experiments carried out under different conditions, from which he finds the specific rotation of barley starch to vary between $[\alpha]_D$ +198° and $[\alpha]_D$ +202·43°, according to the acid employed, the temperature, and period of the reaction. F. M. G. M.

Polarimetric Estimation of Starch in Potatoes. FRANZ HERLES (*Zeitsch. Zuckerind. Böhm.*, 1913, **37**, 466—471).—The rotatory power of pure potato starch was estimated by stirring weighed amounts of the fine powder with 25 c.c. of water and adding 25 c.c. of fuming hydrochloric acid (D 1·188); after one hour it is diluted to 100 c.c. To produce 100% polarisation the amount of dry, ash-free starch was found to be 8·821 grams; $[\alpha]_D^{20}$ +196·25°.

To estimate the starch in potatoes, 8·82 or 8·80 grams (for Mohr's or for metric c.c. respectively) of very finely pulped substance are washed with 25 c.c. of water into a 100 c.c. flask, and treated with 25 c.c. of the fuming hydrochloric acid (D 1·188). After an hour it is diluted to 100·35 c.c., filtered, and polarised. The reading gives the percentage of starch direct.

When the potatoes are supposed to contain sugar, or other polarising substances, the usual amount is transferred to a 100 c.c. flask and diluted with water to 100·35 c.c. A portion of the filtrate (50 c.c.) is then treated with 25 c.c. of fuming acid in another flask, diluted to 100 c.c., and polarised.

In the case of meals and finely crushed cereals, it is advisable to employ phosphotungstic acid. N. H. J. M.

Estimation of Glycogen in Muscle. HENRI BIERRY and (Mme.) Z. GATIN-GRUZEWSKA (*Compt. rend.*, 1913, **156**, 1491—1493).—The method for the estimation of glycogen in liver (compare this vol., ii, 160) is applicable for its estimation in muscle. The fresh

meat is taken without any prior extraction and digested with potassium hydroxide solution (35%), the glycogen so dissolved is hydrolysed with hydrochloric acid, and the dextrose estimated after precipitation of the proteins with mercuric nitrate. W. G.

Detection of Acetaldehyde in Paraldehyde. GEORG HEYL (*Chem. Zentr.*, 1913, i, 1363—1364; from *Apoth. Zeit.*, 1913, **28**, 165—166).—Pure paraldehyde does not give the Gentian-blue coloration with sodium nitroprusside and piperidine (Lewin, A., 1900, ii, 179), but traces of acetaldehyde do react. The coloration is transient, but may be used to determine whether the paraldehyde is up to the official standard. J. C. W.

The Detection and Estimation of Formic Acid. HEINRICH FINCKE (*Biochem. Zeitsch.*, 1913, **51**, 253—287).—Steam is passed first through a flask containing the liquid under examination, and the steam and other volatile products are then passed through a second heated flask containing a suspension of calcium carbonate, which neutralises the formic acid. When all the formic acid has been distilled over, the distillate in the second flask is filtered and concentrated, and the formic acid is then estimated by heating the slightly acid liquid with mercuric chloride in the presence of sodium chloride and sodium acetate. The reaction proceeds according to the equation:

$$HCO_2Na + 2HgCl_2 = 2HgCl + CO_2 + NaCl + HCl.$$

The mercurous chloride thus formed is weighed. Certain precautions must be taken when the following acids are present in the distillate: sulphurous, sorbic, glyoxylic, lævulic, cinnamic, salicylic, and fumaric acids. The first-named is oxidised by hydrogen peroxide, the excess of which is destroyed by mercuric oxide. Methods are also given for eliminating errors due to the other acids, which occur, however, only seldom. Formic acid is also formed as a decomposition product of sugars, etc., which may be present in the substance under examination. In this case formic acid will be continuously formed during the distillation, and this fact affords a method for ascertaining whether the acid is a decomposition product, or exists preformed. The experimental methods are given in detail, and the steam distillation apparatus is figured in the text. S. B. S.

Detection of Formic and Acetic Acids. Application in the Analysis of Glycerol. LÉO BONNES (*Chem. Zentr.*, 1913, i, 1364; from *Bull. Sci. Pharmacol.*, 1913, **20**, 99—101).—The liquid is boiled down to one-quarter with sulphuric acid, the distillate neutralised with calcium carbonate, evaporated to dryness without filtering, and then submitted to dry distillation. The distillate is tested for aldehyde with Leys's magenta-bisulphite solution, and for acetone by means of Legal's sodium nitroprusside reaction. J. C. W.

Estimation of Lactic Acid. A. BELLET (*Bull. Soc. chim.*, 1913, [iv], **13**, 565—572 *).—The method is intended for the estimation of

* and *J. Pharm. Chim.*, 1913, [vii], **8**, 21—29.

lactic acid in presence of much organic matter, and involves (1) the elimination of proteins, (2) extraction of the lactic acid by means of ether, and (3) estimation of the acid by conversion into acetaldehyde, and determination of the latter by means of ammoniacal silver nitrate.

For the removal of proteins, Patein and Dufau's reagent is used, which leaves the lactic acid in the mother liquor in the form of sodium lactate. The mother liquor is evaporated to syrupy consistence, mixed with 1 or 2 c.c. of 20% sulphuric acid, and then with enough dry washed sand to enable it to be packed in a Soxhlet extractor of slightly modified form and extracted with dry ether. The partly purified lactic acid thus obtained is carefully oxidised in a special apparatus with permanganate, and the acetaldehyde formed aspirated into a known volume of ammoniacal silver nitrate of known strength. When the reaction is complete the unreduced silver is determined by the Charpentier-Volhard method. The apparatus used is figured in the original, which also gives exact experimental details and a series of typical results. T. A. H.

The Estimation of Lactic Acid in Urine. MAX DAPPER (*Biochem. Zeitsch.*, 1913, **51**, 398—406).—Lactic acid cannot be estimated directly in urine by the method of von Fürth and Charnass, but the urine must be first concentrated, and the acid extracted by ether. The details of the manipulation are described, and estimations of lactic acid from various pathological cases are quoted. S. B. S.

Detection of Hydrocyanic Acid. C. PERTUSI and E. GASTALDI (*Chem. Zeit.*, 1913, **37**, 609—610).—The test proposed depends on the blue coloration or precipitate which is obtained when copper acetate, potassium cyanide, and benzidine acetate are mixed together in solution. The reaction is also given by other substances, and is only characteristic of hydrocyanic acid under the following conditions. After the removal of metals from the solution under examination, the latter is boiled with sodium carbonate, filtered, and carbon dioxide is passed into the filtrate; this is then added to a mixture consisting of 1 drop of a 3% copper acetate solution, 1 c.c. of a 10% disodium phosphate solution, and 4 drops of a saturated benzidine acetate solution. The test will detect 0·007 mg. of hydrocyanic acid in 10 c.c. of solution. W. P. S.

Detection of Benzoic Acid in the Presence of Phenols and Salicylic Acid. LUCIEN ROBIN (*Ann. Falsif.*, 1913, **6**, 277—278).—As phenol, salicylic acid, etc., yield a red coloration when submitted to the test for benzoic acid described previously by the author (A., 1908, ii, 1078), the test must be modified in order to remove the influence of these substances. For this purpose the residue of benzoic acid extracted from the material under examination is dissolved in water, the solution is acidified with sulphuric acid, heated to 80°, and treated with potassium permanganate; this

destroys any phenol or salicylic acid which may be present, and the benzoic acid is then extracted and identified as described.

W. P. S.

The Estimation of Benzoic Acid in Milk. JOHN F. LIVERSEEGE and NORMAN EVERS (*J. Soc. Chem. Ind.*, 1913, **32**, 319—320).—A milk preservative is now on the market, consisting of a mixture of sodium benzoate and sodium carbonate, and the authors have consequently investigated methods for the detection and estimation of benzoic acid in milk. It was found that if a solution of sodium benzoate is acidified with sulphuric acid, distilled with steam, and the distillate extracted with ether, all the benzoic acid could not be recovered. Also, in the case of milk containing no benzoic acid, the steam distillate, when acidified and extracted with ether, yielded a certain residue.

The following empirical method, by means of which about 45% of the benzoic acid is obtained, is recommended: 100 c.c. of the milk are mixed with 10 c.c. of concentrated sulphuric acid, and distilled in a current of steam until 600 c.c. have passed over. The distillate is acidified with 5 c.c. of concentrated hydrochloric acid, and extracted successively with 100, 35, and 35 c.c. of ether, after which the ether is allowed to evaporate and the residue weighed after drying for twenty-four hours in a desiccator; 5 mg. are subtracted from the weight to correct for the blank obtained with milk free from the preservative in question.

A modification of Halphen's test (A., 1908, ii, 906) for benzoic acid is also recommended as giving fair quantitative results. To the residue from the ethereal extract are added 1 c.c. of concentrated sulphuric acid and 0·2 c.c. of concentrated nitric acid, and the dish heated, so that it fumes moderately for three minutes, unless a deep yellow colour forms, when the heating is stopped at once. When cool, 5 c.c. of water are added, and the liquid poured into a 50 c.c. Nessler cylinder, washing the dish with about 3 c.c. of water. One c.c. of a saturated solution of sodium sulphite is then mixed with the liquid, and afterwards 10 c.c. of 6*N*-ammonia. A brown colour indicates benzoic acid. Two c.c. of ammonium sulphite are then added, producing a deep red colour, the solution is diluted to 50 c.c., and the colour compared with standards prepared in the same manner.

T. S. P.

Estimation of Glycyrrhizic Acid in Sweetmeats and in Liquorice Juice. E. DURIER (*Ann. Falsif.*, 1913, **6**, 252—255).—Twenty grams of the sample are dissolved in 50 c.c. of 10% ammonia, and 150 c.c. of 95% alcohol are added gradually; after the lapse of about five hours, the precipitate is separated by filtration, and washed with about 100 c.c. of 70% alcohol. The filtrate and washings are evaporated to dryness, the residue is dissolved in 50 c.c. of water and 1 c.c. of ammonia, the solution is acidified by the addition of 2 c.c. of hydrochloric acid, and set aside for twenty-four hours. The precipitate is then collected on a filter, washed with 25 c.c. of water, dried partially, dissolved in

ammonia, the solution evaporated, and the residue weighed; 0·320 gram of ammonium glycyrrhizate corresponds with 4 grams of liquorice juice, the minimum quantity which, according to French law, should be present in 100 grams of liquorice sweetmeats. To the quantity of ammonium glycyrrhizate found, however, must be added 23 mg. to correct for the solubility of the compound. In the case of liquorice juice (sticks), 2 grams are taken for the estimation, and it is necessary to make repeated extractions with alcoholic ammonia in order to obtain the glycyrrhizic acid in solution. W. P. S.

Comparative Investigation of Different Methods for the Estimation of Uric Acid. LUCIEN BERNARD (*Chem. Zentr.*, 1913, i, 1364; from *Bull. Sci. Pharmacol.*, 1913, **20**, 65—69).—The author finds that Salkowski's method (A., 1895, ii, 538) gives the best results. J. C. W.

The Titration of Uric Acid in Urine after Precipitation with Silver Reagent. ERICH KRETSCHMER (*Biochem. Zeitsch.*, 1913, **50**, 223—232).—For clinical purposes, uric acid can be estimated with sufficient accuracy and rapidly, by precipitating it by Salkowski's method as magnesium silver urate; the precipitate is first treated with sulphuric acid, the precipitated silver sulphate is filtered off, and the filtrate is then titrated with $N/20$-potassium permanganate solution. The values obtained by this method were somewhat too high, and this is due to the fact that the purine substances are also precipitated and obtained in a form in which they are completely oxidised by permanganate. S. B. S.

Estimation of Uric Acid in Urine and Blood JULIUS SCHNELLER (*Chem. Zentr.*, 1913, i, 1234: from *Zeitsch. exp. Path. Ther.*, 1913, **12**, 341—347).—To avoid the loss of uric acid, which is carried down in precipitating the protein, it is converted into its soluble formaldehyde compound. For this purpose, 100 c.c. of blood are introduced into 1 litre of water containing 10 grams of acid potassium phosphate and 10 c.c. of 40% formaldehyde, previously neutralised with sodium carbonate. After separation of the protein, the solid filtrate is concentrated to 100 c.c., and 2 grams of sodium acetate and 10 c.c. of commercial sodium hydrogen bisulphite solution are added. The mixture is then heated, and 10 c.c. of 70% copper sulphate are added. The precipitated copper compound is decomposed by hydrogen sulphide, 10 c.c. of hydrochloric acid are added, and the liquid, after filtration, is concentrated. For quantitative work a further precipitation with ammoniacal silver nitrate is recommended. S. B. S.

Precipitation of Uric Acid and Purine Bases by Zinc Salts. ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1913, **85**, 346).—Both the uric acid and purine bases of urine are completely precipitated by zinc salts. In concentrated acid urine zinc salts occasion a slight flocculent precipitate of zinc phosphate, which

slowly becomes crystalline, and may then be easily mistaken for uric acid. E. F. A.

Some Peroxydase Reactions of Milk. TEMISTOCLE JONA (*Chem. Zentr.*, 1913, i, 1790—1792; from *Arch. Farmacol. sperim.*, 1913, **15**, 122—130).—The usual preservatives do not influence the peroxydase reactions with guaiacol or *p*-phenylenediamine and hydrogen peroxide for the discrimination between fresh and boiled milk. Ammoniacal copper sulphate is not a good preservative, but milk which had been kept at $-10°$ gave a good reaction. On heating the milk, the peroxydase reaction failed earlier with the preserved than with the fresh samples, salicylic acid and mercuric chloride being most marked in this respect. The reaction is influenced by acids in quite different ways, and since the failure of the reaction with old milk depends on the development of acids, it cannot be used to determine the age of the sample. J. C. W.

The Oxidation-Number of Milk. TEMISTOCLE JONA (*Chem. Zentr.*, 1913, i, 1234; from *Giorn. Farm. Chim.*, 1913, **62**, 59—63. Compare A., 1911, ii, 233).—The number of c.c. of 0·1*N*-potassium permanganate required for the oxidation of 1 c.c. of milk is called the "oxidation number," and should be 50 to 52. It is sensibly affected by watering the milk. J. C. W.

Detection of Sesame Oil. G. F. A. TEN BOSCH (*Pharm. Weekblad*, 1913, **50**, 526—527).—The author describes a modification of Kreis's test for sesame oil. One drop of the oil is dissolved in 1 c.c. of light petroleum, benzene, or chloroform, and mixed with 1 c.c. of sulphuric acid containng one-third of its volume of hydrogen peroxide. A green coloration due to the presence of sesamin is developed. A. J. W.

A Rapid Clinical Method for Estimating Urea in Urine. ELI K. MARSHALL, jun. (*J. Biol. Chem.*, 1913, **14**, 283—290).—The urine is treated with extract of soy bean; the urea is by the urease in the extract rapidly converted into ammonium carbonate, and the alkalinity of the solution is then determined by titration, methyl-orange being used as indicator. W. D. H.

Folin's Microchemical Method for Estimating Urea. JOSEPH C. BOCK (*J. Biol. Chem.*, 1913, **14**, 295—298).—In Folin and Farmer's method (A., 1912, ii, 702) the ammonia can be estimated by titration or colorimetrically; titration, however, gives results which are too low. This is due to increase of acidity, which is greater when air is blown through the mixture whilst still hot, and even below room temperature an odour of acetic acid is still noticed. If, however, an extra tube containing strong alkali is introduced so that the air passes through it before going into the standard acid, and the air current is kept up for fifteen minutes, all the acetic acid is retained, and satisfactory results obtained. W. D. H.

Estimation of Urea in Urine by means of Sodium Hypobromite. MARIE KROGH (*Zeitsch. physiol. Chem.*, 1913, **84**, 379—407).—When urea is decomposed with sodium hypobromite part of the nitrogen is set free, and the rest converted into oxides of nitrogen. The carbon is, in part, oxidised to carbon dioxide, and the rest oxidised only to carbon monoxide. The oxidation is the more complete the smaller the proportion of bromine to sodium hydroxide. On adding dextrose, there is still less oxidation, all the nitrogen being eliminated as such, and the greater part of the carbon escaping as monoxide.

Similarly, when ammonium chloride is decomposed by sodium hypobromite, the nitrogen is only in part liberated as such, and the rest as oxides of nitrogen. When dextrose is added, the elimination of nitrogen is lessened, and some of the ammonia is not decomposed, but the total gas evolved is greater as carbon monoxide is set free from the sugar.

The estimation of urea in urine is carried out as follows. After precipitation with phosphotungstic acid and neutralisation, sodium hypobromite is added in the proportion of 1 c.c. of bromine in 24·5 c.c. of 30% sodium hydroxide and 70 c.c. of water. The volume of gas evolved multiplied by 100/96·5 gives the urea nitrogen. When the hypobromite consists of 1 c.c. of bromine in 196 c.c. of 30% sodium hydroxide, the total gas evolved is equal to the urea nitrogen. Duplicate experiments only differ by 1%. The amount of urea so estimated is less than when it is determined by Folin's method. E. F. A.

A Ureometer for Estimation of Urea in Urine, Blood, and Cerebro-spinal Fluid. The Activity of Kidneys and Liver. HEYNINX (*Biochem. Zeitsch.*, 1913, **51**, 355—368).—A ureometer is described by means of which an estimation of urea in 2—10 drops of urine, or 5 c.c. of blood-serum or cerebrospinal fluid, is possible; by this means, it is claimed that it is possible to make a clinical estimation of the activity of the liver. The nitrogen produced by the hypobromite reaction is measured in a small apparatus (which is figured in the text), consisting of two parts—a lower part where the hypobromite reagent is mixed with the liquid under examination, and an upper part, which fits on to this, in which the nitrogen evolved is measured by the displacement of the water in a calibrated tube. S. B. S.

Precipitating Alkaloids by Lloyd's Reagent. SIGMUND WALDBOTT (*J. Amer. Chem. Soc.*, 1913, **35**, 837—838).—Lloyd's reagent for precipitating alkaloids (*Chem. Abstr.*, 1913, **7**, 683) consists essentially of hydrated aluminium silicate, and has the composition: H_2O, 17·41; SiO_2, 55·30; Al_2O_3, 9·82; Fe_2O_3, 14·18; CaO, 1·58; CO_2, not estimated. The activity of the reagent is not destroyed by heating it to 130°, but at a red heat water is expelled, and the reagent becomes inert. If the material is extracted with hydrochloric acid, the residue is still effective. Treatment with concentrated nitric acid or aqua regia does not

impair its activity. The reagent is capable of removing alkaloids completely from neutral or acid solutions, and the alkaloid can be recovered by treating the precipitate with alkali and an alkaloidal solvent. The residue thus obtained is a jelly-like mass which still retains activity towards alkaloids and can also precipitate inorganic salts, such as barium chloride, lead nitrate, and zinc sulphate.

The action is colloidal; it has been found that colloidal silicic acid and colloidal arsenious sulphide are also capable of precipitating quinine sulphate. E. G.

Controls for the Folin Method of Estimating Creatinine. WILLIAM H. THOMPSON (*Proc. physiol. Soc.*, 1913, i—ii; *J. Physiol.*, **46**).—The double picrate of creatinine and potassium was found to act as a more satisfactory control than a solution of creatinine. W. D. H.

Estimation of "Saccharin" in Foods. JOHANN KARAS (*Zeitsch. Nahr. Genussm.*, 1913, **25**, 559—560).—The solution, or aqueous extract of a solid substance, is concentrated, cooled, and treated with about 10 c.c. of a 10% tannin solution and 8 c.c. of basic lead acetate solution. After filtration, the filtrate is acidified with phosphoric acid, the lead phosphate is separated by filtration, and the filtrate is extracted with a mixture consisting of equal volumes of ether and light petroleum. The residue obtained on evaporating the solvent will consist of "saccharin." Substances containing much fat may be rendered alkaline and extracted with ether before the saccharin is extracted with water. W. P. S.

Method of Distinguishing Natural from Artificial Colouring Matters by Estimating their Electrical Conductivity. W. G. CHLOPIN and P. J. VASSILIEVA (*Zeitsch. Nahr. Genussm.*, 1913, **25**, 596—598).—The authors outline a method which depends on the fact that vegetable and animal colouring matters, such as cochineal, catechu, saffron, turmeric, etc., have a much greater electrical resistance than artificial colouring matters; this difference in conductivity is more marked in alcoholic than in aqueous solution. The process will probably be of use in the analysis of mixtures of the two classes of colours. W. P. S.

New Reaction for the Detection of Aniline Colours in Foods and Especially in Wines. PHILIPPE MALVEZIN (*Ann. Chim. anal.*, 1913, **18**, 193).—The reagent is prepared by passing sulphur dioxide into formaldehyde solution; the substance formed, $OH{\cdot}CH_2{\cdot}SO_3H$, yields a violet coloration when mixed with a solution containing a very small quantity of magenta or other aniline colouring matter even when these have been decolorised previously with sulphur dioxide or animal charcoal. The wine to be tested is mixed with a small quantity of animal charcoal, filtered, and a portion of the colourless filtrate mixed with an equal volume of the reagent. If the wine contains magenta or similar colouring

matter, a violet coloration develops; natural wines yield a faint pink coloration. The test is rendered more sensitive by heating the filtrate with the reagent. W. P. S.

Identification of Small Amounts of Dyes by Oxidation with Bromine. WALTER E. MATHEWSON (*Chem. News*, 1913, **107**, 265).—The test consists in adding to the dye solution twice as much bromine water, drop by drop, as is required to decolorise it, followed by solution of hydrazine sulphate, and finally excess of sodium carbonate solution (*A*). A second test portion is treated similarly, except that a few drops of α-naphthol solution (10% in 50% alcohol) are added just before making alkaline (*B*).

Typical examples of the following groups of dyes give the colours mentioned with the tests *A* and *B*: *Nitro-dyes*, both yellowish-brown. *Monazo-dyes*, *A*, colourless, pale olive, blue, or bluish-red; *B*, red or purplish-red. *Disazo-dyes*, *A*, brown; *B*, purple to brown. *Triphenylmethane dyes*, both nearly colourless. *Xanthen dyes*, both red with green fluorescence to bluish-red. *Alizarin*, both purplish-red. *Azine dyes*, both red. *Quinoline dyes*, both yellow to pale brown. *Natural dyes*, both pale yellow to pale brown. The dye should be purified, if necessary, by extracting with amyl alcohol, before applying the tests. T. A. H.

Detection of Saffron in Farinaceous Foods. CARLO MARTINI (*Boll. chim. Farm.*, 1913, **52**, 37—41).—The colour reactions of saffron with sulphuric acid or with nitric acid do not give satisfactory results when they are directly applied to farinaceous matter. A good preliminary indication is afforded by the characteristic aromatic odour produced when the material is boiled with acid. If artificial colouring matters are not present, the suspected material may then be extracted thoroughly with alcohol, the residue after evaporation purified by extraction with ether at least twice, then treated with alcohol again. The residue obtained when this is evaporated yields the fugitive blue coloration with nitric acid. The reaction with sulphuric acid can only be obtained with certainty if the above treatment with ether has been repeated a third time with anhydrous ether, and even then a definite blue coloration is not always seen, but more frequently a green coloration becoming brown. With sulphuric acid a violet coloration appears later, even in the absence of saffron. R. V. S.

The Triketohydrindene Hydrate [Reaction] (Ruhemann). EMIL ABDERHALDEN and HUBERT SCHMIDT (*Zeitsch. physiol. Chem.*, 1913, **85**, 143—147. Compare Abderhalden and Schmidt, A., 1911, ii, 674).—The sensitiveness of the triketohydrindene hydrate reagent depends on the concentration of the reacting products—a blue coloration is often obtained on concentration when it was not at first visible. Fresh milk, urine, saliva, blood plasma, lymph, sweat, fresh and boiled egg-white, fresh and cooked meat when dialysed give up substances which show no biuret reaction, but react with triketohydrindene. A glass rod which has been handled with the

fingers for some time will give a reaction with triketohydrindene. The reagent shows 1 part of glycine in 65,000 and about 1 in 15,000 to 25,000 of the other monoamino-acids. Proteins must be purified by dialysis until the dialysate no longer reacts with the reagent before being used for anaphylaxical studies. E. F. A.

A Colour Reaction for Proteins. LOUIS LEWIN (*Ber.*, 1913, **46**, 1796—1798).—A 0·1% solution of triformoxime (trioximinomethylene) in commercial sulphuric acid gives a pure violet, persistent coloration with proteins. The reaction is very delicate, and takes place with 1 c.c. of a 0·05% solution of egg-albumin or even with diluted saliva. A solution of the reagent in pure sulphuric acid gives a yellow colour, which, however, shows the same absorption band, $\lambda = 536$ $\mu\mu$. Traces of selenium or, to a lesser extent, arsenic are the cause of the violet coloration. Paraformaldehyde gives similar effects, but it is not so sensitive. Indole and codeine also give characteristic violet or gentian-blue colours, but glue does not respond to the test. J. C. W.

The Conditions for Precipitation of Albumin by Picric Acid. HENRI LABBÉ and R. MAGUIN (*Compt. rend.*, 1913, **156**, 1415—1417). —Using Esbach's citro-picric reagent, the authors have determined the amount of picric acid fixed by varying amounts of ovoalbumin during their precipitation by a given volume of the reagent. The process consists in estimating the acidity of the liquid before and after the admixture of the albumin solution. By plotting the weights of albumin used against the amounts of picric acid fixed, the points are found to lie on the branch of a hyperbola, and by means of this curve, in conjunction with two acidimetric titrations, unknown amounts of albumin can be estimated. W. G.

Estimation of the True Reaction of the Blood by the Electric Method. A. P. KONIKOV (*Biochem. Zeitsch.*, 1913, **51**, 200—210).—Attention is called to the influence of the dissolved oxygen and carbon dioxide in the blood when the reaction of the latter is measured electrometrically. The oxygen acts in that it reduces the hydrogen, and the carbon dioxide in that on evolution it increases the alkalinity of the blood. To eliminate the latter effect an apparatus is described, whereby the blood is shaken in the presence of hydrogen, and into the hydrogen–carbon dioxide atmosphere thus produced containing the electrode, fresh blood is introduced (compare Hasselbalch, this vol., ii, 379). The readings are taken when the potential differences are constant, that is, when the evolved oxygen has combined with the hydrogen, which process is accelerated by shaking and warming slightly. If the blood is laked, by alternate freezing and thawing, the acidity is increased. The reaction of the formed elements is therefore different to that of the serum S. B. S.

General and Physical Chemistry.

The Optical Properties of Water and its Physical Constitution. C. CHÉNEVEAU (*Compt. rend.*, 1913, **156**, 1972—1974).—The author has measured the refractive power of water at 0° and 100°, and finds that the results are in agreement with the hypothesis that water is a mixture, in a proportion varying with the temperature, of two substances, one of which is analogous to ice. Measurements on solutions of different concentrations of potassium chloride at 15° showed that the specific refractive power of the water was constant, although the proportion of "ice" varies with the concentration. T. S. P.

Relationship between Physical Properties of Solutions. IV. Refraction, Dispersion, and Dissociation of Salts in Water. ADOLF HEYDWEILLER (*Ann. Physik*, 1913 [iv], **41**, 499—542. Compare Abstr., 1910, ii, 106, 398; 1912, ii, 433).—The refractive indices of solutions of a number of salts at concentrations from 0·1—4·0 *n* for sodium light at 18° are given together with the corresponding values for λ_α. λ_β, and λ_γ for hydrogen. From these the value for equivalent solutions is calculated by means of the formula $\Delta_n = 100(n-n_0)/mn_0$, in which Δ_n is the refractive index for an equivalent solution, m the molecular concentration of the solution, n_0 the refractive index of water, and n that of the solution. The salts examined consist of a number of acetates, iodates, chlorates, nitrates, thiocyanates, fluorides, chlorides, bromides, iodides, sulphates, chromates, and metasilicates. It is shown that by means of the Δ_n value, which changes only slightly with concentration, n can be calculated for any concentration by means of the expression $n = 1{\cdot}33327 + 4m/300{\cdot}\Delta_n$. It is shown that Δ_n runs parallel with the corresponding density value Δ_s, and that the following relationship exists between the electro-conductivity and the refraction: $\Delta_n = B_n + (A_n - B_n)i$, in which i represents the electrolytic dissociation, A_n the value of Δ_n for a normal solution of ions, and B_n the corresponding value for a normal solution of undissociated molecules. The values of A_n, B_n, and $(A_n - B_n)$ are calculated for the cases examined. The author calculates a number of ionic moduli for the refraction, on the assumption that the refraction of a dissolved compound is the mean of the sum of the refractions of its ions. Thus $A_n = A_{n\eta} + A_{na}$, in which $A_{n\eta}$ and A_{na} are the ion constants. In this way the following values have been obtained: $H^{\bullet} = -119$, $Li = -55$, $Na' = 61$, $Ag' = 679$, $NH_4' = 60$, $K' = 85$, $Rb' = 154$, $\frac{1}{2}Mg' = 208$, $\frac{1}{2}Zn' = 389$, $\frac{1}{2}Cd' = 381$, $\frac{1}{2}Cu' = 421$, $\frac{1}{2}Ca' = 319$, $\frac{1}{2}Sr' = 396$, $\frac{1}{2}Ba' = 495$, $C_2H_5{\cdot}COO' = 1025$, $CH_3{\cdot}COO' = 846$, $H{\cdot}CO{\cdot}O' = 664$, $IO_3' = 1985$, $BrO_3' = 1254$, $ClO_3' = 778$, $CNS' = 1316$, $NO_3' = 718$, $F' = 480$, $Cl' = 777$, $Br' = 1063$, $I' = 1619$, $OH' = 795$, $\frac{1}{2}SO_4' = 1026$, and $\frac{1}{2}CrO_4 = 1665$. The above

numbers are all multiplied by 1000. It is shown that the cation moduli can be represented with very close approximation by a multiple of the figure 0·029. The author calculates the refraction equivalents of the undissociated and completely dissociated salts by means of the Lorenz-Lorentz formula, and finds generally that the latter quantity is about $3\frac{1}{2}\%$ larger than the former. The true ionic volumes are calculated from considerations based on the ionic refraction, and the following values for the cross-section of the following ions obtained: $d \times 10^8 =$ H 1·65, Li 1·75, Na 1·93, K 2·38, Rb 2·62, Ag 2·74, Cs 2·93, Tl 3·27, Mg 2·01, Zn 2·38, Cu 2·38, Ca 2·43, Sr 2·62, Cd 2·70, Ba 3·00, Pb 3·46, F 1·39, Cl 2·74, Br 3·15, and I 3·70. From these values it is shown that the true ionic volume is not, like the apparent atomic volume, a periodic function of the atomic weight. It is shown that the dispersion and constitution are related; the author represents the dispersion by $10^3(\Delta_{n\gamma} - \Delta_{n\alpha})$, and from these values it is shown that the dispersion in the visible spectrum is practically independent of the nature of the cation, and consequently depends practically entirely on the anion. Measurements similar to the whole of the foregoing are recorded for the ultraviolet part of the spectrum. J. F. S.

Band Spectrum of Barium Fluoride in the Electric Arc and Line Spectrum of Barium from 7059—8200 A.U. HANS GEORGE (*Zeitsch. Wiss. Photochem.*, 1913, **12**, 237—258).—The band spectrum was measured from photographs by a measuring machine. The spectrum was produced by means of a Rowland concave grating 6·34 metre radius of curvature and 20,000 lines per inch. The incandescent vapour was obtained by filling hollow carbon rods with powdered barium fluoride and feeding the arc with 2·5 amperes at 220 volts. In some cases, to avoid the carbon bands, the carbon electrodes were replaced by copper tubes. Ten visible bands are described, together with one in the infra-red and one due to barium oxide. The line spectrum of barium from 7059 to 8200 is measured with the international normal. Discussion of the previous work and results on this subject is given in the paper. J. F. S.

Displacement of the Spectral Lines of Certain Metals Produced by the Presence of the Vapour of Another Metal. KEIVIN BURNS (*Compt. rend.*, 1913, **156**, 1976—1978).—The lines of the spectrum of barium or manganese, as obtained in the spectrum of an arc between iron electrodes containing these metals as impurities, are found to have suffered a displacement, as compared with the lines obtained from an arc between carbon electrodes which have been impregnated with salts of the metals. The same holds for cadmium in the presence of mercury, as, for example, when a quartz lamp containing a cadmium amalgam is used as the source of light.

This phenomenon may possibly account for the differences observed between the wave-lengths of lines in the solar and arc spectra.

It follows that it is not safe to take the wave-lengths of lines due to impurities as spectral standards. T. S. P.

Method of Observing the Flame Spectra of Halogen Salts. E. N. DA C. ANDRADE (*Proc. London Physical Soc.*, 1913, **25**, 230—234).—If metals such as copper, nickel, iron, etc., be held in a bunsen flame containing chlorine, produced by leading the air supply through chloroform, characteristic colours are imparted to the different zones of the flame. These colours are due to the chlorides of the metals which can exist in the flame undissociated in the presence of excess of chlorine. This method makes it comparatively easy to observe the different emissions which occur in the different zones. The electrical migration of the vapour can also be observed in such flames. All the chloride spectra have common characteristics. Smithells (*Phil. Trans.*, 1900, *A*, **193**, 121) showed that the colour of lithium and strontium flames is destroyed by the presence of chlorine. In such cases the vapours are not electrically charged, whilst in the case of those metals which give coloured flames in the presence of chlorine the vapours are charged. Compound spectra were observed in some cases on introducing wires into flames containing bromine or iodine vapour.
J. F. S.

Different Band Spectra of Mercury. JOHANNES STARK and GEORG WENDT (*Physikal. Zeitsch.*, 1913, **14**, 562—566).—It is shown that there are at least three band spectra of mercury. The first is obtained in the positive light of a mercury lamp at a pressure of 1—10 mm. and a current of 10—30 milliamps. It consists of five bands, which have maxima at λ 490 $\mu\mu$—400 $\mu\mu$, λ 350 $\mu\mu$—310 $\mu\mu$, λ 270 $\mu\mu$—250 $\mu\mu$, λ 248 $\mu\mu$, and λ 234 $\mu\mu$. The second band spectrum is obtained in the positive light in hydrogen of 10—20 mm. pressure and a current of 12—20 milliamps. This consists of thirteen bands and of three other bands of a quite different nature. A third band spectrum is observed in the negative light, but details of this are reserved for a future publication. The author considers that the first spectrum is caused by the neutral system univalent mercury-ion-electron in the process of recombining to form a neutral atom. The second spectrum is probably due to an electron which is combining with bi- or ter-valent mercury ions. The third spectrum is regarded as being due to either a ter- or quadri-valent mercury ion combining with an electron. J. F. S.

Differentiation between the Mercury Lines λ 2536·7 and 2345·5 Å and the Mercury Bands λ 2540 and λ 2346 Å. JOHANNES STARK and GEORG WENDT (*Physikal. Zeitsch.*, 1913, **14**, 567—568. Compare last abstract).—A comparison of the characteristics of the above-mentioned bands and lines is given, which enables the one to be identified in the presence or absence of the other. J. F. S.

Normal System of Wave-lengths in the Arc Spectrum of Iron. F. Goos (*Zeitsch. wiss. Photochem.*, 1913, **12**, 259—275).—The author points out that in determining the arc spectrum of iron second order, it is not sufficient to say that the arc was using a current between 5 and 10 amperes, but every condition, particularly the pressure, must be characterised. Measurements of Fabry and Buisson, Eversheim, and Pfund are quoted as showing differences which have arisen in the second order iron spectrum from differences in the arc. The normal third order for the iron arc spectrum is discussed. The influence of pressure on the width of lines and the sensitiveness of certain lines to changes in pressure are discussed by the author, and measurements are given. Suggestions are made for the determination of the normal third order for the iron spectrum. J. F. S.

Arc Spectrum of Platinum Measured on the International Normal. Erich Symons (*Zeitsch. wiss. Photochem.*, 1913, **12**, 277—295).—The author has photographed and measured the arc spectrum of platinum; the measurements in the region λ 6945—λ 4282 were made on the international normal, and the regions below and above this on Buisson and Fabry's normal measurements. The measurements were made by means of a Rowland concave grating 6·4 metre radius of curvature and 20,000 lines to the inch. The measurements in the region λ 6500—λ 2500 were made on the second order spectrum, whilst those above and below were made on the first order spectrum. The illumination was obtained by placing small pieces of platinum foil in the crater of a carbon arc fed by 5 amperes at 220 volt direct current. A full list of the lines is given, ranging from $\lambda = 6710{\cdot}44$ to $\lambda = 2144{\cdot}19$. These values are compared with the measurements of Rowland and Tatnall, Exner and Haschek, and Kayser. J. F. S.

The Absorption of Water Vapour and New Residual Ray Groups in the Region of Long Wave-lengths. Heinrich Rubens (*Sitzungsber K. Akad. Wiss. Berlin*, 1913, **28**, 513—549. Compare A., 1910, ii, 172, 262).—Experiments are made on the influence of water-vapour on the residual rays obtained by reflexion from four surfaces of rock salt, sylvine, and potassium bromide. It is shown that water-vapour has a very marked influence on the energy distribution of the residual rays, and that existence of two maxima in the energy curves of these substances is entirely due to the water-vapour in the atmosphere through which the rays pass. The mean wave-length is but slightly influenced by the presence of water-vapour. The residual rays from silver chloride, lead chloride, calomel, and silver bromide were examined, and shown to have mean wave-lengths of $81{\cdot}5\mu$, $91{\cdot}0\mu$, $98{\cdot}8\mu$, and $112{\cdot}7\mu$ respectively. The energy distribution curves of these substances also show peculiarities which must, from a study of the interference curves, be attributed to water vapour. Water vapour shows a strong absorption over the spectrum range 45μ—120μ, with specially strong absorption at 50μ, 66μ, 79μ, and probably also

at 58μ and 103μ. Water vapour is particularly transmissive at 47μ, 54μ, 62μ, 75μ, 91μ, and 115μ. In the region 53μ—113μ quartz exhibits a strong dichroism in the sense that the residual rays are more strongly absorbed when the electric vector swings at right angles to the axis than when the vector is parallel to the axis.
J. F. S.

The Absorption of Light by Inorganic Salts. IX. Solutions of Copper, Nickel, and Cobalt Salts in Alcohol and Acetone. ROBERT A. HOUSTON and A. H. GRAY (*Proc. Roy. Soc. Edin.*, 1913, **33**, 137—146. Compare A., 1911, ii, 785, 786; 1912, ii, 507).—The authors investigate the absorption spectra of the salts of nickel cobalt and copper salts in solution in acetone and alcohol. The measurements are made by means of a spectrophotometer, and are all in the visible region. In many cases, particularly the nitrates, it was impossible to obtain the salts anhydrous owing to decomposition, and in other cases, that is, sulphates, the anhydrous salts were found to be insoluble in alcohol and acetone. In these cases the hydrated salts were used for measurement of the extinction-coefficient, whilst in other cases the anhydrous salts were used. The general result is drawn from the measurements, that when copper, nickel, and cobalt salts are dissolved in acetone or alcohol their absorption is much greater, and at the same time more characteristic of the molecule than when they are dissolved in water. The addition of water to a solution of cobalt bromide in alcohol was next studied, and an attempt made to show that the change in colour of the solution is due to a balanced action:

$$CoBr_2 + xH_2O \rightleftharpoons CoBr_2,xH_2O.$$

The values of x do, it is true, in most cases approximate to 6, and consequently make it extremely likely that the colour change is brought about by the anhydrous salt changing into the hexahydrate.
J. F. S.

The Absorption of Light by Inorganic Salts. X. ROBERT A. HOUSTON and CHARLES COCHRANE (*Proc. Roy. Soc. Edin.*, 1913, **33**, 147—155. Compare preceding abstract.).—The present paper deals with four points arising out of previous papers. (1) Ewan (A., 1895, ii, 433, 471) had pointed out that the molecular-coefficient of copper acetate varied with the wave-length in the same way as the molecular extinction-coefficients of other salts of copper, but its value was approximately two and a-half times the value of the latter. Curves showing the relationship between the sulphates and acetates of copper, nickel, and cobalt are given, which show the abnormality of copper acetate. This is attributed to a difference in chemical constitution. (2) With respect to the colour of ions the authors show that the molecular extinction-coefficient remains constant at low concentrations, and increases asymptotically as saturation is reached. The behaviour is entirely different from that of the molecular conductivity; consequently there is no connexion between the two quantities. The authors draw the conclusion, therefore, that ionisation has nothing whatever to do with the

colour changes of copper, nickel, cobalt and iron salts in solution. (3) It is shown from the shape of the curve for the extinction-coefficient of anhydrous cobalt chloride in acetone that the acetone doubtless combines with the cobalt chloride; and (4) the absorption of cobalt and nickel iodides had been previously shown to have very large absorptions approaching that of iodine. The results were redetermined and shown to vary with the age of the solution. Eventually it is shown that the two iodides break up in solution into iodine and oxyiodides of the formulæ Co_2I_3O and

$$NiI_2,9NiO,15H_2O$$

respectively, thus explaining the high absorptive values of the solutions. J. F. S.

The Absorption of Light by Inorganic Salts. XI. Conclusion. ROBERT A. HOUSTON (*Proc. Roy. Soc. Edin.*, 1913, **33**, 156—165. Compare preceding abstracts).—A theoretical paper in which the work published in the preceding papers is criticised, together with the various theories of absorption. The author states that there is no spectroscopic evidence in favour of the theory of electrolytic dissociation, but there is some evidence against it which can, however, be surmounted by the assumption of hydrolysis, complex ions, hydration, etc. J. F. S.

Quantitative Investigation of the Absorption of the Ultraviolet Rays by Aliphatic Monamines, Diamines, Nitriles, Carbylamines, Amides, and Oximes. JEAN BIELECKI and VICTOR HENRI (*Compt. rend.*, 1913, **156**, 1860—1863).—The authors have studied the influence of the different groups containing nitrogen in the above substances on the absorption of ultraviolet rays, the determinations being made in alcoholic solution. They are led to the following conclusions: (1) In all the cases examined, absorption takes place in a regular manner, the value of the molecular absorption constant increasing with diminishing wave-length of light up to $\lambda = 2144$; (2) absorption of ultraviolet rays by primary amines of the series $C_nH_{2n+1}NH_2$ increases with the value of n. When compared with the corresponding alcohols, the replacement of -OH by -NH_2 causes a considerable increase in absorption. The absorptive power of the hydroxyl group is small, so that, for the alcohols, the influence of the alkyl group is the predominant factor. The absorption of alcohols of the series $C_nH_{2n+1}OH$ increases with the value of "n" according to an exponential law. On the other hand, the influence of the amino-group in primary amines is very considerable, and masks the absorption due to the alkyl group in such a manner that the relative variations of the absorption with regard to the value of "n" are small; (3) secondary and tertiary amines resemble primary amines in their general behaviour; (4) when the hydrogen atoms in ammonia are successively replaced by alkyl groups of the formula C_nH_{2n+1}, a strongly marked increase of absorption is noticed which follows an exponential law; thus, for $\lambda = 2389$ the values of ϵ are 0·66 for methylamine, 1·8 for dimethylamine, and 15·8 for trimethylamine; (5) the absorption curve of

ethylenediamine resembles that of ammonia; (6) substances in which nitrogen is triply linked to carbon or is quinquevalent have very little absorptive power; (7) the absorption of amides resembles that of the corresponding acids. Substitution of the hydroxyl by the amino-group produces an increase in absorption, which, however, is of relatively less importance than in the case of alcohols and primary amines, since the absorption due to the acyl group is itself considerable; (8) the absorption of oximes is greater than that of amines, and substitution of the two atoms of hydrogen of the NH_2 group by alkyl radicles produces a very marked increase in absorptive power. H. W.

Action of Radiations on a Mixture of Coloured Substances. P. A. DANGEARD (*Compt. rend.*, 1913, **156**, 1844—1845).—It has been previously shown that only the rays actually absorbed are causative of the decolorisation of chlorophyll. When light is allowed to act on a mixture of chlorophyll and pinaverdol, the latter is first decolorised at the first absorption band of the chlorophyll, later at its own absorption band; in the absence of chlorophyll, pinaverdol is only decolorised at its own absorption band, from which it follows that the latter is attacked and finally destroyed through the energy absorbed by the chlorophyll, and not by that absorbed by itself. The experiments have been extended to a variety of coloured substances, with the general result that radiations which are completely inactive towards a pure substance are found to become active in the presence of a second pigment. Since chlorophyll in the plant is accompanied by various yellow pigments, such as carotine and xanthophyll, and decolorisation is complete at the bands I, II, III, and IV, it follows that these pigments are also attacked and ultimately decomposed through the energy absorbed by the chlorophyll. H. W.

Colorimetric Dilution Law. ARTHUR HANTZSCH (*Annalen*, 1913, **398**, 379—384).—Several examples have been given by the author of substances which attain a state of isomerism-equilibrium in solution and exhibit variations from Beer's Law. It is now stated that these abnormalities are due to the presence of traces of impurities in the solvent or in the solute. Ethyl acetoacetate in very carefully purified hexane follows the law, although in ordinary hexane it exhibits abnormalities. Optical abnormality is shown by the colourless and the yellow modifications of ethyl dichlorodihydroxyterephthalate in all solvents; this is due to an impurity in the solute, because the more easily purified methyl ester obeys Beer's law in all solvents. Doubtless the same explanation accounts for the abnormal optical behaviour of the colourless and the yellow modifications of nitro-*p*-acetotoluidide.

The variations of the chromoisomeric pyridine, quinoline, and acridine salts from the colorimetric dilution law can be explained by the ionic hypothesis in the case of dissociating solvents; a satisfactory explanation of the abnormalities in non-dissociating media cannot be given. C. S

Interference Phenomena of Pleochroic Liquid Crystals in Convergent Polarised Light. DANIEL VORLÄNDER and M. E. HUTH (*Zeitsch. physikal. Chem.*, 1913, **83**, 723—727).—It is shown from a study of the interference figures of liquid crystals that they are analogous to uniaxial crystal plates cut at right angles to the crystal axis. Mixtures of liquid crystals when examined under crossed nicols do not show the same colours in all four quadrants of the interference figure. This was noticed first with a mixture of *p*-cyanobenzylideneaminocinnamic active amyl ester and *p*-cyanobenzylideneanisidine. This behaviour is found in the case of all strongly pleochroic and circularly polarising liquid crystals. A number of coloured diagrams of interference figures are appended to the paper. J. F. S.

Studies of the Processes Operative in Solutions. XXVIII. The Influence of Acids on the Rotatory Power of Cane Sugar, of Glucose, and of Fructose. FREDERICK P. WORLEY (*Proc. Roy. Soc.*, 1913, *A*, **88**, 439—443).—The author has studied the effect of adding benzenesulphonic acid in different dilutions to solutions of sucrose, dextrose, and lævulose with respect to the rotatory power. It is shown that the large alteration produced by the acid in the value of the ratio of the final to the initial rotation in experiments on the hydrolysis of sucrose can be completely and satisfactorily explained by the changes produced by the acid on the rotatory powers of the three sugars involved. J. F. S.

Energy Changes during Photochemical Reactions in Gases. III. Photochemical Deozonisation. EMIL WARBURG (*Sitzungsber K. Akad. Wiss. Berlin*, 1913, 644—659. Compare A., 1911, ii, 834; 1912, ii, 315).—The author has investigated the decomposition of ozone by light of known wave-length. The ozone was mixed with oxygen, nitrogen, and helium respectively. It is shown that the Einstein photochemical equivalent law (*Ann. Physik*, 1912, [iv], **37**, 832) holds for the cases examined. It is also shown that the specific photochemical deozonising is approximately twice as large in moist ozone–oxygen mixtures as in the corresponding dry mixtures. The spontaneous decomposition of ozone is increased by the presence of aqueous vapour. The photochemical action in concentrated ozone–oxygen mixtures decreases with the intensity of the illumination. J. F. S.

Photochemical Decomposition of Solutions of Oxalic Acid in Presence of Uranyl Nitrate. MARCEL BOLL (*Compt. rend.*, 1913, **156**, 1891—1894).—It has been shown previously (Fay, A., 1896, i, 464) that oxalic acid is decomposed by uranyl nitrate in presence of light, and that the nitrate is unchanged at the end of the reactions. The author finds that the acid is oxidised to carbon dioxide. Examined by the method already described (this vol., ii, 171, 265) and the change being measured by conductivity determinations, the reaction was found to be unimolecular, and this was confirmed by determinations of the initial velocity of reaction If

uranyl nitrate takes any part in the reaction, it must therefore be re-formed as quickly as it is decomposed. The coefficient of absorption of light for the mixture is practically the sum of those of the two components, and the energy absorbed is inferior to that required by Einstein's rule (*J. Phys.*, [v], **3**, 277). In this and the case examined by Henri and Wurmser (this vol., ii, 171) systems of false equilibrium are concerned, in which a spontaneous reaction proceeds feebly and is accelerated by light. T. A. H.

Photocatalysis. MARC LANDAU (*Compt. rend.*, 1913, **156**, 1894—1896. Compare preceding abstract).—The decomposition of oxalic acid by uranium and its compounds has been investigated, and shown not to be parallel with the radioactivity of the substances used. The lightest and heaviest metal of each of six groups of the periodic table (I, II, III, VI, VII, VIII) were also tried in the form of nitrates, and of these only chromium and uranium (group VI) proved to be active, uranium being three times as active as chromium. A mercury lamp was used as the source of light.

T. A. H.

Quantitative Investigation of the Action of Monochromatic Ultra-violet Rays on Amylase. A. CHAUCHARD and Mme. CHAUCHARD (*Compt. rend.*, 1913, **156**, 1858—1860).—Two methods have been employed in the study of the effect of variation in the wave-length of the ultraviolet light employed on the rate of destruction of amylase. In the first of these, the source of light is the spark passing between cadmium electrodes. The light is filtered by suitable screens and allowed to traverse the solution of amylase, when it is found that the rays $\lambda = 2469$, 2300, and 2195 are more active than those of greater wave-length. In the second series the light from a spark passing between magnesium, cadmium, or zinc poles is resolved by two quartz prisms, and the individual rays are allowed to act on the amylase solution. The amount of decomposition is found to increase as the wave-length of the light employed decreases.

By a comparison of these results with the absorption of the different rays by the amylase solution, the authors are led to the conclusions that: (i) the photochemical action of ultraviolet rays on a solution of amylase is proportional to the absorption of these rays by the solution, and (ii) an amount of radiant energy sufficient to raise the temperature of the solution through only $\frac{1}{4}$ degree is capable of bringing about the destruction of 40% of the amylase.

H. W.

Light-Reactions Observable in the Cardioid Ultramicroscope. WILHELM BILTZ (*Zeitsch. Chem. Ind. Kolloid.*, 1913, **12**, 296—299).—The author records a number of reactions which take place in the strong illumination of the cardioid ultramicroscope (compare Siedentopf, A., 1910, ii, 289). It is shown that a drop of a carbon disulphide solution of sulphur precipitates amorphous sulphur in two to five minutes, and that Fehling solution rapidly

changes from blue to green, yellow, and finally red. Sodium nitroprusside quickly shows the presence of rapidly-moving submicrons the nature of which is unknown, but the author considers that they are not substances of the iron cyanide groups, since they are red in colour. A mixture of mercurous chloride and ammonium oxalate on illumination with white or blue light rapidly shows the formation of feathery crystal-aggregates. Dichromated gelatin, malachite-green, and uranin all show rapid formation of submicrons, indicating that a chemical change has been induced by the light.

J. F. S.

Biochemical Catalysis of a Luminescent Oxidation. Jules Ville and Eugène Derrien (*Compt. rend.*, 1913, **156**, 2021—2022).—It has been known for some years that the atmospheric oxidation of lophine in solution in alcoholic potassium hydroxide is accompanied by luminescence (Radziszewski, A., 1881, 488). Luminescence in a much more marked degree is observed if the same quantity of lophine in alcoholic solution is treated with a much smaller quantity of sodium hydroxide, some dilute hydrogen peroxide, and a little hæmatin solution. The peroxydase character on which the effect of the hæmatin depends can be also supplied by hæmin or a little diluted blood. A similar luminescence can be observed during oxidation in pyridine solution, but in this case tartaric acid must be present, and the effect is produced only by hæmatin and hæmin.

D. F. T.

The Equivalence of Ionisation and Chemical Action under the Influence of α-Rays. Samuel C. Lind (*Le Radium*, 1913, **10**, 174).—In the previous paper (*ibid.*, 1912, **9**, 426) the values given for the total number of ions furnished by the α-particle should have referred to pairs of ions. This correction does not affect the general conclusions, but necessitates a modification in the mechanism proposed for the formation of ozone in that four ions instead of two are required per molecule of ozone.

F. S.

The Passage of β-Rays Through Matter. J. Gedult von Jungenfeld (*Physikal. Zeitsch.*, 1913, **14**, 507—514).—Measurements of the absorption-coefficient μ of the β-rays of uranium-X have been made for a number of new materials (iridium, tantalum, antimony, cadmium, rhodium, sulphur, and sodium), and the results are considered from the point of view of Schmidt's theory of absorption. A number of mixtures and compounds were also studied. Comparison is made between the observed and calculated values of $(\mu/D)_0$, the initial value of the absorption-coefficient divided by the density, for alloys of lead and tin, mixtures of powdered metals, the halogen salts of potassium, and the sulphates of the alkaline-earth elements.

F. S.

Some Experiments to Detect β Rays from Radium-A. Walter Makower and Sydney Russ (*Proc. Physical Soc.*, 1913, **25**, 253—255).—Since when an atom of radium-A disintegrates, the

atom of radium-*B* formed carries a single positive charge, and the α-particle expelled carries two positive charges, it must be supposed that three negative electrons are also expelled. Attempts to detect a β-radiation from radium-*A* were made by two methods without success. The curve of the rise of β-rays from pure radium emanation with time, through a thickness of material only just sufficient to absorb the α-rays of radium-*C*, agreed with the theoretical curve calculated on the assumption that radium-*A* gives no β-rays. The magnetic spectrum of the β-rays from a bare wire covered with radium-*A*, by exposing it for five minutes to the emanation, showed only the known β-rays due to radium-*B*. Possibly negative electrons may be expelled as δ-rays which would escape detection by these methods. F. S.

Origin of Penetrating Rays. VIKTOR F. HESS (*Physikal. Zeitsch.*, 1913, **14**, 610—617).—The author, making use of ionisation experiments at a height of 5350 metres and other controlling experiments (*Physikal. Zeitsch.*, 1912, **13**, 1084), develops a theory of the very penetrating atmospheric rays. It is shown that at a height of above 1000 metres, the penetrating rays operative at the earth's surface are inoperative. The measurements were made by means of a Wulf apparatus, and a formula is developed which gives the quantity of γ-rays emanating from the radium-*C* particles in the air. Special experiments were made with a radium standard, which enables conclusions to be drawn with respect to the quantity of radium-*C* and emanation in the air. The value obtained is between $1{\cdot}6$—$1{\cdot}9 \times 10^{-16}$ Curie per c.c., whereas the quantity present at the earth surface is about 1/20th of this amount. Since the concentration of the emanation in the air cannot be more than that at the surface, it follows that the radium-*C* particles in the air are responsible for only 1/20th of the penetrating rays. Consequently it follows that a very large portion of the penetrating rays are not caused by the known radioactive substances on the earth's surface or in the atmosphere. J. F. S.

A Cathode-ray Vacuum Furnace. ERICH TIEDE (*Ber.*, 1913, **46**, 2229—2233).—A description of a furnace which is so arranged that the cathode rays fall directly on a crucible containing the substance to be investigated. Full dimensions are given, since it was only with these particular dimensions that success was attained.

Iron, nickel, chromium, platinum, tantalum, boron, etc., were readily melted in the furnace. Calcium carbide was dissociated at the temperatures produced, giving metallic calcium. T. S. P.

Secondary Rays from Canal Rays. HANS BAERWALD (*Ann. Physik*, 1913, [iv], **41**, 643—669).—Using an aluminium electrode in hydrogen, the author arrives at the following conclusions: (1) That with increasing velocity of the primary rays the velocity of all secondary rays is increased to a definite maximum velocity. (2) The quantity of the secondary radiation is proportional to the intensity of the primary radiation. (3) The velocity of the free secondary

electrons is independent of the intensity of the primary canal rays. (4) The ability of hydrogen canal rays to produce secondary radiation demands a minimum potential of 900 volts. (5) At the highest discharge potentials, 95% of the secondary radiation has a velocity of less than that corresponding with 10 volts. (6) A higher velocity of the primary ray particles corresponds with a higher velocity of the secondary electrons. A series of experiments were made in air and hydrogen with the metals iron, copper, zinc, silver, platinum, gold, and lead, and a further series in hydrogen alone with carbon, magnesium, sulphur, calcium, thallium, bismuth, uranium, and copper oxide, and in this connexion it is shown that the influence of the primary radiation on the velocity distribution of the secondary radiation at a definite discharge potential depends on the atomic weight, and not on the chemical characteristics of the metal, and, further, that the influence of the primary radiation on the quantity of the secondary radiation does not depend on the atomic weight or the chemical character of the metal, but on the number of particles in unit volume composing the ray. The nature of the metal on which the canal rays strike, is without influence on the velocity and quantity of the secondary radiation. J. F. S.

Bending of Rubidium Rays in a Magnetic Field. KARL BERGWITZ (*Physikal. Zeitsch.*, 1913, **14**, 655—658).—It is shown that the radiation from rubidium consists of β-rays. The velocity of these rays approximates to $1·85 \times 10^{10}$ cm. per sec. J. F. S.

Energy Required to Ionise an Atom. R. T. BEATTY (*Phil. Mag.*, 1913, [vi], **26**, 183—186).—The author deduces an expression for calculating the energy required to remove an electron from an atom; for helium the expression has the form $Ee = 1·5 \, . \, e^2/a$, where E is the energy required, $2e$ is the central positive charge of the helium atom, and a is the radius at the end of which the electrons are situated. Values of E are calculated for helium, neon, and argon, and they are very near the values experimentally determined by Franck and Hertz (this vol., ii, 174). J. F. S.

Ionisation Potential in Gases. R. T. BEATTY (*Physikal. Zeitsch.*, 1913, **14**, 622).—The energy required to remove an electron from an atom is worked out by the author. A series of figures denoting the molecular radius and the observed and calculated *E.M.F.* required to effect the separation of atom and electron in the case of the inactive gases is given. J. F. S.

The Spontaneous Ionisation of the Air in a Closed Vessel. J. J. REY (*Le Radium*, 1913, **10**, 137—141).—Contrary to the experience of other workers, but in conformity with those of Patterson (A., 1903, ii, 194), the spontaneous ionisation in a large vessel was found to be nearly proportional to the pressure for pressures below 15 cm. of mercury, and to be nearly independent of the pressure above 30 cm. of mercury. The closed vessel was a cylindrical brass receptacle of 13 litres capacity, thickly coated on the

inside with solder, and giving a production of about 100 ions per c.c. per second. The exact form of the curve connecting ionisation with pressure revealed an ill-defined maximum of ionisation at about 50 cm. of mercury. The curve is easily explained as being formed by the superposition of two radiations, the one very easily absorbed producing most of the ionisation at low pressures and the other very penetrating, producing ionisation small at low pressure, but increasing proportionately to the pressure.

The spontaneous fluctuations of the ionisation current in the chamber, the effect of dust, and of the presence of radium emanation initially in the air were also studied. F. S.

Recombination of Ions Produced by Röntgen Rays in Gases and Vapours. H. THIRKILL (*Proc. Roy. Soc.*, 1913, **88**, *A*, 477—494).—Experiments are described on the recombination of ions in air, carbon dioxide, carbon monoxide, sulphur dioxide, and nitrous oxide. The measurements were made at 15° under varying conditions of pressure, electric field, and intensity of ionisation. The experiments were rendered uniform by producing the ionisation by means of a single flash from a Röntgen ray bulb. The experiments show that recombination takes place according to the expression $dn/dt = -\alpha n^2$ when both ions are present in equal concentrations, or generally $dn_1/dt = -\alpha n_1 n_2 = dn_2/dt$, in which n_1 and n_2 represent the number of positive and negative ions respectively, t is the time, and α the coefficient of recombination. The coefficient of recombination varies with the pressure, and throughout a considerable range of pressure is proportional to the pressure. J. F. S.

Measurement of the Valency of Ions in Gases. P. LANGEVIN (*Le Radium*, 1913, **10**, 113—118).—The theory is discussed of a method for determining K/D, the ratio of the mobility to the coefficient of diffusion of gaseous ions, with the object of determining the valency of the ions. The gas between two parallel metal plates, placed very near together, is ionised by an exterior radiation traversing the gas normally to the surface of the plates. The production of ions in the volume of the gas may be considered uniform, provided that the distance between the plates is of the same order as the average path of the secondary rays in the gas, which is fulfilled even in the case of X-rays when the thickness of the gaseous layer is of the order of a millimetre. In these conditions the permanent regime which establishes itself between the plates is determined, in the first place, by the loss of ions by diffusion rather than by recombination, and the quotients K/D and K'/D' for positive and negative ions can be determined by following the variation of current with the difference of potential established between the plates. Expressions for the variation of current with potential are worked out to the first and second degree of approximation, and obtained in a form such as to admit of the experimental determination of the valency of the ions. F. S.

Researches on the Valency of Ions in Gases. EDOUARD SALLES (*Le Radium*, 1913, **10**, 119—122).—Langevin's method of

determining K/D has been put into practice, using the β-rays of 7 mg. of a radium salt. The comparison of the curves obtained, representing current and voltage, with those theoretically to be expected for the case of univalent ions, for thicknesses of air ranging from 2·7 to 0·3 mm., gave values for K/D, for different portions of the curve, from 1·0 to $1·23 \times 10^4$, whereas, if any ions of higher valency had been present, the effect would have been to increase the value beyond $1·23 \times 10^4$, the value theoretically to be expected for univalent ions. The results bear out those of Millikan and of Franck and Westphal. F. S.

The Magnetic Separation of Ions Emitted by the Spark in a Rarefied Gas. AUGUSTO RIGHI (*Le Radium*, 1913, **10**, 134—136).—At one end of a tube are two electrodes connected with an influence machine, furnishing about 0·3 milliampere, two condensers of capacity about 37,620 *E.S.U.*, and a spark-gap of from 2 to 4 mm. between brass balls 5 cm. diameter. The tube is exhausted to 0·04 mm. pressure, and a magnetic field established across it to deviate the positive and negative ions produced by the spark in the tube to two electrodes suitably placed. Under these circumstances, a current passes between the electrodes, reaching a maximum of about 30 micro-amperes as the strength of the magnetic field is increased. The effect is somewhat analogous to the Hall effect, the rarefied gas replacing the metallic plate. Using an induction coil instead of an influence machine, the current may be increased ten or twenty times, and an ordinary galvanometer of medium sensitiveness used to demonstrate them. F. S.

The Ionisation of Liquid Dielectrics by the Radium Emanation. GEORGE JAFFÉ (*Le Radium*, 1913, **10**, 126—134. Compare Abstr., 1910, ii, 481).—The ionisation produced by the emanation of radium in carefully purified hexane, carbon tetrachloride, and carbon disulphide has been studied in a glass condenser. An unknown quantity of emanation was introduced into the liquid, and the current for various potentials measured; an unknown fraction of the emanation was withdrawn by an air stream, and its quantity measured in an air condenser; the current in the liquid was again measured, and the difference between the two currents thus found for a known quantity of emanation. The currents so observed were very small, and for the α-rays were only of the order of one thousandth of that produced by the emanation in air. The effects due to the α- and β-rays of the several products were separated, and the effects due to the β-rays were of the order of one-tenth of that produced in air. Tables are given showing the number of ions produced per second per curie in the three liquids by the α-rays of radium-*A* and radium-*C*, and by the β-rays of radium-*B* and radium-*C*. The results are compared mathematically, and shown to be in agreement with what is to be expected from the theory of columnar ionisation applied to liquids. The only essential difference between ionisation in liquids and in gases is regarded as being that in the former only an insignificant fraction of the ions formed

escape recombination in the columns in which they are produced, but this part, in spite of the great density of the ions in the columns in liquids, obeys the same laws of mobility, recombination, and diffusion as are valid for ions in gases. F. S.

The Fractional Adsorption of Radium-Barium Salts, and the Fractional Electro-dialysis of the Adsorption Compounds thus Obtained. ERICH EBLER (*Eighth Inter. Cong. App. Chem.*, 1912, **2**, 91—93).—An extension of the method previously described (A., 1911, ii, 957) to other colloids indicates that they do not all show a like selective adsorption towards radium salts, and also that the adsorption depends on the nature of the radium salt used. Of the colloids investigated, manganese dioxide hydrate shows marked adsorptive power for nearly all radium salts; basic ferric carbonate acts similarly towards radium carbonate, so that when a solution containing radium salts and an excess of ferric salt is precipitated with sodium carbonate, all the radium is carried down with the iron precipitate. If this precipitate is then dissolved in the necessary amount of dilute hydrochloric acid to give the colloidal sol, $Fe(OH)_2Cl$, and the sol dialysed, the radium salts can be separated; barium salts, if present, pass through the dialyser at a different rate from the radium salts, and thus fractionation can be brought about. The dialysis can be accelerated, in an obvious manner, by electrolysis, the phenomenon of electro-cataphoresis often aiding the process.

The adsorption compounds with manganese dioxide and silicic acid gels may be submitted directly to dialysis or electrodialysis, without being first brought into the sol condition. T. S. P.

The Solubility of the Active Deposit of Radium. EVA RAMSTEDT (*Le Radium*, 1913, **10**, 159—165).—Plates were exposed to dried radium emanation overnight, without application of an electric field, and the activity two hours after removal compared with that remaining after treating a certain time with a solvent. From the curves the loss of activity of both radium-*B* and -*C* could be separately deduced. Glass surfaces give better and more regular results than those of gold and platinum. Only about one-half (mean 0·52) of the active deposit on a glass surface is readily dissolved; the other half is not dissolved at all on boiling with acid, but with gold and platinum the soluble part amounts to 60—70%. This is explained by the recoil of the radium-*B* particle in its formation from radium-*A*, driving it into the surface. For radium-*B* deposited on a plate by projection from a radium-*A* surface the whole is soluble.

The measurements of solubility were carried out with two similar plates, one of which was subjected to standard treatment, the same in all cases. Radium-*C* is soluble in the common acids, less so in alkaline liquids and in water, and very little in organic solvents. Radium-*B* dissolves more quickly than radium-*C* in water and acids, especially when dilute, less quickly in alkaline liquids, and very little in organic solvents. Radium-*A* is more soluble than

radium-*B* and -*C*, and dissolves even in organic solvents, especially carbon disulphide, which confirms its position in the sulphur family of elements. The speed of solution increases with the temperature of the solvent, and Arrhenius's formula applies approximately. It was found by depositing the active material on plates of gold and platinum previously saturated electrolytically with hydrogen and oxygen that oxygen enormously diminishes the solubility, especially of radium-*C*, whilst hydrogen diminishes the relative speed of solution of radium-*A*. The influence of oxygen on solubility is analogous to that on volatility. F. S.

Position of the Radioactive Elements in the Periodic System. KASIMIR FAJANS (*Le Radium*, 1913, **10**, 171—174).—Owing to the discovery of a short-lived product of uranium-*X*, called uranium-X_2 (Fajans and Göhring, *Naturwissenschaften*, 1913, **1**, 339) of half period 1·1 minutes, the only remaining possibility as regards the origin of actinium is that it comes from a β-ray change of radium, and the atomic weight of actinium will then be equal to that of radium. On this assumption, the following generalisation holds. The α-ray-giving members of a non-separable group of elements have longer periods of life according as their atomic weight is higher For the β-ray-giving members the reverse is the case. For the α-ray rule radium-*F* is an exception. For the β-ray rule actinium-*B* and -*X* are exceptions. This point of view explains the small content of lead in thorium minerals, free from uranium, because the end-product of thorium in the lead place in the periodic table, with atomic weight 208·4, ought to have a shorter period of life than radium-*G* (lead), atomic weight 206·5, although longer than that of radium-*D*, atomic weight 210·5. F. S.

Activity of Subsoil and Atmospheric Air in November and December, 1912. JOSÉ MUÑOZ DEL CASTILLO and JOSÉ BARRIO FERNÁNDEZ (*Anal. Quim. Fis.*, 1913, **11**, 294—307).—It is suggested that probably the activity of the sub-soil may be related to the pressure and temperature, but it is not influenced by the wind. Up to 0·5 metre depth the activity of the air and of the sub-soil appear to be related. Below 2 metres this activity increases with the depth, and the activity is greater in firm than in loose soil.

G. D. L.

Relation between the Limiting Values of the Molecular Conductivity and Internal Friction in Non-aqueous and Aqueous Solutions. PAUL WALDEN (*Bull. Acad. Sci. St. Pétersbourg*, 1913, 559—582).—In order to investigate the extent to which the law $\lambda_\infty . \eta_\infty$ = constant (see A., 1906, ii, 335; 1912, ii, 23) is applicable, the author has examined the following cases.

(1) Tetramethylammonium iodide in benzyl cyanide. (2) Tetra-amylammonium iodide in methyl and ethyl alcohols, acetonitrile, ethyl cyanoacetate, and acetone; with ethyl alcohol, $\lambda_\infty . \eta_\infty$ = 0·524, whilst with the other four solvents the values lie within the limits 0·562 and 0·567. These results show that, in the solvents

employed, the above salt containing the complex cation, $N(C_5H_{11})_4$, behaves in exactly the same way as potassium iodide, only the absolute value of the product changing from salt to salt; thus, the four homologous tetralkylammonium iodides give the values: methyl, 0·745; ethyl, 0·700; propyl, 0·624; amyl, 0·557. It is found also that, if V is the molecular volume of a large ion, the law $\lambda_\infty \cdot \eta_\infty \cdot \sqrt[3]{V}=\text{const.}$ holds for different salts of a homologous series, independently of the solvent (see Herzog, A., 1911, ii, 23).

(3) Piperidine picrate in water, propionitrile, acetone, furfuraldehyde, ethyl cyanoacetate, nitromethane, acetylacetone, benzonitrile, methyl thiocyanate, methyl and ethyl alcohols and acetonitrile. With all these solvents except ethyl alcohol, the differences from the mean value of 0·632 are less than ±2%. Although fundamentally different in their chemical relations, piperidine picrate and tetrapropylammonium iodide differ little in molecular weight, number of atoms in the molecule, and value of the product $\lambda_\infty \cdot \eta_\infty$; the conclusion is therefore drawn that, also with organic solvents, the sum of the velocities of migration or the molecular conductivity depends principally on the number of atoms composing the salt.

(4) Triamylamine picrate in ethyl and methyl alcohols, water, ethyl cyanoacetate, acetonitrile, and nitrobenzene. In this case $\lambda_\infty \cdot \eta_\infty = 0{\cdot}509 \pm 0{\cdot}005$, the values for tetra-amylammonium iodide and sodium iodide being 0·557 and 0·556 respectively. The fact that the simple cation, $Na^{\bullet}$, exhibits the same velocity of migration as the complex one, $N(C_5H_{11})_4^{\bullet}$, is understandable only if the former is surrounded by an extensive atmosphere of molecules of the solvent.

(5) The values of $\lambda_\infty \cdot \eta_\infty$ for tetramethylammonium nitrate in acetonitrile (0·759), methyl alcohol (0·753), nitromethane (0·774), and ethyl cyanoacetate (0·758), and (6) those for tetramethylammonium thiocyanate in acetone (0·755), acetonitrile (0·769), methyl alcohol (0·770), and ethyl cyanoacetate (0·775) are given in brackets.

Hence, if the value of the product $\lambda_\infty \cdot \eta_\infty$ for a given salt in an efficient and readily accessible solvent of considerable ionising power is known, the value of the limiting molecular conductivity for the same salt in a second solvent can be calculated from the expression:

$$\lambda^1_\infty = \lambda_\infty \cdot \eta_\infty / \eta^1_\infty = \text{const.}/\eta^1_\infty .$$

Such a method of calculating is of value in determining the degree of dissociation at any dilution, $v(\gamma = \lambda^1_v/\lambda^1_\infty)$, either of slightly dissociated salts or of good electrolytes in solvents of low ionising power. T. H. P.

Electrical Emissivity and Disintegration of Hot Metals. JOHN A. HARKER and GEORGE W. C. KAYE (*Proc. Roy. Soc.*, 1913, *A*, **88**, 522—538. Compare A., 1912, ii, 525).—The authors describe experiments on the metals platinum, iridium, iron, tantalum, copper, nickel, and brass. The metals were heated by an alternating current, and no potential was applied; the experiments were carried out in

nitrogen at low pressures. It is shown that the emission of positive electricity occurs at temperatures from 1000° to 1400°. For metals which melt within this range, a sudden and marked increase in the positive current often occurred at the melting point, due probably to a sudden release of occluded gas. The presence of oxygen augments the positive current. At higher temperatures negative electricity predominates, and increases rapidly with the temperature. The negative current attained with iridium at the melting point was 80 milliamps., with tantalum at 1670°, 220 microamps., with iron at the melting point, 90 microamps. In the case of carbon in air at 760 mm. an ionisation current of $3\frac{1}{2}$ amps. was obtained. The negative current at moderate pressures appears to be largely increased if the conditions are such that considerable "sputtering" of the metal occurs. The negative currents are probably a consequence of chemical action between the metal and the surrounding gas. Carbon becomes plastic in the neighbourhood of 2500°, and readily sublimes at the same temperature. J. F. S.

New Processes for the Production of Electricity which Explain Some Bioelectrical Phenomena. II. REINHARD BEUTNER (*Zeitsch. Elektrochem*, 1913, **19**, 467—477. Compare this vol., ii, 468).—A continuation of the work published in part I (*loc. cit.*). Experiments are described which show that at the surface of salicylaldehyde and aqueous salt solutions, potential differences exist which vary reversibly with the concentration in the same way, no matter which salt is in the aqueous solution. This is as was to be expected from the theory deduced previously (*loc. cit.*). Equally concentrated solutions of different cations give large, although different, potential differences. It is shown how the potential difference of cells containing several such single potential differences may be calculated from thermodynamical considerations. It is shown that both the strength and concentration of the acid in the non-aqueous phase influence the dimensions of the potential variations with concentration change. The addition of non-electrolytes, such as sugar, which are soluble only in the aqueous phase, do not affect the potential difference, but the addition of substances, like alcohol and ether, which are soluble in both phases, and thereby change the distribution-coefficient of the salts, cause a change in the potential difference, and this is the same as that observed for plant membranes. Finally, measurements were carried out with basic substances insoluble in water; these substances give rise to *E.M.F.*'s which change in the opposite direction to that observed for acidic substances, that is, there is a reversibility for the anion. The *E.M.F.* in these cases is analogous to the *E.M.F.* obtained for acidic substances, and can be treated by the mathematical expressions given in the earlier paper (*loc. cit.*). J. F. S.

[Measurement of Polarisation Potential.] DAVID REICHINSTEIN (*Zeitsch. Elektrochem.*, 1913, **19**, 518—520).—The author shows that in his measurements on polarisation potentials (A., 1912, ii, 1037) an error was introduced by measuring this with a hydrogen elec-

trode. The value thus obtained gave the sum of two potentials, namely, that of the polarisation and that of the polarising current. It is shown that by using the Haber-Luggins capillary method quite different values are obtained, and these represent the true values.

J. F. S.

Theory of Chemical Polarisation of Reversible Electrodes. Anodic Behaviour of Mercury, Copper, and Silver Copper Alloys. DAVID REICHINSTEIN (*Zeitsch. Elektrochem.*, 1913, **19**, 520—530. Compare preceding abstract).—The author puts forward an hypothesis which considers the positive and negative polarisations as similar and comparable processes. The reasons for the deposition of alloys on the cathode in electrolysis are developed, and the solution of an anode alloy is treated as a special case of negative depolarisation. The second part of the paper is experimental, and deals with the polarisation of the electrodes Cu | $CuSO_4$, CuHg | $CuSO_4$, and CuAg | $CuSO_4$, in the presence of sulphuric acid of various concentrations. The current density potential curve and the time potential curves of these elements are determined.

J. F. S.

Influence of the Addition of Free Sulphuric Acid and its Neutral Salts on the Cathodic Polarisation of the Cu | $CuSO_4$ Electrode. DAVID REICHINSTEIN and A. ZIEREN (*Zeitsch. Elektrochem.*, 1913, **19**, 530—534. Compare preceding abstracts).—It is shown that the cathodic polarisation of a Cu | $CuSO_4$ electrode gives an entirely different current density potential curve when a measureable quantity of hydrogen ions are present. The addition of free sulphuric acid or neutral sulphates [K_2SO_4, $MgSO_4$, $ZnSO_4$, Na_2SO_4, and $(NH_4)_2SO_4$] brings about a considerable increase in the polarisation. The nature of the current-density concentration curve leads to the conclusion that the addition of the sulphates brings about a decrease of the $Cu^{\cdot\cdot}$ ion concentration in the electrolyte, and the slow reaction, on which the chemical polarisation depends, consists in the reduction of the $Cu^{\cdot\cdot}$ ions by a cathodically produced reducing agent, and not in the slow production of $Cu^{\cdot\cdot}$ ions from the undissociated copper sulphate in the solution. J. F. S.

Minimum Potential of Electrolytic Valves in the [Direction of the Current]. GÜNTHER SCHULZE (*Ann. Physik*, 1913, **41**, [iv], 593—608. Compare A., 1907, ii, 842; 1908, ii, 350, 560, 658; 1909, ii, 371).—Electrolytic valves are shown to prevent the passage of current in the direction of flow as long as the applied potential does not reach a given minimum value. The size of the minimum potential depends on the metal of which the valve is made, the thickness of the gas layer on the metal, and the nature of the electrolyte. The minimum potential of tantalum is 1·51 times that of aluminium when both metals have been prepared at the same potential. The minimum potential increases slightly with the preparation potential and the thickness of the active layer. The minimum potential increases about 7% when the ionic concentration

of the electrolyte is decreased by one-half. In 0·2N-solutions of nitrates, after preparation of the valves by a direct current of 85 volts, the minimum potential of tantalum for alkali cations is about 10 volts, and for most other cations about 30 volts. The minimum potential for H ions is particularly high, 46·3 volts. Of the anions the aluminate anion AlO_2' has an abnormally low minimum potential, 4·3 volts, and the Cl' and NO_3' ions relatively high values, namely, 18·2 and 11·7 volts for 0·05N-solutions of the sodium salts. Tables of values for a large number of anions and cations, with and without addition of other substances, are given in the paper. J. F. S.

Normal and Liquid Potentials in Non-aqueous Solutions. Correction. N. ISGARISCHEV (*Zeitsch. Elektrochem.*, 1913, **19**, 491)—Correction to the author's paper (A., 1912, ii, 729). The value of E_h for silver in methyl-alcoholic solution is shown to be 0·9100 volts instead of the lower figure published previously. J. F. S.

Electrocapillary Phenomena at the Surface [of Contact] of Immiscible Liquids. P. KANDIDOV (*Zeitsch. physikal. Chem.*, 1913, **83**, 587—591).—The author has determined the relationship which exists between the capillarity of two liquids to which definite but variable potentials are applied. The apparatus is a modified Lippmann electrometer, having three limbs; this contains one of the liquids; the other is contained in a capillary tube which dips into the central limb. Electrodes are introduced into the two liquids so that they are as near as is possible to the surface of separation. The liquids used in the experiments were ether and a 5% solution of uranium nitrate in water. The potentials applied varied from 1 to 20 volts. It is shown that with increasing potential difference the surface tension increases to what is apparently a limiting value at about 12 volts. J. F. S.

Passivity of Metals and its Dependence on the Solvent. N. ISGARISCHEV (*Zeitsch. Elektrochem.*, 1913, **19**, 491—498).—The author has studied the conditions under which the metals nickel, cobalt, iron, cadmium, copper, and zinc become passive in alcohol solutions and also in water solutions. The process is followed by means of *E.M.F.* measurements. The *E.M.F.* of nickel against a solution of nickel chloride in alcohol was measured, and the value found to increase rapidly, that is, the metal became passive; on removing the metal and cleaning it, it showed its original potential on again immersing in the liquid, but became passive much more rapidly than before, and on repeating the process the rate at which it became passive continued to increase. A fresh piece of nickel dipped in the solution which had been used became passive very rapidly. A solution of nickel chloride in alcohol was left for two days in contact with a piece of nickel; on using this solution for the *E.M.F.* measurements, it was shown that the nickel became passive very rapidly. If all oxygen was removed from the solution and the measurements were made in a current of hydrogen, the

E.M.F. was constant, and consequently the metal showed no signs of becoming passive; thus it is shown that the passivity of nickel in solution is due to the presence of a soluble substance of the nature of a peroxide, and the main cause of the passivity of nickel in alcoholic solution is the formation of an oxide coating on the metal. Similar results were arrived at for cobalt, iron and cadmium. In the case of copper in cupric chloride solution it is shown that the presence of a complex compound of alcohol and cuprous chloride, $Cu(C_2H_5O)_2 \cdot CuCl_2$, conditions the passivity of copper. Hypotheses concerning the action of this complex in the case of copper passivity are considered. J. F. S.

Acid and Base as Expressions of the Intensity of Electrons ERNST CRATO (*Ber. Deut. pharm. Ges*, 1913, **23**, 331—355).—A theoretical paper, in which the author seeks to show that acidity is not a chemical property of H ions, but a physical property of all anions, and probably an expression of the intensity of the electrons in the anions, basicity in the same way being an expression of the intensity of electrons in cations. The intensity depends on the nature of the substance, and is probably the source of energy in electrolytic dissociation and in the chemical action of ions. Some reactions which are anomalous when viewed from the point of view of the ordinary electrolytic dissociation theory, are described and discussed on the new basis. T. A. H.

Electrolysis of Solutions of Lithium Hydroxide. WILLIAM ŒCHSNER DE CONINCK and A. BOUTARIC (*Ann. Chim. Phys*, 1913, [viii], **29**, 471—472).—It has been previously observed by Duter (*Compt. rend.*, 1887, **104**, 354) that the volume of oxygen obtained during the electrolysis of solutions of potassium, sodium, barium, and calcium hydroxides is sensibly less than one half of that of the hydrogen evolved. These observations have been confirmed by Berson and Destrem (A., 1888, 1007). The authors have therefore electrolysed solutions of lithium hydroxide, the cathode being a platinum wire and the anode a platinum plate. The volume of hydrogen liberated is always more than double that of the oxygen, varying from 2·30 for low-current densities to 2·06 for higher current densities. The phenomenon is not dependent on an absorption of oxygen at the anode, since it does not show an appreciable variation if the latter has been previously used or recently heated. Hydrogen peroxide could not be detected in the liquid surrounding the anode, nor does a peroxide of lithium appear to be formed. H. W.

The Electrolysis of Silver Nitrite and the Transport Number of the Nitrite Ion. NILRATAN DHAR and DEVENDRA NATH BHATTACHARYYA (*Zeitsch. anorg. Chem.*, 1913, **82**, 141–144).—Silver nitrite has been electrolysed, using a platinum cathode and silver anode. The transport number found for the nitrite ion is 0·539 in 0·01—0·017*N*-solution, and 0·519 in 0·002*N*-solution at 25°. Vogel (A., 1903, ii, 591) found 0·5877 from a 0·05*N*-solution of barium nitrite. C. H. D.

Concentration Changes in the Electrolysis of Copper Sulphate Solutions. CHARLES W. BENNETT and C. O. BROWN (*J. Physical Chem.*, 1913, **17**, 373—385. Compare A., 1912, ii, 646). —The anode–cathode potential in a cell with a rotating cathode depositing copper increases regularly with the speed of rotation of the cathode. By means of Sand's auxiliary electrode it was found that the solution pressure of the copper cathode increases by upwards of 0·014 volt when the speed of the cathode is increased.

Fine-grained copper produced by electrolysis or by mechanical treatment has a higher solution potential than cast copper. The *E.M.F.* of the cell cast copper | copper sulphate solution | electrolytic copper is 0·006 volt, which is increased to 0·014 volt with rapid stirring. The increase in solution pressure of the rotating cathode during electrolysis is attributed, however, to the increased rate of removal of cuprous salt (ions) with the more efficient stirring, as no such increase occurs when the electrolyte is dilute sulphuric acid free from copper.

The increase in back *E.M.F.* at the cathode does not explain the whole of the increase in the anode–cathode potential, part of which must be attributed to an increased resistance due to air bubbles being drawn down into the solution when the speed of rotation is high.

The variations in anode–cathode potential and cathode solution potential with variations in temperature and in concentration of acid and copper salt and the influence of alcohol are in harmony with the authors' hypothesis. The back *E.M.F.* in acid cuprous chloride solution, however, falls with increased cathode speed. This is attributed to a more rapid removal of the cupric ions from the vicinity of the cathode, but it is not explained why they should tend to collect there.

The solution potential of a rotating copper electrode in nitric acid diminishes with increased speed of rotation owing to the more rapid removal of the active film of nitrous acid (compare Stansbie, *Proc. Faraday Soc.*, November, 1912). R. J. C.

Photoelectric Phenomenon Shown by Liquid Sulphur Dioxide. JACQUES CARVALLO (*Compt. rend.*, 1913, **156**, 1882—1884). —It has been shown already (A., 1910, ii, 1026) that when a current is passed between platinum electrodes in liquid sulphur dioxide in the dark, the current-intensity falls to a constant minimum. If at this stage the liquid is alternately illuminated and darkened, the current intensity rises to a greater extent at each successive illumination, reaching a maximum at the seventh, and falls at each extinction of the light, the limit of the fall being higher at each successive extinction. These changes are shown by a curve in the original. After the final extinction the current gradually falls to the original minimum.

These two effects occur in the mass of the liquid, and are produced by ultraviolet rays. The positive effect is chemical, and is due to the change represented by the equation $3SO_2 = S + 2SO_3$; the negative effect, which takes place in the dark, is due to the removal of

the impurities by the current. This negative effect is not exhibited when an alternating current is used. T. A. H.

Thermoelectric Power of Silicon. JOHANN G. KOENIGSBERGER (*Physikal. Zeitsch.*, 1913, **14**, 658—659).—The author has examined specimens of silicon which have both negative and positive values for the thermoelectric power when in contact with copper. It is shown that this property increases in both cases with the iron content of the silicon. It is determined by the number of electrons on the silicon, and the number of electrons determines the absolute dimensions of the Hall effect, the conductivity, the thermoelectric power, and the Peltier heat effect. J. F. S.

Magnetic Properties of the Alloys of Iron, Cobalt, Nickel, and Manganese with Boron. ARMAND BINET DU JASSONNEIX (*Eighth Inter. Cong. App. Chem.*, 1912, **2**, 165—170).—Measurement of the magnetic permeability of the various alloys of iron with boron (compare A., 1909, ii, 569) shows that it attains a maximum when the composition corresponds with that of the boride, Fe_2B. Similar series of measurements could not be made with alloys of nickel and cobalt, owing to the small quantities of them available, but the few results obtained indicated that the magnetic permeability of nickel is diminished by alloying with boron, at all events at the ordinary temperature; the boride Ni_2B is not attracted even by a strong magnet.

Of the manganese borides, MnB and MnB_2, only the former possesses magnetic properties other than those possessed by manganese itself. The permeability of the various alloys reaches a maximum at 13—15% of boron.

Hysteresis measurements showed that the various alloys of iron and manganese with boron, as also the borides Fe_2B, MnB, MnB_2, and CoB, gives flatter cycles than soft iron filings.

Iron boride, Fe_2B, becomes non-magnetic at 740°; with falling temperature, it becomes magnetic at 730°. Both the borides of iron and cobalt lose their magnetism at a lower temperature than the respective metals. T. S. P.

Additive Character of Physical Properties in Organo-metallic Compounds. PAUL PASCAL (*Compt. rend.*, 1913, **156**, 1904—1906).—It has been shown previously (this vol., ii, 182) that in the case of organo-metallic compounds of the aliphatic series the conservation of diamagnetic properties follows a limit law, but that there are anomalies in the case of aromatic organo-metallic compounds. These anomalies have now been investigated by the determination of the density, refractive index, and coefficient of magnetisation for a number of compounds of both types. Lists of the values obtained are given in the original.

In general, there is an exaltation of the optical properties of the metal (or corresponding multivalent element) in the case of the aromatic compounds and a lowering of the coefficient of magnetisa-

tion. There is therefore no generally additive character in the physical properties in the case of organo-metallic compounds. They may be exceptional in this respect, but the existence of these anomalies indicates that the additive character of physical constants in purely organic substances may be due, not only to the relative independence of the constituent atoms, but also to their low atomic weights and to the constant character of the valencies concerned.

T. A. H.

The Thermo-electricity of Steel. WITOLD BRONIEWSKI (*Compt. rend.*, 1913, **156**, 1983—1985).—The author has extended his previous work (this vol., ii, 288) to steels containing respectively 0·07, 0·24, 0·44, 0·79, and 1·12% of carbon; manganese, silicon, sulphur, and phosphorus were also present. The results show that the various critical points and points of recalescence are as readily determined by this method as by any other.

Formulæ are given which represent the thermo-electric power of the different steels over a range of temperature between 0° and 700°.

T. S. P.

Relation between the Law of the Compressibility of Gases and the Coefficients of Dilatation. THADDÉE PECZALSKI (*Compt. rend.*, 1913, **156**, 1884—1886).—A mathematical paper in which it is shown that the values of pv for hydrogen, nitrogen, and air, calculated from a knowledge of the values of α and β, the coefficients of dilatation at constant pressure and at constant volume respectively, are in good agreement with the experimental values found by Amagat and Witkowski. T. A. H.

The Adiabatic Expansion of Liquids. L. GAY (*Compt. rend.*, 1913, **156**, 1978—1979).—Using the method previously described (this vol., ii, 382) the author has determined, at different temperatures, the coefficient of adiabatic compressibility of the following liquids: ethyl bromide, *iso*pentane, *cyclo*hexane, carbon disulphide, toluene, carbon tetrachloride, chloroform, and ethyl acetate. From the results obtained the coefficient of isothermal compressibility has been calculated, and found to be in agreement with the results of other observers. T. S. P.

The Equilibrium Diagram of Both Modifications of Sulphur. WALTHER NERNST (*Zeitsch. physikal. Chem.*, 1913, **83**, 546—550).—A theoretical paper in which it is shown that there is no reason for attributing a value other than zero to the integration constant C of the expression of the second law of thermodynamics as applied to the maximum work of condensed systems, namely,

$$A = -T {}_0\!\int^T U / T^2 . dT + CT.$$

Kruyt's paper (this vol., ii, 132) is criticised, and an answer given to his method of using the Nernst theorem for calculating the transition point of sulphur (see also Smits, this vol., ii, 499).

J. F. S.

Determination of Specific Heats at Low Temperatures and their Use in the Calculation of Electromotive Force. II. FRANZ POLLITZER (*Zeitsch. Elektrochem.*, 1913, **19**, 513—518. Compare A., 1911, ii, 180).—The author has determined the specific heats of mercury, heptahydrated zinc sulphate, mercurous sulphate, mercurous chloride, thallous chloride, and ice at temperatures from the boiling point of hydrogen to about $-100°$. The values were used to calculate the atomic and molecular heats of the substances, and figures obtained which agree well with those obtained by means of the Nernst-Lindemann-Einstein formula. By means of the specific heats found the author calculates the *E.M.F.* of the elements, $Hg|HgCl|PbCl_2|Pb$, $Hg|HgCl|AgCl|Ag$, and $Pb|PbCl_2|AgCl|Ag$, making use of the Nernst heat theory. The calculated values agree well with the best experimentally determined values. J. F. S.

Melting Points, Specific Heats, and Heats of Fusion of the Alkali Metals. ÉTIENNE RENGADE (*Compt. rend*, 1913, **156**, 1897—1899).—A short description is given of the methods used in purifying the metals, and in determining the constants. The following results were obtained:

Sodium.—Specific heat (solid) $0·2811 + 0·000233t$; (liquid) 0·330 at 98°; heat of fusion 27·21; m. p. 97·9°; L/T (ratio of atomic heat of fusion to absolute m. p.) 1·69.

Potassium.—Specific heat (solid) $0·1728 + 0·000142t$; (liquid) $0·1422 + 0·000668t$; heat of fusion 14·67; m. p. 63·5°; L/T 1·70.

Rubidium.—Specific heat (solid) $0·0802 + 0·000153t$; (liquid) $0·0921 - 0·000026t$; heat of fusion 6·144; m. p. 39·0°; L/T 1·68.

Caesium.—Specific heat (solid) $0·0522 + 0·000137t$; (liquid) $0·0604 - 0·000034t$; heat of fusion 3·766; m. p. 28·45°; L/T 1·66.

T. A. H.

Cryoscopy in Molten Hydrated Salts. CH. LEENHARDT and A. BOUTARIC (*Bull. Soc. chim.*, 1913, [iv], **13**, 651—657).—An elaboration of work already published on the cryoscopy of the fused pentahydrate of sodium thiosulphate (compare A., 1912, ii, 234) and an extension of the study to the decahydrate of sodium sulphate. For the latter the latent heat of fusion at 31·3° is found to be 56·9, which gives $K = 32·5$ in van't Hoff's formula, a value which agrees well with the experimental figure. W. G.

Lowering of the Freezing Points of Reacting Solvents. PETRUS H. J. HOENEN (*Zeitsch. physikal. Chem.*, 1913, **83**, 513—545. Compare this vol., ii, 394).—A theoretical mathematical paper containing a continuation of the author's calculations (*loc. cit.*) applied especially to freezing-point lowerings. It is shown that the freezing point of a salt (acting as solvent) is only lowered by the unlike portion of an added salt containing one ion the same as the solvent; for example, the lowering of the freezing point of potassium chloride is brought about by the SO_4 ion on the addition of potassium sulphate. The dissociation of dissolved salts is not

complete, or is it zero. Only when the ionisation of the solvent is very small can the dissolved substance at very great dilution be completely dissociated, and only under these conditions can the unlike ions lower the freezing point. The rule, "that only the unlike ions lower the freezing point of a primary system," is evolved mathematically for a solvent of any complexity. It is also shown that this rule is a special case of a general law, concerning the lowering of an $(n+1)$ phase-point in a system of n components. This is fully worked out in the paper. The theoretical points evolved in the paper are illustrated, and proved by a consideration of the freezing-point lowerings of potassium chloride, sodium chloride, potassium fluoride, sodium fluoride, potassium nitrate, sodium chlorate, barium chloride, strontium chloride, calcium chloride, and formic acid, by the addition of salts containing one or other of the ions of the solvent, and by the addition of salts containing ions which are both dissimilar. The change in the transition point of Glauber's salt by the addition of various substances (Löwenherz, A., 1896, ii, 149) is considered, and shown to be in accord with the theory evolved. J. F. S.

Vapour Pressure of Metals. H. von Wartenberg (*Zeitsch. Elektrochem.*, 1913, **19**, 482—489).—The author has determined the vapour pressure of lead, silver, thallium, platinum, and copper by the method previously used by him for the determination of the vapour pressure of silicon (A., 1912, ii, 1137; this vol., ii, 47). The following values were obtained: Lead, vapour pressure (p) at $808° = 1{\cdot}05 \times 10^{-4}$ atm., $996° = 2{\cdot}30 \times 10^{-3}$ atm., and $1178° = 2{\cdot}20 \times 10^{-2}$ atm. The boiling point (b) and the heat of vaporisation (λ) were calculated in each case, $\lambda = 44{,}000$ cal. and $b = 1630° \pm 20°$. For silver, p at $1178° = 1{\cdot}90 \times 10^{-4}$ atm., $1316° = 1{\cdot}08 \times 10^{-3}$; $1435°$ $5{\cdot}10 \times 10^{-3}$: $\lambda = 60800$ cal., $b = 2100°$. For thallium, p at $634° = 7{\cdot}40 \times 10^{-5}$; $783° = 1{\cdot}75 \times 10^{-3}$; $970° = 3{\cdot}20 \times 10^{-2}$: $\lambda = 3800$ and $b = 1306°$. Platinum and copper showed no loss in weight when heated at 1360°. Hence their vapour pressure at this temperature was less than 10^{-5} atm.; tin, however, gave a notable pressure at this temperature, and preliminary experiments are recorded.

J. F. S.

Vapour Pressure of Binary Mixtures. Johannes J. van Laar (*Zeitsch. physikal. Chem.*, 1913, **83**, 599—608).—Polemical against Dolezalek (this vol., ii, 481). The author takes exception to ten points in Dolezalek's criticism of his paper (A., 1910, ii, 583), which he argues at length. J. F. S.

Regularities in the Steam Distillation of Organic Acids. Albr. Stein (*J. pr. Chem.*, 1913, [ii], **88**, 83—89).—It has been shown by Naumann and Müller (A., 1901, i, 204) that at constant temperature and pressure the velocity of steam distillation of a volatile substance, as measured by the amount contained in unit volume of the distillate, is proportional to the amount of the substance in the distillation flask, provided that the volume of

liquid in the latter remains constant. From this the author deduces the equation $1/v \log a/(a-x)=c$, where a is the amount of the substance originally present in the distillation flask, v the volume of the distillate, x the amount of substance in the distillate, and c a constant, which is termed the distillation constant. The value of this constant has been determined for a number of organic acids, using a volume of 150 c.c.

In the case of acetic acid it is found that the velocity of distillation is independent of the concentration, and inversely proportional to the volume of the liquid in the distillation flask.

Substitution of a hydrogen atom in acetic acid by methyl increases the volatility, whilst substitution by phenyl, chlorine, carboxyl, and hydroxyl diminishes it in the order given.

Of the isomeric toluic acids, all of which have a greater volatility than phenylacetic acid, the ortho-compound is the most volatile and the para the least.

*iso*Butyric acid is more readily volatile than *n*-butyric acid.

F. B.

Small Rods for Preventing Superheating. E. P. HÄUSSLER (*Zeitsch. angew. Chem.*, 1913, **26**, 400).—The end of a glass rod is softened in the Bunsen flame and then a piece of platinum wire pushed into it. When the glass is cold the wire is bent backwards and forwards so as to break it off as near to the glass as possible. Such rods act extremely well in preventing the superheating of a boiling liquid. T. S. P.

Polymorphism of Zinc. P. N. LASCHTSCHENKO (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 552—557).—The author has measured the amounts of heat developed during the cooling of zinc in a tube of quartz glass from various temperatures ranging from 200° to 540° down to 15—15·5°. The curve having amounts of heat as ordinates and initial temperatures as abscissæ suddenly increases in steepness at 340—350°, which is in good agreement with the temperature of transformation as given by other observers. At the melting point, 419—420°, the curve rises vertically through a certain distance, and then becomes virtually a straight line. The heat of transformation is about 0·19 Cal. per gram-atom, and the latent heat of fusion about 1·73 Cal.

Although quartz exhibits a definite temperature of transformation at 575—580°, quartz glass contains no crystalline quartz, and hence shows no transformation point. T. H. P.

Thermochemical Researches on Solution. III. NICOLAS DE KOLOSSOVSKI (*Bull. Acad. roy. Belg.*, 1913, 329—339. Compare this vol., ii, 22, 308).—The author has determined the heat of solution of sodium and potassium iodides and bromides in aqueous solutions of ethyl and methyl alcohols, the object of the work being to see if there existed in these cases the same regularity between the corresponding sodium and potassium salts as was found by Thomsen for aqueous solutions. For a 33·83% ethyl alcohol–water mixture,

that is, $200H_2O+40Et{\cdot}OH$, the following heats of solution are found: $NaBr=-1866$ cal.; $NaI=+151$ cal.; $KBr=-6384$ cal., and $KI=-6076$ cal. The differences between the heats of solution of corresponding sodium and potassium salts are of the same order as the corresponding differences obtained for aqueous solutions; on the other hand, the differences between these figures are about double the values obtained for aqueous solutions. For a 30·77% methyl alcohol–water mixture, that is, $200H_2O+50Me{\cdot}OH$, the following heats of solution were obtained: $NaCl=-2234$ cal.; $NaNO_3=-6064$ cal.; $KCl=-5429$ cal., and $KNO_3=-9300$ cal. The difference between the heats of solution of the corresponding sodium and potassium salts is -3850 cal., and between nitrate and chloride in each case -3215 cal.; this shows the additive nature of the heat of solution in alcohol–water solutions. The author then proceeds to examine certain solutions as to their suitability as freezing or cooling mixtures. It is shown that the following temperature lowerings are obtained: $50NaCl+100H_2O$, 2·5°; $50NaCl+100EtOH$, 5·5°; $100C_{12}H_{22}O_{11}+100H_2O$, 2·4°; $100C_{12}H_{22}O_{11}+100EtOH$, 5·5°; $100NH_4NO_3+100H_2O$, 25·5°; $100NH_4NO_3+100EtOH$, 19·0°; $50KNO_3+100H_2O$, 10·9°; $50KNO_3+100EtOH$, 4·1°; $100EtOH+100H_2O$, 6·4°; $100PhOH+100$, 33·83% alcohol, 18·4°; $100PhOH+100$, 95% alcohol, 14 4°; and $200PhOH+100$, 95% alcohol, 22·5°. J. F. S.

Thermochemical Researches on Solution. IV. NICOLAS DE KOLOSSOVSKI (*Bull. Acad. Roy. Belg.*, 1913, 340—357. Compare last abstract).—The present paper deals with the relationship of the heat of solution in water and aqueous alcohol, and the degree of dissociation of the dissolved substance in these solvents; and for this purpose a number of heats of solution in water and 33·83% alcohol were determined. The following values were obtained: $C_3H_5(OH)_3+200H_2O=+1339$ cal.; $C_3H_5(OH)_3+200H_2O+40EtOH=-412$ cal.; tannin $+400H_2O=+325$ cal.; tannin $+400H_2O+80EtOH=+206$ cal.; $C_{12}H_{22}O_{11}$(sucrose) $+400H_2O=-913$ cal.; $C_{12}H_{22}O_{11}+400H_2O+80EtOH=-4290$ cal.; $PhOH+200H_2O=-2730$ cal.; and $PhOH+200H_2O+40EtOH=-4578$ cal. On comparing these values with the corresponding values of strong electrolytes it is seen that there is no obvious difference in the heat change for electrolytes and non-electrolytes. The author shows that the heat of solution of phenol in alcohol–water mixture and in pure water furnishes evidence in favour of the existence of a phenol hydrate in the latter case, and not in the former. J. F. S.

Anhydrous Sodium Sulphate and Water. D. T. WILBER (*J. Physical Chem.*, 1913, **17**, 556—557).—The dissolution of anhydrous sodium sulphate in water above the transition point (32·6°) is accompanied by a rise in temperature which is greater the higher the initial temperature. The explanation which connects the positive heat of solution with the falling solubility curve of the anhydrous salt is correct, but it does not explain the effect of the initial temperature on the temperature rise. Dammer suggested

an increasing heat of solution with rise in temperature, but it is sufficient explanation that the temperature rise depends on the ratio of the rate of dissolution to the rate at which heat is lost by radiation, etc., and that this ratio is higher at 90° than at 40°.

R. J. C.

Trouton's Quotient and the Heat of Vaporisation of Pure Substances Boiling at Low Temperatures. Data for Helium. ROBERT DE FORCRAND (*Compt. rend.*, 1913, **156**, 1809—1813).—The author has calculated the molecular heats of vaporisation of a number of substances of low b. p. (chlorine, radium emanation, oxygen, nitrogen, hydrogen, and helium) by means of his formula (this vol., ii, 556). The values obtained are in satisfactory agreement with those deduced from the vapour tension, and also with those obtained by direct experiment. Trouton's law only appears to be exact at moderate temperatures (from 300° to 900° absolute).

The method of calculating the molecular heat of vaporisation from measurement of vapour tension is fully explained in the instance of helium.

H. W.

A Safe Thermostat for Use with Coal-gas. WILLEM P. JORISSEN (*Chem. Weekblad*, 1913, **10**, 532—537).—A description of a thermostat and stirrer actuated by hot air. The important features are use of "compo" pipe for the gas leads instead of indiarubber, and the complete enclosure of the gas-jets in a chamber of wire-gauze, on the principle of the Davy lamp.

A. J. W.

Constant Temperature Apparatus. FREDERICK H. DUPRÉ and PERCY V. DUPRÉ (*Analyst*, 1913, **38**, 308—311).—An apparatus is described and figured, in which a constant temperature is obtained by regulating the pressure; this may be effected by cautiously withdrawing (or supplying) air after (or before) generating steam.

The apparatus consists of a boiler filled one-third with water, a reflux condenser, a water-jacketed pressure bulb, and a screw valve. When the latter is shut the apparatus is absolutely air-tight; a safety plug of fusible metal is supplied. The pressure determines the temperature of the steam evolved in the boiler, and so long as sufficient heat is supplied to keep the water boiling without producing more steam than can be dealt with by the condenser, the temperature remains practically constant.

L. DE K.

Molecular Constitution of the Free Surfaces of Liquids. MADISON M. GARVER (*J. Physical Chem.*, 1913, **17**, 386—389. Compare A., 1912, ii, 831).—The conclusion previously drawn from Maxwell's law of the distribution of molecular energies, namely, that attraction in the surface film of a liquid depends on the number of molecules irrespective of their mass, is now shown to be unnecessary. The equation is satisfied if it is assumed that the density of a liquid is determined solely by the molecular forces acting between individual molecules in the surface film. In the interior of the liquid the average force acting on a molecule in any

given direction is nil, but owing to the relatively crowded condition complexes are formed which act temporarily as single molecules.

The molecular weight in the surface film is the same as that of the saturated vapour. R. J. C.

Gay and Ducelliez's Chemical Interpretation of Singular Points. NICOLAS DE KOLOSSOVSKI (*Bull. Soc. chim.*, 1913, [iv], **13**, 648—650).—A criticism of Gay and Ducelliez's inferences (compare this vol., ii, 387). W. G.

Significance of the Relationship between Molecular Cohesion and the Product of the Molecular Weight and the Number of Valencies. ALBERT P. MATHEWS (*J. Physical Chem.*, 1913, **17**, 481—500. Compare this vol., ii, 300, 494, 495).—According to Drude, the electron couples constituting molecules are of two kinds, namely, those of the atoms which when added together give the molecular weight, and the valency electrons, which have a different degree of liberty and can vibrate synchronously with light. Pascal has shown (A., 1911, ii, 367, 679) that magnetic susceptibility is a function of atomic weight and valency; thus refractive index, diamagnetism, and molecular cohesion are cognate properties.

The fact that cohesion is determined by the number of electron couples (atomic and valency) in the molecule suggests that it is electrostatic or electromagnetic in nature. The author adopts the latter view, and supposes that magnetic attraction is molecular cohesion made apparent at distances more than molecular by reason of the orientation of polarised molecules.

If a molecule is of such a nature that its electron couples co-operate to produce polarity, it is paramagnetic, but if the molecule has many poles it is diamagnetic, and its magnetic field coincides with its cohesive field.

In non-magnetic substances the cohesive field is completely neutralised by the surrounding molecules. R. J. C.

Do Molecules Attract Cohesively Inversely as the Square of the Distance? ALBERT P. MATHEWS (*J. Physical Chem.*, 1913, **17**, 520—535. Compare preceding abstract).—The empirical equation, $A = L - E = k(\sqrt[3]{d} - \sqrt[3]{D})$, where A represents the internal latent heat employed in overcoming molecular cohesion on passing from liquid at density D to vapour at density d, was considered by Mills (A., 1911, ii, 711; 1912, ii, 1041) as evidence that molecular cohesion, like gravitation, follows an inverse square law. Mills' equation is not valid in the neighbourhood of the critical temperature, whereas the equation given by van der Waals is valid only at the critical temperature. This equation, $L - E = a(d - D)$, indicates, according to Sutherland, that molecular cohesion varies inversely as the fourth power of the distance between molecular centres.

The total latent heat L must be equal to the sum of three factors, namely, E, the external work, A, the work against molecular cohesion, and I, the energy absorbed in expanding the actual

molecules and increasing their rotation; thus the correct equation should be $L-E-I=a(d-D)$ on Sutherland's hypothesis, and in any case Mills' equation cannot be correct, as it takes no account of I, so that the inference drawn from it, that the molecules attract inversely as the square of the distance, is not justified. The equation $L-E-I=a(d-D)$ reduces to that of van der Waals near the critical temperature, where I is very small. It cannot be verified at other temperatures in the absence of an independent estimate of the value of I, but in accordance with it the ratio $(L-E)/(d-D)$ increases progressively from a on passing from the critical to lower temperatures. The value of I for hexane is nil at the critical point (234·5°) and 28·21 Cal. at 0°.

It is urged that the known variations in the constant b of van der Waals' equation indicate that the factor I cannot be neglected. At low temperatures, when b decreases on vaporisation it must be supposed that association or quasi-association occurs in the vapour and I retains a positive value. R. J. C.

Fluidity and the Hydrate Theory. II. EUGENE C. BINGHAM, GEORGE F. WHITE, ADRIAN THOMAS, and J. L. CADWELL (*Zeitsch. physikal. Chem.*, 1913, **83**, 641—673. Compare A., 1912, ii, 1144).—A continuation of the previous work; the authors have measured the fluidity of the following series of binary liquid mixtures at a series of temperatures: Ethyl alcohol and water, acetic acid and water, methyl alcohol and water, formic acid and water, *n*-hexane and di*iso*amyl, methyl alcohol and ethyl alcohol, acetic acid and ethyl alcohol, and also the ternary mixtures ethyl alcohol, water, and acetic acid, and ethyl alcohol, methyl alcohol, and water. The measurements of other observers are recorded, compared with the authors' values, and criticised. An hypothesis is put forward to explain the relationship between fluidity and other physico-chemical properties. It is shown that in comparing the fluidity of mixtures, volume concentration must be used instead of the usually adopted weight concentration. It is also shown that normally the fluidity concentration curve is linear, and that changes from the linear curve in certain mixtures can be explained by chemical changes, association, etc. The cases examined indicate that many so-called solvates are, strictly speaking, chemical compounds of one molecule of each of the components of the mixture, and in this they are directly opposed to the general theory that a solvate is undetermined in its composition. This is explained by the statement that at any given moment only a small fraction of the components are combined, and that an equilibrium exists between the compound and the components. It is shown that taking μ_{∞} as a measure of the anions and cations in the ionic migration, in ethyl alcohol–water mixtures this value decreases when the concentration of the alcohol is slowly increased, but no minimum is to be found which corresponds with the fluidity minimum. Assuming that the "atmosphere" surrounding the ions is of uniform size it would follow that the conductivity would be proportional to the fluidity. But in mixtures with small fluidity the components are combined to the

largest extent; consequently, the atmosphere surrounding these atoms or groups is diminished, and the ionic velocity is correspondingly large. It is also shown that when an acid and an alcohol are mixed an additive compound of the two components is first formed, and that this then decomposes to form the ester. Also it is shown that a maximum in a viscosity-weight concentration curve does not necessarily give the composition of the solvate; consequently, until some other evidence is forthcoming as to the existence of hydrates in solution than this, the results must be received cautiously. J. F. S.

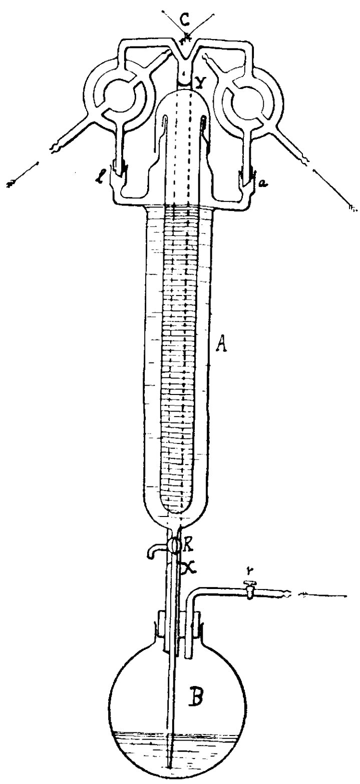
Association in Some Gaseous Mixtures. ALFRED SCHULZE (*Ber. Deut. physikal. Ges.*, 1913, **15**, 488—496. Compare A., 1912, ii, 108).—Experiments are described on the vapour pressure of the following vapour mixtures: acetone–chloroform, ethyl ether–benzene, benzene–chloroform, and ethyl ether–carbon disulphide. It is shown that on mixing acetone and chloroform a mutual association takes place, and at 80° under a total pressure of 1 atm. the two substances combine to the extent of 0·37 mol. %. From this it follows of necessity that the same compound exists in the liquid mixture and to a much larger extent, as has been shown by the divergence of the mixture from the mixture laws. With regard to the mixtures ethyl ether–benzene and benzene–chloroform a chemical compound of the two substances could also be detected in the gaseous phase. By the same method it is shown that in the mixture ethyl ether–carbon disulphide on account of the increase in pressure on mixing the vapours that carbon disulphide must be strongly associated; probably ter- or quadri-molecular complexes are present. Finally, a series of other properties are detailed, which allow of conclusions being drawn as to association in liquids and vapours. J. F. S.

Related Absorption Curves. I. WERNER MECKLENBURG (*Zeitsch. physikal. Chem.*, 1913, **83**, 609—624. Compare A., 1912, ii, 355).—The author had previously shown that if the absorption curves of phosphoric acid by stannic oxide are plotted for different temperatures, a series of curves are obtained such that if one be taken as the normal curve then by multiplying the ordinate values of that curve by a given figure and leaving the abscissæ values alone the other curves can be obtained. Such a series of curves the author calls "related" (affine) curves. The object of the present paper is to see if such curves are general for other absorbing colloids, and for this purpose the absorption curves of arsenious oxide by ferric hydroxide gels at a number of temperatures is determined. It is shown here that such related curves are obtained. The meaning of the relationship between the curves is held to be due to the specific surface of the adsorbent, and consequently the constants for the various curves can be taken as a relative measure of the specific surface of the different specimens of the absorbent. It is also shown that similar related curves can be obtained when a given substance is adsorbed by a series of different adsorbing colloids. J. F. S.

Adsorption. IV. GERHARD C. SCHMIDT (*Zeitich. physikal. Chem.*, 1913, **83**, 674—682. Compare A., 1910, ii, 1041; 1911, ii, 969; 1912, ii, 236).—The author gives a new and stricter proof of his adsorption isothermal formula $(a-x)/v \,.\, S = Ke^{A \cdot (S-x)/x} \,.\, x$, in which x represents the quantity of adsorbed substance, v the volume, $(a-x)/v$ the concentration, S the concentration at saturation, and A and K constants. The analogy between adsorption and reactions of the first and second orders is illustrated by consideration of the decomposition of calcium carbonate in the absence and presence of carbon dioxide. It is shown that absorption of gases runs parallel to the power of those gases in reducing and destroying the fluorescence of iodine and mercury vapours. J. F. S.

Tension of Metal Ammonias. FRITZ EPHRAIM (*Zeitsch. physikal. Chem.*, 1913, **84**, 98—100).—Polemical: an answer to Biltz (this vol., ii, 129, 130). J. F. S.

An Analytical Dialyser. LADISLAS KOPACZEWSKI (*Compt. rend.*, 1913, **156**, 1853—1855).—The author has devised an apparatus in which (1) rapid dialysis in a stream of pure water, (2) distillation of the water, and (3) condensation of the dialysable portion can be effected. It may be readily understood from the annexed diagram.



A is a modified dialyser provided with a glass tube; by means of the three-way cock, R, communication can be established between A and the flask B, or water may be drawn off by the lateral tube to enable the operator to determine the end of the reaction. The Jena-glass flask, B, is provided with a cork carrying three tubes; two of these, made of glass, communicate with the dialyser and pump respectively, whilst the third, of tin, leads to the condensers. The latter are connected by a Y-tube, and so arranged that the water condensed in them flows into A. In use, the flask is filled with a suitable quantity of water, and the dialyser placed in position. The apparatus is then exhausted through the stopcock r, and the latter closed. The flask is heated at about 40°. Under these circumstances between three and four litres of water distil per day, and the water in the dialyser is renewed from ten to twenty times.

It is claimed that dialyses can be effected much more rapidly in this apparatus than in the usual manner, and further, that, if the dialyser is removed, the apparatus can be used for the preparation of water in a high state of purity. H. W.

Passage of Nascent Hydrogen through Iron M. BELLATI and SILVIO LUSSANA (*Nuovo Cim.*, 1913, [vi], **5**, i, 389—392).—The recent paper of Charpy and Bonnerot (A., 1912, ii, 336) only confirms the authors' results published twenty years since (*Atti Istituto Veneto*, 1888—1891). R. V. S.

Osmotic Pressure of Colloids. IV. The Theory of Colloidal Electrolytes. WILHELM BILTZ (*Zeitsch. physikal. Chem.*, 1913, **83**, 625—639. Compare A., 1910, ii, 22, 693; 1911, ii, 702).—The author criticises and compares the views of Donnan and Harris (T., 1911, **99**, 1554) and Donnan (A., 1911, ii, 848) with his own. It is shown that in connexion with the wandering in of electrolytes in the measurement of osmotic pressure of colour substances against water of equal electro-conductivity, that the theories of Donnan and the author agree qualitatively, and in some cases quantitatively. Hydrolysis is discussed in connexion with the older theories and with Donnan's theory of membrane hydrolysis chiefly in the following points: (*a*) hydrolysis in the preparation and purification of colloids; (*b*) lowering of osmotic pressure by hydrolysis, and the accompanying formation and polymerisation of free colour acids; (*c*) driving back of hydrolysis in osmotic experiments by the addition of the products of hydrolysis. The author concludes that even in the light of the more general theory of Donnan, his conclusions, as stated in his last paper (*loc. cit.*) with regard to characteristics of the solutions of colour substances, sufficiently express the observed conditions. J. F. S.

Dispersological Theory of True Solutions. PETR P. VON WEIMARN (*Zeitsch. Chem. Ind. Kolloid*, 1913, **12**, 298—308. Compare this vol., ii, 307).—The author starts from the statement that solids are practically insoluble in those liquids in which they are unable to form solvates, and toward which they are chemically indifferent. The conclusion is drawn that solution in water is brought about by a weakened (dynamic chemical) linking between the water and the dissolved substance; the intensity of the linking must lie between fixed limits, an increase leading to static chemical linking (that is, the formation of definite hydrates) as well as a diminution causing a diminished solubility. From a consideration of the ultramicroscopic structure of solutions the author comes to the conclusion that the dimensions of the viscosity of the solvate particle tend to approach those of the particles of the solvate without ever actually reaching them. In the ideal case at the maximum of the solubility curve the dissolved particles have their maximum dimensions and minimum density, and at this point the viscosity of the dissolved particles most nearly approaches the viscosity of the solvent particles. In connexion with the mechanism of solutions it is shown

that the process of solution consists in a diminution of the surface energy by means of a diminution of the surface tension and a compensating of the tendency to contract by the residual surface energy, by means of the kinetic energy of the solution. In a typical case of a true solution the contractive tendency of the surface energy is entirely compensated by the kinetic energy of the solvent, and consequently the homogeneous distribution of the dissolved substance cannot change with time. Similarly, in the case of a substance which is absolutely indifferent to the solvent the contractive tendency of the extremely large surface energy cannot be compensated by the kinetic energy of the solvent, and consequently such solutions can only maintain their homogeneous distribution for any length of time when they are very dilute. J. F. S.

Electrolytic Dissociation of a Salt Governed by the Mass Law. PAUL TH. MULLER and R. ROMANN (*Compt. rend.*, 1913, **156**, 1889—1891).—It has been assumed recently that the failure of salts and good electrolytes in general to dissociate electrolytically in accordance with the mass law, is due to gradual hydration of the ions which accompanies dilution. If this is so the mobility of the ions will become constant when hydration is complete, and the conductivity will then no longer depend only on the ionisation, and under these conditions the mass law should govern the change. This hypothesis has been verified for piperidine cyanoacetate.

T. A. H.

A New Theory of Allotropy. GUSTAV TAMMANN (*Zeitsch. physikal. Chem.*, 1913, **83**, 728—734).—Polemical against Smits (compare Smits, A., 1910, ii, 195, 400; this vol., ii, 393; Tammann, A., 1913, ii, 193). J. F. S.

Colloidal Suspension of Graphite. HENRY L. DOYLE (*J. Physical Chem.*, 1913, **17**, 390—401).—Crystalloids, such as sodium chloride, sodium hydroxide, acetic acid, etc., have no appreciable influence on the rate of settling of suspensions of bone-black and graphite. Bone black and graphite decolorise saturated solutions of iodine in water, but iodine has no influence on the rate of settling of these substances in benzene and absolute alcohol.

Good suspensions of graphite and bone-black in water were obtained by the use of caseinogen dissolved in sodium phosphate, dilute ferric acetate which had been boiled to promote hydrolysis, and sodium oleate. Concentrated sugar solutions, gelatin solutions, and an ammoniacal suspension of catechu have a little influence in stabilising suspensions of graphite, which in the case of catechu is increased by the presence of iron oxide.

An excellent suspension of graphite in oil was obtained by the use of a dry iron soap prepared by heating ferric chloride solution with sodium oleate. Sodium and magnesium oleates and precipitated ferric hydroxide give good suspensions, but only in presence of a small proportion of water. A dark gummy product obtained by heating "paraffin" in air had some effect, but resin and shellac were without influence.

A sample of Acheson's "Aquadag" was found to contain 3·2% of ferric oxide and 1·2% of copper in a total ash of 8%.

R. J. C.

Indirect Analysis of a Ferric Oxide Gel. HARRY B. WEISER (*J. Physical Chem.*, 1913, **17**, 536—555).—The calculation of the composition of a deposited gel from that of its mother liquor (Bancroft, A., 1905, ii, 685) depends on the assumption that one constituent of the mother liquor is entirely absent from the gel. Gelatinous ferric hydroxide precipitated from a known amount of ferric chloride solution by a known excess of sodium hydroxide solution cannot be analysed by this method, as both sodium and chlorine are found in the gel. A modification of the method is possible in this case, as the hydroxide is matted into a compact mass by long-continued centrifuging, and the mother liquor may be decanted practically without loss. The weight and composition of the mother liquor are the data necessary for calculating the composition of the gel. The indirect method avoids the estimation of small amounts of sodium and chlorine in presence of excess of iron.

The quantities of sodium hydroxide, chloride, and water adsorbed in ferric hydroxide gel vary widely with the composition of the mother liquor and the age and amount of centrifugal treatment of the gel. The absorption of chloride is diminished by an excess of sodium hydroxide.

R. J. C.

Proof of the Applicability of the Boyle-Mariotte and Gay-Lussac Laws to Emulsions. B. ILJIN (*Zeitsch. physikal. Chem.*, 1913, **83**, 592—598).—The author has examined emulsions of gamboge in water, castor oil, and gum arabic in water, and from the results draws the conclusions that in emulsions the variation in concentration follows the theoretical laws within the limits of experimental error; also that at the concentrations employed in the work the compressibility ratio β/β_0 is very nearly unity, or, in other words, that the movements of a given particle are quite independent of the movements of the other particles.

J. F. S.

Theory of Emulsification. V. WILDER D. BANCROFT (*J. Physical Chem.*, 1913, **17**, 501—519. Compare this vol., ii, 121).—In an emulsion the surface film surrounding the dispersed drops must be considered as a separate phase. This film adsorbs each of the two liquid phases, and its surface tension is not the same on each side. The film becomes concave, and envelopes the liquid on the side with the higher surface tension. Hence a hydrophile colloid will make water the dispersing phase, and a hydrophobe colloid will make water the dispersed phase.

Examples of emulsions in which water is dispersed are lanolin (which contains 25% of water), emulsions of water in mineral oil containing resin, greases, or solidified oils in which a lime soap is usually the emulsifying agent, and ready-mixed paints to which water has been added to keep the solid ingredients in suspension.

In the last case the dispersing phase is linseed oil, and the emulsifying agent probably rosin. Experiments made by F. R. Newman showed that an emulsion of water in white lead paint could contain as much as 70% of water. Water can be dispersed in carbon disulphide to the extent of 90%, using magnesium oleate with a little sodium oleate as protective colloid. In order to emulsify two liquids which are completely miscible it is necessary to add some soluble substance which will cause the two liquids to separate, as well as an emulsifying colloid or powder. The cracking of emulsions with age is often due to the shrinkage of the jelly-like colloidal film. In some emulsions, however, the protective film is a layer of ions due to an electrical charge. R. J. C.

Kinetics of Chemical Reactions of the First, Second, and Third Orders. V. EGOR I. ORLOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 457—488. Compare this vol., ii, 127, 128).—The author arrives analytically at the following results.

The chemical reactions characterised by the fundamental differential equations (I) $dx/dt=k(A-x)$, (II) $dx/dt=k(A-x)(B+x)$, and (III) $dx/dt=k(A-x)(B-x)$ or $dx/dt=k(A-x)$, represent the summation of at least three reactions, the observed values of x being composite magnitudes.

Mathematical analysis of the equations (II) and (III) renders possible their resolution into: (1) An equation of a reaction of the first order, $dx_1/dt=k_1(A-x_1)$. (2) An equation representing the action of a newly-formed substance, different from A, and increasing in concentration x^1; on its formation, the new compound immediately decomposes into fresh groupings. The reaction proceeds with velocity k_2, and is represented in the fully developed differential equation by the term $+k_2x'(A-x_1)$. (3) An equation of the counter-reaction of the new compound x^1, this proceeding with velocity k_3, and being represented in the complete equation by the term $-k_3x^1(A-x_1)$.

For a reaction with the fundamental differential equation, $dx/dt=k(A-x)(B+x)$, k_2 is always greater than k_3 and $k_2-k_3=k$. For one with the equation $dx/dt=k(A-x)^2$ or

$$dx/dt=k(A-x)(B-x),$$

k_2 is always less than k_3 and $k_2-k_3=-k$, whilst for one with the equation $dx/dt=k(A-x)$, k_2 is equal to k_3.

The term $k_1(A-x_1)$ of the complete equation is present in every differential equation representing a chemical reaction, and characterises a process of change of the initial substance into one of different nature; for instance, an ionised into a non-ionised complex. This change is a time-change, and when complete is immediately followed by further resolution into new groups or ionic groupings. The interaction of these new groups with the remaining initial compound and the corresponding counter-reaction proceed simultaneously with the first reaction, and are also time-reactions.

The velocity constant k of the fundamental equation represents the difference k_2-k_3, and may be either positive, or negative, or zero. T. H. P

Kinetics of Reactions of the Second and Third Orders. VI. EGOR I. ORLOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 489—511. Compare this vol., ii, 127, 128).—The author considers the derivation of the differential equation $dx/dt=k(A-mx)^3$ from $dx/dt=k(A-x)^3+k_1\phi(x)$. Writing k_1 for $k(1-m)$, k_2 for $1+m$, and k_3 for $1+m+m^2$, it is shown that $\phi(x)=x\{3A(A-k_2x)+k_3x^2\}$. So that, $dx/dt=k(A-mx)^3$ is derived from $dx/dt=k(A-x)^3+k_1x\{3A(A-k_2x)+k_3x^2\}$. The second term of the right-hand side has a positive sign if m is less than 1, whereas if m is greater than 1 the equation becomes

$$dx/dt=k(A-x)^3-k_1x\{3A(A-k_2x)+k_3x^2\}.$$

The reactions (1) $2FeCl_3+2KI=2FeCl_2+2KCl+I_2$ and (2) $Fe_2(SO_4)_3+2KI=2FeSO_4+K_2SO_4+I_2$ (compare Seubert and Dorrer, A., 1894, ii, 140, 191) are shown to be capable of representation thus: (1) $[FeCl_2]Cl+KI=[FeCl_2]I+KCl$ and

$$2[FeCl_2]I=2FeCl_2+I_2,$$

and (2) $\begin{bmatrix}FeSO_4\\FeSO_4\end{bmatrix}SO_4+2KI=2[FeSO_4{\cdot}I]+K_2SO_4$ and

$$2[FeSO_4{\cdot}I]=2FeSO_4+I_2.$$

Since, on the one hand, the reaction does not proceed to completion but attains a limit, and, on the other, the iodine separated combines, as it is liberated, with potassium iodide to form the complex KI_3, and so removes a corresponding quantity of potassium iodide from the sphere of the reaction, it is regarded as justifiable to apply to the process either the equation

$$dx/dt=k(A-mx)(B-mx)$$

or $dx/dt=k(A-mx)^2$. The integral of this equation under such conditions that $x=0$ when $t=0$ is $mk=mx/tA(A-mx)$, where k and m are constants and A the amount of iodine corresponding with the whole of the ferric chloride or sulphate, independently of whether the whole or only part of the salt takes part in the reaction. The magnitude of m depends on the concentration of the potassium iodide, and is, in most cases, greater than 1, so that in the differential equation $dx/dt=k(A-x)^2+k_1\phi(x)$ the constant k_1 is negative in sign. Hence the change proceeds with retardation of the principal reaction, $k(A-x)^2$, owing to union of the iodine and potassium iodide to form the complex KI_3 and to its reversibility. The magnitude of k increases in approximate proportion to the square of the concentration of the potassium iodide. When k_1 is negative the smaller the concentration of potassium iodide the greater is the absolute magnitude of k_1 and the more marked will be the negative catalysis.

Bodenstein and Kranendieck (A., 1912, ii, 747) attempted to explain the results of their investigations on the decomposition of sulphur trioxide in quartz vessels at high temperatures by assuming that the course of the reaction is represented by an equation of the first order, $dx/dt=k(A-x)-k_1x$. Such an assumption is open to criticism, especially as it is not easy to explain why, under certain conditions, a reaction of the third order should proceed as one of the first order. To explain the divergence of this reaction from the usual type, the author applies the equation for a

reaction of the third order in its general form, namely,

$$dx/dt = k(A - mx)^3,$$

integration of which gives $2A^2mk = mx(2A - mx)/(A - mx)^3$. Recalculation of Bodenstein and Kranendieck's experimental results gives constant values for A^2mk.

In his investigations on the oxidation of sulphur dioxide in aqueous and dilute sulphuric acid solutions by means of oxides of nitrogen, Trautz (A., 1904, ii, 328) obtained time-curves which he could not explain satisfactorily. The author shows that application of the differential equation in its general form,

$$dx/dt = k(A - xm)^2,$$

and calculation of the corresponding integral,

$$Amk = mx/t(A - mx),$$

give constant results. The oxidation of sulphur dioxide in presence of oxides of nitrogen is, indeed, a reaction of the second order, complicated by negative catalysis. The influence of the latter is explained by the author as follows: The oxidation of sulphur dioxide in presence of oxides of nitrogen is expressed by

$$SO_2 + HNO_3 = SO_3 + HNO_2,$$

which is a reaction of the second order. Hence the reaction would proceed according to the equation $dx/dt = k(A - x)^2$ if the nitrous acid did not remain in the solution and if other reactions did not proceed at the same time. But the nitrous acid undergoes the change represented by: $3HNO_2 \rightleftarrows 2NO + HNO_3 + H_2O$, the nitric acid then oxidising $1SO_2$ and being itself reduced to nitrous acid, whilst 2NO is oxidised in the atmosphere to $2NO_2$, which then dissolves again, giving $HNO_3 + HNO_2$. The equilibrium between nitrous acid, nitric oxide, nitric acid, and water is established, not instantaneously, but only after a certain time, and it is to this circumstance that the negative catalysis of the reaction is due.

T. H. P.

Kinetics of Chemical Reactions of Oxidation, Combination, and Deoxidation. VII. EGOR I. ORLOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 511—551).—The author applies the results previously obtained to elucidate the mechanism of various oxidation changes (compare this vol., ii, 127, 128).

The oxidation of hydriodic acid by potassium dichromate in presence of sulphuric acid is a reaction of the first order proceeding according to the equation $dx/dt = k(A - mx)$, the value of m being 1·01—1·05. If the concentrations of the potassium iodide and sulphuric acid are each doubled, the value of k is increased approximately $8(2^3)$ times; further, if the concentration of the potassium iodide only is halved, k is almost doubled, whereas the reaction velocity is increased sixteen times (2^4) when the concentration of the sulphuric acid is doubled.

In presence of arsenic acid the oxidation of hydriodic acid by potassium dichromate is a unimolecular reaction of either the first or the second order, being represented by $dx/dt = k(A - mx)$ or $dx/dt = k(A - mx)(B + mx)$. When the second law holds, it is

assumed that an intermediate compound is formed by the chromate and the iodine liberated, this being, on the one hand, a double compound of iodine with a salt of tervalent chromium, and on the other a compound having the properties of sexavalent chromium and hence possessing oxidising properties.

In the oxidation of potassium iodide by potassium bromate in presence of arsenic acid, no direct proportionality exists between the magnitudes of the velocity constant and the concentrations of the iodide and the arsenic acid, the action of the bromic acid being, not quantitative, but only partial. The oxidation by bromic acid in presence of potassium dichromate, ferric chloride, or sodium tungstate, and oxidation by hydrogen peroxide in presence of acetic acid either alone or together with potassium dichromate, ferric chloride, sodium tungstate, or ammonium molybdate have also been studied.

The oxidation of hydriodic acid by means of bromic acid, hydrogen peroxide, or potassium dichromate in an acid medium and either with or without an accelerator may be regarded as a chemical process obeying a law expressed by the general equation $dx/dt = k(A - mx)$, which has been shown previously to be derived from $dx/dt = k(A - x) \pm k_1 x$. This equation shows that the process comprises, besides the principal reaction of the first order expressed by $k(A - x)$, also another reaction with velocity k_1, which may either accelerate the principal reaction, k_1 being then positive, or retard it, in which case k_1 is negative; in the general equation this difference is shown by the factor m being less or greater than 1. In presence of an accelerator the values of both k and k_1 are altered T. H. P.

The Effect of Incombustible Dusts on the Explosion of Gases. HAROLD B. DIXON and COLIN CAMPBELL (*J. Soc. Chem. Ind.*, 1913, **32**, 684—687).—The experimental results which led Abel to his view that the presence of inert dust could promote the combustion of firedamp by a catalytic surface effect and so increase the danger of explosion, are shown to have been due to incomplete mixing of the firedamp and air used; there could thus be streams of gas richer in combustible constituents than the samples drawn for analysis. In experiments by the authors it was found impossible to render explosive, by the addition of incombustible dust, a gaseous mixture which under ordinary conditions would not propagate flame when sparked. Even heating such a mixture by an electrically-heated platinum wire did not render it explosive.

The experiment of Mallard and Le Chatelier (*Ann. des. Mines*, 1882) may easily be modified to show the inertness of magnesia and other incombustible dusts. A glass tube 5 feet long and 3 inches in diameter is fed from below with a mixture of gas and air from a Mecker burner and an adjustible orifice, whilst a Bunsen flame burns across the upper end. When the gaseous mixture is just below the explosive limit particles of magnesia (heated by passage through the Bunsen uame) carry down a small flame cap with them, but when the mixture is above this limit and would propa-

gate a flame if it was not moving upwards faster than the flame can travel down, a heated particle carries a real flame in its wake as it falls, and the flame spreads outwards in an inverted cone. When the mixture is just strong enough to propagate a flame downwards the heterogeneity of the mixture is revealed by curious round films of flame which slide over one another. D. F. T.

Reactions in Aqueous and Colloidal Systems. WILLIAM P. DREAPER (*J. Soc. Chem. Ind.*, 1913, **32**, 678—684).—Experiments on the formation of insoluble substances, in which the reacting solutions are contained in glass capillary tubes, demonstrate the fact that stratification can occur in the absence of any gel. Stratified layers were obtained of lead chloride, lead ferrocyanide, lead sulphate, silver ferrocyanide, barium sulphate, and barium carbonate. In one experiment a crystal of lead chloride 4 mm. in length was produced as one layer. Precipitation in the form of spherulites was not observed. The results indicate that the presence of a gel is not necessary to stratification, but that the diffusion process is primarily responsible; local supersaturation may exert some effect, but this can only be subsidiary because if a tube of stratified lead chloride crystals is heated until the precipitate dissolves, recrystallisation without stratification occurs on cooling.

When potassium sulphate is allowed to diffuse into a capillary tube containing barium chloride solution in which gelatin has been dissolved (or ammonium chloride may replace the gelatin) an opaque band of deposited barium sulphate appears to advance through the tube, leaving a clear space behind. This appearance is due to the gradual change of the finely divided opaque precipitate into an almost invisible crystalline salt, which could be easily examined under the microscope. D. F. T.

Colorimetric Investigation of Neutral Salt Action. II. Hydrogen Bromide. BOHDAN VON SZYSZKOWSKI (*Zeitsch. physikal. Chem.*, 1913, **84**, 91—97. Compare A., 1912, ii, 146).—The author has investigated the influence of sodium and potassium bromides on the colour reaction between methyl-orange and hydrogen bromide. The influence of these substances is compared with the corresponding influence of chlorides on hydrogen chloride, and it is shown that the sodium ion has a stronger influence than the potassium ion, and bromine than chlorine, the general nature of the influence being additive. But with sodium bromide the additive character vanishes entirely, and a very much smaller effect is observed; this is explained by assuming a removal of hydrogen bromide by the formation of a complex of the type nNaBrmHBr.

J. F. S.

Equilibria in Systems Containing Alcohols, Salts, and Water, Including a New Method of Alcohol Analysis. GEORGE B. FRANKFORTER and FRANCIS C. FRARY (*J. Physical Chem.*, 1913, **17**, 402—473).—The equilibrium diagrams of the ternary systems of water with methyl alcohol–potassium carbonate, ethyl alcohol–potassium carbonate and fluoride, propyl alcohol–potassium carbon-

ate and fluoride and sodium chloride have been plotted in triangular co-ordinates. Each of these six systems becomes heterogeneous within certain limits of concentration, and the alcohol phase may be rendered visible with phenolphthalein in the case of potassium carbonate systems and with °spirit-blue] in the others. The tie lines are straight, whether in triangular or rectangular co-ordinates.

In general, the solubility of the hydrated salts in absolute alcohol is about the same as in 60—70% alcohol, and greater than in alcohol of intermediate dilutions. The influence of temperature on the position of the binodal curves is small with methyl and ethyl alcohols, but considerable in propyl alcohol mixtures, particularly with sodium chloride. Propyl alcohol has a minimum solubility in 2·28% sodium chloride solution at about 37°. Some of the heterogeneous solutions had both upper and lower critical temperatures, outside of which they were homogeneous.

The relative salting out powers of potassium fluoride and carbonate for ethyl and propyl alcohols are opposite, and sodium chloride, which is a good precipitant for propyl alcohol, does not affect ethyl alcohol. The precipitating action does not depend on the ions of the salt, but rather on its affinity for water.

Anhydrous potassium fluoride is an excellent dehydrant for alcohols, acting rapidly on account of its solubility in the alcohols, and absorbing a large proportion of water (62%) to form its lowest hydrate, $KF,2H_2O$. The limit of dehydration of ethyl alcohol is at 97·5% when the vapour pressure, 3·5 mm., corresponds with that of the hydrate, $KF,2H_2O$.

Saturated potassium fluoride solution is superior to saturated potassium carbonate as a dehydrant as it has a lower vapour pressure.

Ethyl alcohol in aqueous solution may be estimated by adding sufficient potassium fluoride to salt out part of the alcohol, and then adding water, drop by drop, until the solution is just homogeneous again at 25°. The proportion of alcohol is found by reference to the solubility curve of the salt in alcohol–water mixtures.

The method is not applicable to liquors such as beer, which contain dissolved solids, but is fairly accurate in presence of small proportions of methyl alcohol. R. J. C.

The Velocity of Evolution of Oxygen from Bleaching Powder Solutions in Presence of Small Quantities of Cobalt Nitrate and the Influence of Different Compounds on it. N. M. Bell (*Zeitsch. anorg. Chem.*, 1913, **82**, 145—163).—An apparatus is described by means of which a 0·5078*N*-solution of cobalt nitrate may be added to a solution of bleaching powder in a thermostat, and the volume of escaping oxygen measured. The velocity accords well with a unimolecular reaction, but is modified by shaking and by the order in which the solutions are mixed. Acids accelerate the reaction by about one-half for *N*/50-solutions of the acid, and alkalis retard it by one-half for a *N*/2000-solution. Salts accelerate or retard it, and a relation between the nature of the salt and its catalytic influence has not been found. Nickel sulphate has about

the same influence as cobalt nitrate, but ferrous sulphate has only about 1·5% of the catalytic influence of the cobalt salt. C. H. D.

Piezochemical Studies. X. The Influence of Pressure on the Velocity of Reaction of Condensed Systems. I. ERNST COHEN and R. B. DE BOER (*Zeitsch. physikal. Chem.*, 1913, **84**, 41—82. Compare last abstract).—The authors give a long critical review of the older work on the influence of pressure on the velocity of chemical reactions, and follow this with a description of experiments on the velocity of hydrolysis of sucrose at 25° by $N/8$- and $N/16$-hydrochloric acid at pressures varying from 1 to 1500 atms. The authors have also determined the compressibility of sucrose solutions, and this value is used in the calculations of the velocity constant. The measurements by this method can be made with the same accuracy as at ordinary pressures. It is shown that the reaction velocity is decreased by 8% at a pressure of 500 atms., by 19% at 1000 atms., and 26% at 1500 atms. The influence of pressure can be expressed by the equation $d\log k/dp=$const. and also by the linear equation $k_p=a+bp$. The compressibility of a solution of sucrose containing 20 grams in 100 c.c. of solution at 25° is found to be 238·5—423·1 atms. $\beta\times10^6=36·7$, 1252·0—1509·0 atms. $\beta\times10^6=29·1$. J. F. S.

Hydrolysis of Esters of Substituted Aliphatic Acids. VI. Saponification by Sodium Hydroxide of Hydroxy- and Alkyloxy-acetates and -propionates. E. W. DEAN (*Amer. J. Sci.*, 1913, [iv], **35**, 605—610. Compare Findlay and others, T., 1905, **87**, 747; 1909, **95**, 1004).—The velocity of saponification by sodium hydroxide at 0° and 25° of the following ethyl esters has been determined: Ethyl acetate, glycollate, methoxyacetate, ethoxyacetate, propoxyacetate, propionate, lactate, glycerate, α-ethoxypropionate, and β-ethoxypropionate.

The presence of an hydroxyl group in aliphatic esters produces an acceleration in the velocity of saponification, which, however, is variable in its magnitude. The presence of alkyloxy-groups has a very varying effect, in some cases resulting in a considerable acceleration, in others in a slight retardation. With alkyloxy-esters of similar constitution the velocity of saponification decreases as the molecular weight of the alkyloxy-group increases.

β-Substituted esters are saponified less rapidly than the α-isomerides, in this respect behaving the same as in acid hydrolysis; generally, however, the relative velocities of saponification of the esters studied are quite different from the relative velocities of their acid hydrolysis.

The velocity of saponification seems to be closely connected with the strength of the acid from which the ester is derived; a quantitative relation could not be found at present, but, in general, the stronger the acid the greater the velocity of saponification.

T. S. P.

The Forces which Determine the Velocity of Removal of Soluble Colloids from Colloidal Media in Aqueous Solutions. T. BRAILSFORD ROBERTSON (*Pflüger's Archiv*, 1913, **152**, 524—534. Compare A., 1910, i, 528).—The author shows that the velocity of extraction of proteins from colloidal media by means of aqueous solutions is determined by forces of a capillary nature. The capillary forces regulate the reaction velocity, not because they determine the velocity with which the solvent penetrates the colloid particles and moistens their internal surface, but because they control the velocity with which the protein passes from the inside of the colloid particles to the outside solvent. The following relationship between the time and amount of protein dissolved is deduced; $x = kt^m$, in which x is the amount of protein extracted in the time t; k and m are constants. From the form of the relationship it is clear that although the extraction of the protein is very rapid at first it decreases so rapidly that it cannot be regarded as complete in an experimentally finite time. The above relationship is confirmed by the results of experiments on the rate of extraction of casein by dilute solutions of acids, and the extraction of protamine from the dried spermatozoa of *Oncorhynchus tschawytscha*, Walbaum (*loc. cit.*). J. F. S.

Catalytic Hydrogenisation by Finely Divided Metals. ANTONIO MADINAVEITIA (*Anal. Fis. Quim.*, 1913, **11**, 328—333).—Ruthenium and iridium determine the catalytic hydrogenisation of cinnamic acid, but not of toluene, whereas rhodium acts on both substances. Osmium is inactive. G. D. L.

Catalysis. XVII. Reactions of Both the Ions and the Non-ionised Forms of Electrolytes. Reactions of Sodium Phenoxide with Methyl Iodide and Ethyl Iodide in Absolute Ethyl Alcohol at 25° and 35°. H. C. ROBERTSON, jun. and SOLOMON F. ACREE (*Amer. Chem. J.*, 1913, **49**, 474—520. Compare Acree, this vol., ii, 576; Marshall, Harrison, and Acree, this vol., ii, 577).—In continuation of the work on catalysis, a study has been made of the velocities of reaction of sodium phenoxide with methyl iodide and with ethyl iodide at 25° and 35° in absolute alcohol at concentrations ranging between N and $N/40$. Constant values have been obtained for K_i and K_m, which represent the velocity of transformation of unit concentrations of phenoxide ions, and of non-ionised sodium phenoxide with alkyl iodides. This is regarded as evidence that both the phenoxide ions and the non-ionised sodium phenoxide react with the non-ionised alkyl iodides, and is supported by the fact that the same value is obtained for K_i with a given alkyl haloid whether the phenoxide ions are derived from the sodium, potassium, or lithium salt. It is probable that the transformation is accompanied by an "abnormal salt effect," and in order to investigate this question it is proposed to determine the reaction velocities in solutions varying in concentration from N to $N/2048$. A similar study has shown that p-bromobenzonitrile and sodium, potassium, and lithium ethoxides in solutions ranging

from $N/32$ to $N/2048$ give the same value for K_i for the ethoxide ion in these ideal solutions, but seem to yield different uncorrected values for K_i and K_m in the more concentrated solutions. The abnormal behaviour of the concentrated alcoholic solutions are being investigated by measurements of their fluidities, the effect of added salts on the reaction velocities, and the probable extent of the alcoholation of the reacting constituents. E. G.

Constitution of Atoms and Molecules. I. N. BOHR (*Phil. Mag.*, 1913, [vi], **26**, 1—24).—The author, making use of Rutherford's theory of the constitution of the atom, considers the mechanism by which the revolving electrons are bound to the positive nucleus. The considerations are made in relation to Planck's hypothesis of energy quanta. It is shown that in any molecular system consisting of positive nucleii and electrons in which the nucleii are at rest relatively to each other and the electrons move in circular orbits, the angular momentum of every electron round the centre of its orbit will in the permanent state of the system be equal to $h/2\pi$, where h is the Planck constant.

On the assumption that the hydrogen atom consists of a positive nucleus and a single electron of charge e, the author deduces the expression $\nu = 2\pi^2 me^4/h^3(1/\tau_2^2 - 1/\tau_1^2)$, where m is the mass of an electron, τ_1 and τ_2 are whole numbers, h is the Planck constant, and ν is the atomic vibration frequency. This expression accounts for the law connexion of the lines in the hydrogen spectrum. If $\tau_2=2$ and τ_1 varies, the expression gives the Balmer series, and if $\tau_2=3$ the ultra-red series of Paschen is obtained. If $\tau_2=1$ and $\tau_2=4$, 5 respectively, series are given in the extreme ultraviolet and infra-red. These have not yet been observed. J. F. S.

Formation of the Molecules of the Elements and their Compounds with Atoms as Constituted on the Corpuscular-ring Theory. ALBERT C. CREHORE (*Phil. Mag.*, 1913, [vi], **26**, 25—84).—The author first describes experiments made to test the corpuscular-ring theory of the atom. A number of steel balls of uniform size are suspended by long, thin copper wires in castor oil and charged to an equal high potential, allowed to take up their equilibrium position, and photographed. In this way it is shown that the arrangement calculated by Thompson is set up, although other equilibria are possible. The radii, etc., for the arrangements which correspond with hydrogen, carbon, nitrogen, oxygen, and fluorine atoms are worked out from measurements made on the photographs of the equilibrium arrangements. The second part of the paper deals with the combination of atoms to form molecules. It is shown that two atoms take up a position of equilibrium to one another in forming a compound, and that there is an attraction between them varying inversely as the fourth power of the distance. The third part of the paper is mathematical, and deals with the calculation of the necessary formulæ involved in the paper. J. F. S.

Chemical "Lability" and Absorption of Ultraviolet Rays. VICTOR HENRI (*Compt. rend.*, 1913, **156**, 1979—1982).—Substances which are chemically labile are said to possess the property of chemical "lability."

An examination of the work which has been done during the past few years leads the author to the following electronic theory of chemical reactions: a substance which reacts readily contains molecules which are able either to liberate or to exchange electrons readily; the linkings between the atoms in a molecule are brought about by the electrons.

Since the absorption of ultraviolet rays is an electronic property, it should follow that compounds which absorb these rays should be chemically labile, and vice versa. An examination of a number of different compounds shows this to be the case. T. S. P.

Reform of Chemical Calculations. C. J. T. HANSSEN (*Chem. News*, 1913, **108**, 3).—The author has extended the list of atomic weights which are whole numbers (compare A., 1912, ii, 1157) to seventy-six elements. T. S. P.

Piezochemical Studies. IX. An Automatic Pressure Regulator for High Pressures. ERNST COHEN and R. B. DE BOER (*Zeitsch. physikal. Chem.*, 1913, **84**, 32—40).—The authors describe an automatic apparatus which is capable of regulating the pressure in a reaction bomb to within 1% for pressures up to 1800 atms. This apparatus has been used in the authors' previous work (A., 1909, ii, 291, 641, 796, 857, 981; 1910, ii, 1029; 1911, ii, 23).
J. F. S.

An Automatic Apparatus for the Extraction of Solutions Sensitive to Heat. RICHARD KEMPF (*Chem. Zeit.*, 1913, **37**, 774).—The solution to be extracted is contained in a jacketed glass tube, which can be cooled by a current of cold water. Into this glass tube is fitted, at the top, a reflux condenser, and between the lower end of the condenser and upper end of the jacket are sealed two side-tubes, the lower one of which leads to the bottom of a flask containing the extracting liquid, and serves as an overflow for this liquid from the jacketed tube. The upper side-tube serves to conduct the vapour from the flask to the reflux condenser. Just below the end of the condenser is a funnel which is sealed on to a spiral of glass tubing which reaches to the bottom of the jacketed tube. The liquid from the condenser runs down through this spiral, and is forced, by hydrostatic pressure, up through the solution to be extracted, and overflows into the above-mentioned flask. T. S. P.

A New Form of Condenser. RICHARD ASCHER (*Zeitsch. angew. Chem.*, 1913, **26**, 408).—To avoid the instability caused by the introduction of an adapter between a condenser and the flask of boiling liquid the author constructs the inner tube of the condenser with a short T-piece at one end, making an angle of 60° with the cooling

portion of the tube. The two short arms of the T-piece can be fitted to a flask, and with a thermometer or tap-funnel respectively. When the condenser is so disposed that the smaller angle of the T-piece is below, it is in position for ordinary distillation, whilst when turned with the smaller angle above it is ready for refluxing.

D. F. T.

A New Modification of the Liebig Reflux Condenser. WALTHER FRIESE (*Pharm. Zentr.-h.*, 1913, **54**, 670).—The ordinary condenser, in which the inner tube is expanded into a series of bulbs, is modified in such a way that the cooling area of the bulbs is increased by making the upper and lower end of each bulb re-entrant (as the lower end is in the head of an alembic). In order to prevent the condensed liquid collecting in the bottom channel thus formed in each bulb, a tube is sealed into the lowest part and connected with the top portion of the next lower bulb.

T. S. P.

The L-Condenser. KARL LÜDECKE (*Chem. Zeit.*, 1913, **37**, 838). —A condenser has already been described by the author (*ibid.*, 1905, **29**, 1282) in which condensation is effected by internal cooling with an inner tube enlarged into a series of bulbs; it can be used over a water-bath without condensing the steam and so wetting the cork of the flask. The condenser is very effective, and the earlier disadvantage that a little of the condensed liquid in distillations was retained in the lower portion of the condenser is now obviated by attaching the inlet and outlet tubes for the vapour and condensed liquid in a line with the side of the condenser instead of centrally.

D. F. T.

Lecture Experiment to Show the Specific Action of Catalysts. EMIL ABEL (*Zeitsch. Elektrochem.*, 1913, **19**, 480—482. Compare A., 1908, ii, 26; 1912, ii, 927).—The author has shown (*loc. cit.*) that the reaction between hydrogen peroxide and thiosulphate is catalysed differently by iodine and molybdic acid. In the first case the reaction goes as indicated by the scheme:

$$H_2O_2 + 2S_2O_3'' + 2CH_3\cdot CO_2H \longrightarrow S_4O_6'' + 2CH_3\cdot CO_2' + 2H_2O,$$

and in the second case as indicated by the scheme:

$$4H_2O_2 + S_2O_3'' \longrightarrow 2SO_4'' + 2H^{\cdot} + 3H_2O.$$

If both reactions are started and a little barium chloride solution added to each, in the first case there will hardly be a cloudiness, whilst in the second a continuous formation of sulphate will occur. Further, if a drop of hydrochloric acid is added to each reaction and then a drop of methyl-orange solution which is just acid, in the first case the colour will change to yellow as the reaction proceeds, whilst in the second case it will become notably redder. As is visible from the equations, the end of the reaction in the first case is conditioned by the using up of all the thiosulphate, and in the second case by the using up of the hydrogen peroxide. Consequently there is an excess of hydrogen peroxide over thiosulphate in the first case, and vice versa in the second case. This is shown by

adding starch to the first reaction, when a deep blue colour will be formed due to the iodine liberated by the action of the H_2O_2 on the sodium iodide formed in the reaction. In the second case even on adding potassium iodide there is no blue colour formed in the presence of starch, showing the absence of hydrogen peroxide. As a lecture experiment the author recommends the following quantities. The volume of the reaction mixture in each case should be 100 c.c., made up of (I) $0{\cdot}1N H_2O_2$, $0{\cdot}025N Na_2S_2O_3$,

$0{\cdot}025N CH_3{\cdot}CO_2H$,

a little $0{\cdot}025N BaCl_2$ and $0{\cdot}004N HCl$, a few drops of methyl-orange, and a little starch and $0{\cdot}25N KI$; (II) as (I) except that the $0{\cdot}25N KI$ is replaced by 0·0002 mol. Na_2MoO_4. The reaction is complete in a few minutes, and the changes indicated can all be observed J. F. S.

Two Lecture Experiments. [Preparation of (I) Copper Acetylide, (II) the ψ-Nitrole of Nitro*iso*propane.] HANS RUPE (*J. pr. Chem.*, 1913, [ii], **88**, 79—82).—Details are given of the preparation of copper acetylide and the methods adopted to show its explosive character when brought in contact with nitric acid, potassium permanganate and sulphuric acid, bromine, and chlorine.

The second experiment illustrates the formation of the ψ-nitrole of nitro*iso*propane by passing nitrous gases from arsenious oxide and nitric acid into a concentrated ethereal solution of acetoxime. The formation of the ψ-nitrole may be more readily shown in the following manner: An aqueous solution of acetoxime and sodium nitrite is covered with ether, and dilute hydrochloric acid added drop by drop with constant shaking, when the ether rapidly acquires a deep blue colour. F. B.

A Modified Borman's Gas-generating Apparatus. J. MAREK (*Zeitsch. anal. Chem.*, 1913, **52**, 419—421).—An improved form of the apparatus destribed and figured by Borman (A., 1912, ii, 931).

L. DE K.

Inorganic Chemistry.

Bromides. IV. Icilio Guareschi (*Atti R. Accad. Sci. Torino*, 1912–1913, **48**, 735—749. Compare this vol., ii, 333).—The author has continued his investigation of the stability of bromides with the aid of the test previously described. The paper also contains information regarding the hydrates of the salts described.

Anhydrous lithium bromide evolves bromine when heated to its m. p., and also (in small quantity) when it is boiled with water and iodine. Ammonium bromide sublimes and dissociates on heating, but does not yield bromine. Sodium bromide does not evolve bromine (or only in traces) when heated even above its m. p.

Bromine is rapidly eliminated, however, when the salt is heated with excess of iodine. Rubidium bromide loses bromine above its m. p., but only gives the smallest trace of bromine when heated with water and iodine. If the dry salt is heated with iodine, however, much bromine is evolved. Cæsium bromide does not yield bromine on heating, and only gives traces with water and iodine; with iodine in the absence of water, however, bromine is evolved even at the ordinary temperature, and on heating the evolution is very considerable. Thallium bromide does not lose bromine even at high temperatures; it is more stable than the bromides of potassium and sodium. When it is heated with iodine, bromine is evolved. Silver bromide behaves similarly. All the above-mentioned bromides yield bromine when heated with chromic acid.

The action of chromic acid on silver bromide may be used to detect traces of this salt, even in presence of other silver haloids. In the reaction, oxygen and bromine are evolved, and metallic silver and chromium sesquioxide are formed.

Mercurous bromide sublimes when heated, and during the sublimation no bromine is liberated. The salt yields bromine, however, when rapidly heated with excess of iodine or with very concentrated chromic acid. Iodine reacts with mercurous bromide even at the ordinary temperature, and a mixture of mercuric iodide and mercuric bromide is formed. This reaction agrees with Werner's formula, $Hg\cdot Hg{:}Br_2$, for mercurous bromide.

Anhydrous cuprous bromide evolves bromine at its m. p. The salt also yields bromine when heated with 25% chromic acid.

R. V. S.

The Existence of Bromites. J. CLARENS (*Compt. rend.*, 1913, **156**, 1998—2000).—A fresh solution of hypobromite, made by the solution of bromine vapour in a solution of potassium or sodium hydroxide, was divided into two parts; the one was treated with an excess of ammonium chloride, whilst the other was first heated at 80° for a few minutes, and then excess of ammonium chloride added. The first solution was without action on an alkaline arsenite solution in the cold, whilst the second oxidised it, the oxidising power being as much as one-tenth of that originally possessed by the hypobromite solution. The oxidising agent still present in the second solution could not be bromate, since bromate does not oxidise an arsenite in cold alkaline solution; it was probably bromite. This was proved to be the case by analysis, as follows. The hypobromite present in the (second) solution was destroyed with carbamide, and the bromide precipitated as silver bromide. After collecting the precipitate, the filtrate was divided into three portions, which were analysed as follows: In the first portion the oxidising power towards a cold alkaline arsenite solution was determined; in the second portion the oxidising power towards a cold, strongly acid arsenite solution was measured; the third portion was evaporated to dryness, the residue calcined to destroy bromate and bromite, and the amount of bromide estimated. The results of these three analyses gave the formula $MBrO_2$, that is, that

of a bromite, as the oxidising substance present in the second solution. T. S. P.

The Oxidation of Some Inorganic Substances at High Pressures and Temperatures. JAROSLAV MILBAUER (*Eighth. Inter. Cong. App. Chem.*, 1912, **2**, 183—185).—The action of oxygen at 480° and a pressure of 12 atmospheres on various oxides and mixtures of oxides has been investigated. The oxides of the following metals give peroxides: lithium, sodium, potassium, and barium. A small proportion of higher oxides is given by the oxides of cobalt and nickel. Lead oxide gives red lead, antimony oxide gives the tetroxide, and chromium sesquioxide gives chromium chromate. The oxides of the following metals and elements remain unaltered: glucinum, calcium, strontium, zinc, cadmium, aluminium, boron, thallium, silicon, zirconium, tin, bismuth, molybdenum, tungsten, uranium, and iron.

The two-component mixtures investigated all contained chromium oxide as the one component; all of them, with the exception of the mixture with cerium oxide, gave chromates. In the second column of the periodic system the amount of oxygen absorbed diminishes in the inverse ratio of the atomic weight of the metal. T. S. P.

The Action of Carbon Dioxide on the Mineral Sulphides. N. D COSTEANU (*Compt. rend.*, 1913, **156**, 1985—1987).—The action of carbon dioxide on sulphides, at temperatures below that at which dissociation of the carbon dioxide takes place, has been studied.

Silver, copper, cadmium, bismuth, and antimony sulphides were not acted on. Silicon sulphide reacted slowly at 1100° in accordance with the equation: $2CO_2 = SiS_2 = 2CO + 2S + SiO_2$; the same reaction takes place even at 450°. The results show, at the same time, that carbon dioxide has no action on sulphur at these temperatures. T. S. P.

Colloidal Selenium. ALEXANDER GUTBIER and FR. HEINRICH (*Koll. Chem. Beihefte*, 1913, **4**, 411—457).—The authors have studied the reduction of selenious acid to selenium by means of a series of reducing agents, and also the reversibility of the disperse selenium system produced in these actions. It is shown that in the reduction of selenious acid solution by sulphurous acid the maximum reduction occurs when the substances are present in the molecular relationship $1SeO_2 : 2SO_2$. The colour of the solutions in the above case is reddish-yellow when the selenium oxide is above the given relationship, and changes toward the green with an excess of sulphur dioxide. The colour is in this sense dependent on the way the liquids are mixed. When solutions of selenium dioxide are reduced by sodium or ammonium hydrogen sulphite, a maximum reducing action is found to occur at the molecular relationships $1SeO_2 : 2{\cdot}5—2{\cdot}7NaHSO_3$ and $1SeO_2 : 1{\cdot}8—2{\cdot}0NH_4HSO_3$. Just as in the reductions by sulphur dioxide the colour of the

solutions tends towards the green in the presence of excess of the reducing agent. All these reductions take place in the absence of hydrochloric acid. Reduction with sodium hyposulphite ($Na_2S_2O_4$) occurs very rapidly, the velocity increasing with the increasing amount of the reducing agent, and decreasing with increasing dilution of the solution. A maximum reduction relationship could not be observed. A relationship appears to exist between the velocity of sedimentation and the concentration of the hyposulphite, in the sense that sedimentation is more rapid the greater the concentration of hyposulphite. In those cases where there is a large concentration of hyposulphite, the deposited red selenium often changes into the black modification when kept. Hydrazine hydrate reduces solutions of selenious acid very rapidly, but no maximum reduction relationship could be observed, and the coagulation of the selenium sols occurred at about the same time with all quantities of the reducing agent. Hydrazine chloride and sulphate behave exactly like the hydrate. The relative velocity of reduction of the substances investigated is shown to be in the following order: sodium hyposulphite, hydrazine chloride, sulphurous acid, hydrazine sulphate, and hydrazine hydrate. The selenium obtained by reduction with sulphurous acid dissolves in water to form a colloidal solution, and the red disperse system so formed, which can be filtered without a residue, coagulates extremely slowly. During sedimentation, it forms two layers, the upper one being bluish-red to yellowish-green, and the under one turbid red. A solid hydrosol of selenium can be obtained by evaporation of the above-mentioned solution in a vacuum. This is a reddish-brown powder, which partly dissolves in water to form a yellowish-green solution, and a turbid red sol can be formed by rubbing the residue with water. Selenium prepared by reduction with sodium or ammonium hydrogen sulphite forms colloidal solutions, that precipitated by the sodium salt passing more easily into solution than that precipitated by the ammonium salt. Reduction with sodium hyposulphite produces reversible and stable sols so long as the relationship $1SeO_2 : 2—2{\cdot}8Na_2S_2O_4$ is not exceeded in the reduction. Selenium produced by hydrazine hydrate or the hydrazine salts is completely irreversible. J. F. S.

The Atomic Weight of Tellurium; and a Critique of the Basic Nitrate Method of Determination. WILLIAM L. DUDLEY and PAUL C. BOWERS (*J. Amer. Chem. Soc.*, 1913, **35**, 875—880).—A continuation of the earlier investigation (Dudley and Jones, A., 1912, ii, 935). Tellurium, which had been purified in the manner described earlier, was dissolved in nitric acid for the purpose of determining the atomic weight by the basic nitrate method, but it was found to separate, on crystallisation, sometimes as orthorhombic basic nitrate, and sometimes as octahedral dioxide; the latter could be converted into basic nitrate by further treatment (repeatedly if necessary) with nitric acid. The figures calculated from the results of the decomposition of the basic nitrate were, however, so irregular that the method was abandoned. Tellurium

may crystallise from nitric acid solution as tellurous acid, tellurium dioxide, and basic nitrate, and the exact conditions for the separation of pure crystals of any one appear to be very elusive.

In the failure of the basic nitrate method, the tetrabromide method was applied to the determination of the atomic weight of the various fractions of the tellurium precipitated by hydrazine hydrochloride, and also of the element in the various specimens of basic nitrate obtained above. The results indicate the identity of the tellurium in every case. D. F. T.

Effect of Free Chlorine on the Product of Hydrolysis of Tellurous Chloride. PHILIP E. BROWNING and GEORGE O OBERHELMAN (*Eighth. Inter. Cong. App. Chem.*, 1912, **2**, 59–62).—In Harcourt and Baker's discussion (T., 1911, **99**, 1311) of the work of Browning and Flint on the hydrolysis of tellurous chloride, they state that the yellow colour sometimes observed in the hydrolytic fractions was found by them to be due to a small amount of telluric oxide present in their material, presumably because of chlorine set free from the hydrochloric acid by the action of bright sunlight. The authors find that if pure tellurous oxide is dissolved in hydrochloric acid which has been exposed to bright sunlight, the solution hydrolysed with boiling water, and the precipitate thus formed boiled with pure hydrochloric acid, no chlorine is liberated. Moreover, if the solution of tellurous oxide in hydrochloric acid is saturated with chlorine both before and after hydrolysis, the amount of chlorine liberated when the precipitate is boiled with hydrochloric acid is very small, the amount of tellurium trioxide formed being less than 0·5%.

It follows that the results obtained by Browning and Flint cannot be due to an error caused in the way suggested by Harcourt and Baker. T. S. P.

An Active Modification of Nitrogen Produced by the Electric Discharge. V. (HON.) ROBERT J. STRUTT (*Proc. Roy. Soc.*, 1913, *A*, **88**, 539—549. Compare A., 1911, ii, 482; 1912, ii, 153, 477, 935).—An improved method is described for preparing and storing pure nitrogen containing less than 1/150,000 of its volume of oxygen. It is shown that, despite criticisms, the presence of traces of oxygen in the nitrogen used is not essential or even favourable to the formation of active nitrogen. The addition of oxygen hinders the formation, 2% preventing the action altogether. Hydrogen and carbon dioxide as impurities have but little effect on the action, but traces of water vapour are decidedly harmful. Nitrides are formed by passing active nitrogen into vapours of mercury, cadmium, zinc, arsenic, sodium, and sulphur. These nitrides are decomposed by water or potassium hydroxide, giving ammonia. Carbon disulphide yields a blue, polymeric nitrogen sulphide and a polymeric carbon monosulphide. Sulphur chloride gives ordinary yellow nitrogen sulphide. Stannic chloride and titanium chloride also yield solid products; in the latter case nitro-

gen was shown to be present. The following compounds give hydrogen cyanide when treated with active nitrogen: acetylene, benzene, pentane, methyl bromide, ethyl iodide, ethyl chloride, chloroform, ethylene dichloride, ethylidene dichloride, and ether. Carbon tetrachloride and carbon disulphide gave no trace. When chlorine is present, cyanogen chloride is produced, and benzene also gave cyanobenzene. The intensity of the cyanogen spectrum with organic compounds is no index of the quantity of hydrogen cyanide being formed. Preponderance of the real cyanogen bands is associated with cyanogen chloride and bromide. Generally there does not appear to be any definite connection between the development of spectra by active nitrogen and the chemical actions in progress.

J. F. S.

Fixation of Atmospheric Nitrogen by means of Boron Compounds. I. Decompositions under High Pressures. ARTHUR STÄHLER and JOHN JACOB ELBERT (*Ber.*, 1913, **46**, 2060—2077).—The object of the authors' experiments was to determine the conditions under which boron nitride may best be obtained from naturally occurring compounds of boron. Since in such compounds the boron is generally combined with oxygen, it was necessary to investigate first the best methods for their reduction, and then the combination with nitrogen of the boron or boride formed.

The reduction of boron trioxide by carbon begins to take place at 1200°; in the presence of nitrogen, calcium borate (borocalcite) undergoes reduction at 1280°, reaction probably taking place according to the equation:

$$CaB_4O_7 + 8C + 3N_2 = 4BN + CaCN_2 + 7CO.$$

The electrolysis of molten borax gave yields of boron to the extent of 12·1%. Carbon electrodes were first used, but they broke off repeatedly at the surface of the fusion; iron electrodes lasted longer, but they also broke off after a time.

Attempts to reduce boron trioxide by means of calcium carbide at 1625° made it probable that the product of reaction was calcium boride, which has previously been prepared by Moissan.

Before carrying out further experiments on the production of boron nitride it was necessary to determine its stability; it was found that decomposition with evolution of nitrogen only commenced to take place at 2450°; this temperature of decomposition holds only in the presence of carbon, since the boron nitride was contained in a graphite crucible.

The next experiments were confined to mixtures of carbon with either boron trioxide or borocalcite. These were heated to different temperatures in an atmosphere of nitrogen under different pressures, a special electrical furnace having been constructed in which reactions could be carried out at pressures up to 500 kg. per sq. cm., and at temperatures up to 2500°.

With mixtures of boron trioxide and carbon and nitrogen at atmospheric pressure, the best yield, 26—28%, of boron nitride is obtained between 1500° and 1700°. With increasing pressure

the yield increases, more than 85% of boron nitride being obtained at a pressure of 70 kg. per sq. cm. and a temperature of 1600°. When the boron trioxide is replaced by borocalcite, a nearly theoretical yield of boron nitride, according to the equation given above, is obtained when the temperature is maintained at 1850° for thirty minutes and 1400° for fifteen minutes; increase in pressure of the nitrogen has no effect on the yield. At normal pressures the amount of nitrogen absorbed per gram of boron is much greater with borocalcite than with boron trioxide; only at very high pressures are better results obtained with boron trioxide than with borocalcite. T. S. P.

Catalytic Action of Iodine. MORITZ KOHN and ALFONS OSTERSETZER (*Zeitsch. anorg. Chem.*, 1913, **82**, 240—241).—The reaction between phosphorus trichloride and sulphur chloride, $3PCl_3 + S_2Cl_2 = PCl_5 + 2PSCl_3$, is accelerated by iodine, and a yield of 88% of phosphorus pentachloride may be obtained. C. H. D.

The Retention of Small Quantities of Water by Arsenic Pentoxide at Elevated Temperatures. ALAN W. C. MENZIES and PAUL D. POTTER (*Eighth. Inter. Cong. App. Chem.*, 1912, **2**, 179—182).—An investigation of the amount of water lost by the hydrate, $3As_2O_5,5H_2O$, when heated for different lengths of time at different temperatures in a current of dry air or of air of known humidity. T. S. P.

Total Adsorption of Arsenious Oxide by Ferric Hydroxide. GEORG LOCKEMANN and FRANZ LUCIUS (*Zeitsch. physikal. Chem.*, 1913, **83**, 735—758. Compare A., 1911, ii, 485, 720).—A continuation of the work of Lockemann and Paucke, in which the quantity of iron hydroxide required for the total adsorption of arsenious oxide is determined at a series of temperatures, the iron always being exactly precipitated by the theoretical quantity of ammonia. The influence of sodium and ammonium salts in the formation of soluble basic iron salts is examined, and it is shown that sodium nitrate has the least tendency to form such salts, and ammonium sulphate the greatest. It is then shown that in the presence of salts it is better to add the ammonia to the iron salt in two portions; thus, if one-third the required amount of ammonia is added, and then after fifteen minutes the residue, the total adsorption is more regular and reproducible than if other conditions are adopted. The adsorption occurs less perfectly at higher temperatures than at lower temperatures, and the difference in the adsorption is more marked at lower concentrations than at higher. Thus, at 40°, the quantity of iron hydroxide required for the total adsorption of 0·1 mg. arsenic in 100 c.c. is three times as much as is required at 0°, and at 80° six times as much is required; but for the total adsorption of 300 mg. per 100 c.c., the amounts at 40° and 80° are only one and a-half and two and a-half times respectively the quantity required at 0°. The total adsorption of arsenic by ferric hydroxide follows the formula $E = \beta A^p$, in which E represents the

number of mg. of iron hydroxide, A the number of mg. arsenic per 100 c.c., and β and p are constants, which differ for different temperatures. The total adsorption of arsenic is not materially influenced by the presence of sodium and ammonium salts. The precipitation of arsenic by iron hydroxide is a usable process for the purification of concentrated salt solutions, and for the detection of small traces of arsenic in solutions or nitre fusions. J. F. S.

Boron Hydrides. II. A New Boron Hydride, B_2H_6. Carbon Disulphide Cooling Bath for Maintaining a Constant Temperature of −112°. ALFRED STOCK and KURT FRIEDERICI (*Ber.*, 1913, **46**, 1959—1971).—When the boron hydride, B_4H_{10} (compare Stock and Massenez, this vol., ii, 44), is preserved at room temperature over mercury, it slowly undergoes decomposition, with the formation of a new *boron hydride*, B_2H_6, the only other gaseous product of decomposition being hydrogen. The decomposition is not appreciably affected by sunlight, but is accelerated to a great extent by ultra-violet light. At 100° the decomposition is complete in a few hours, whereas at ordinary temperature it takes a month or more.

The composition, B_2H_6, of the new hydride was proved (1) by decomposition with water, which is very rapid, and takes place quantitatively according to the equation: $B_2H_6 + 6H_2O = 2H_3BO_3 + 6H_2$, (2) by explosion with excess of air, (3) by determination of the density, which gave a molecular weight of 27·8 (theory for B_2H_6, 28·0).

B_2H_6 is a colourless gas possessing a characteristic, repulsive odour, resembling that of the hydride B_4H_{10} and to some extent that of hydrogen sulphide. The vapour tensions at the following temperatures, −130°, −120°, −112·1°, −110°, −100°, and −90°, are respectively 4, 10, 22·4, 25, 40, and 65 cm.; the b. p. is −87° to −88°/760 mm., and the m. p. $<$−140°. It is much more stable than B_4H_{10}, but nevertheless decomposes very slowly at ordinary temperatures. When submitted to the action of electrical sparks boron is deposited, and non-volatile boron hydrides of objectionable odour formed. When heated with the bare flame, colourless and yellow solid hydrides are formed, but no liquid products, as is the case with the hydride B_4H_{10}; the chief product crystallises in long, colourless needles, which are not decomposed by water, and dissolve in sodium hydroxide.

B_2H_6 only takes fire in the air when mixed with other boron hydrides. With alkalis, it reacts similarly to B_4H_{10}; for example, with sodium hydroxide it gives solutions in which the presence of hypoborates must be assumed. B_4H_{10} is at first completely absorbed by sodium hydroxide (*loc. cit.*), but B_2H_6 gives some hydrogen immediately it comes in contact with the alkali.

The formula B_2H_6 shows that boron must be at least quadrivalent, and not tervalent as a maximum, as it should be according to its position in the periodic system.

A carbon disulphide cooling bath for maintaining a constant

temperature of $-112°$ is described. It was used in fractionating the decomposition products of the hydride B_4H_{10}. T. S. P.

Borates. System $CaO-B_2O_3-H_2O$ at 30°. II. UMBERTO SBORGI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 715—719).—The paper gives the numerical results of the author's experiments, a discussion of which is to follow. R. V. S.

Composition of the Gaseous Mixtures Resulting from the Action of Water on the Carbides of Uranium and Thorium. PAUL LEBEAU and A. DAMIENS (*Compt. rend.*, 1913, **156**, 1987—1989). —The gas evolved by the action of water on the carbides of uranium and thorium is proved to be a mixture of the following: hydrogen, methane, ethane, propane, butane, ethylene, propylene, and homologues, acetylenic hydrocarbons. Uranium carbide reacts very slowly, the reaction lasting from five to twenty-five days or longer; thorium carbide reacts much more quickly, three to four days.

Two specimens of uranium carbide were used, one containing 1·47% of graphite and the other free from graphite. The reaction is much slower with the latter carbide, and the gases are more completely hydrogenised, as shown by the fact that the proportion of hydrogen diminishes, whilst that of the hydrocarbons, especially methane, propane, butane, and propylene, increases.

The gases were analysed by the method previously described (this vol., ii, 349). T. S. P.

The Composition of Water Gas. LÉO VIGNON (*Compt. rend.*, 1913, **156**, 1995—1998).—The author confirms the observation of Clément and Désormes and of Langlois that water-gas always contains some methane. Further investigation has shown that the formation of the methane is due to the presence of calcium oxide in the coke used. Experiments on the action of steam at 1000° on mixtures of coke and lime showed that the percentage of methane in the water-gas increased with increasing proportions of lime. The formation of the methane is considered to be due to the following reactions: $4CO + 2H_2O = 3CO_2 + CH_4$; $2CO + 2H_2 = CO_2 + CH_4$; $CO_2 + 4H_2 = CH_4 + 2H_2O$. The lime acts as a catalyst on these reactions. T. S. P.

Mixed Crystals of Potassium and Ammonium Chlorides. KENJIRO UYEDA (*Mem. Coll. Sci. Eng. Kyoto*, 1913, **5**, 147—150).— The author has determined the mutual solubilities of potassium and ammonium chlorides at 25°, 65°, and 90° respectively. The mutual solubilities increase with rise in temperature, the increase in the case of ammonium chloride in potassium chloride being much more rapid than in the case of potassium chloride in ammonium chloride. The gaps in the series of mixed crystals lie between the following molar percentages of ammonium chloride: 27—95% at 25°, 46—93% at 65°, and 69—90% at 90°. T. S. P.

The Reduction of Some Metallic Chlorides by Sodium. MATTHEW A. HUNTER (*Eighth. Inter. Cong. App. Chem.*, 1912, **2**, 125—138).—The author has constructed a special steel bomb, capable of withstanding high pressures, in which the action of sodium on various chlorides at high temperatures could be studied. In such an apparatus titanium tetrachloride is readily reduced by sodium; if the amount of material used is great enough, the heat of reaction is sufficient to give the titanium metal in a coherent condition.

Both carbon tetrachloride and carbon disulphide can be reduced by sodium, the temperature and pressure produced during the reaction being considerable. There is no conclusive evidence that fusion of any part of the material takes place during the reaction. A crystalline residue, microscopic in amount, appears to possess some of the properties of crystalline carbon. Some sodium carbide is formed as a by-product of both reactions, and if too little sodium is present for complete reduction of the carbon tetrachloride, some carbon hexachloride is produced.

Glucinum chloride gives glucinum metal, the properties of which are to be investigated further.

Silicon tetrachloride is reduced with difficulty, giving finely-divided silicon. Great difficulty was experienced in maintaining the bomb air-tight.

Neodymium chloride gives finely-divided neodymium, which is not readily separated from the sodium chloride produced during the reaction. T. S. P.

Equilibria in the Systems: Water, Sodium Nitrite and Water, Sodium Nitrite and Sodium Nitrate. MARCEL OSWALD (*Eighth. Inter. Cong. App. Chem.*, 1912, **2**, 205—207).—The author has determined the solubility curve of sodium nitrite, and also the mutual solubilities of sodium nitrate and nitrite at different temperatures.

Sodium nitrite does not give a stable hydrate. Sodium nitrite and nitrate form neither a double salt nor mixed crystals.

T. S. P.

Disodium Monohydrogen Phosphate and its Hydrates. Their Solubilities and Transition Temperatures. ALAN W. C. MENZIES and EDMUND C. HUMPHERY (*Eighth. Inter. Cong. App. Chem.*, 1912, **2**, 175—178).—The determination of the solubility curve of disodium hydrogen phosphate has given the following transition temperatures: dodecahydrate to heptahydrate, 35·2°; heptahydrate to dihydrate, 48·3°; dihydrate to anhydrous salt, 95°. The cyohydric temperature is $-5°$. The solubility of the anhydrous salt diminishes with rise in temperature. T. S. P.

Equilibrium of Lithium Sulphate with the Alkali Sulphates in their Mixed Solutions up to 100°. (Mlle.) CÉCILE SPIELREIN (*Compt. rend.*, 1913, **157**, 46—48. Compare A., 1912, ii, 917).—A continuation of the study of the solubility of lithium sulphate in

water in the presence of alkali sulphates up to 100°. The results show the existence of several double salts. With sodium sulphate it gives salts: $Li_2SO_4,Na_2SO_4,5\frac{1}{2}H_2O$ at 0°, which ceases to exist at 16°; $Li_2SO_4,3Na_2SO_4,12H_2O$ from 16—24°; $4Li_2SO_4,Na_2SO_4,5H_2O$ at 28°, and between 32° and 100° $Li_2SO_4,Na_2SO_4,3H_2O$. With potassium sulphate it forms one double salt, Li_2SO_4,K_2SO_4, and with ammonium sulphate one double salt, $Li_2SO_4,(NH_4)_2SO_4$, up to 100°. W. G.

Forms of Silver. Physico-chemical Morphology. VOLKMAR KOHLSCHÜTTER (*Zeitsch. Chem. Ind. Kolloid*, 1913, **12**, 285—296).—A theoretical paper, in which the relationships between the various forms of silver are discussed. The material contained in the paper has all been previously published (compare A., 1908, ii, 182; 1912, ii, 253, 731, 845; this vol., ii, 285, 286, 287). J. F. S.

Silver Oxide. H. VON WARTENBERG (*Zeitsch. Elektrochem.*, 1913, **19**, 489—491).—The author shows that silver vapourises more easily in oxygen than in nitrogen, which he explains by the formation of an oxide, probably Ag_2O. The stability of the oxide is explained from its large heat of vaporisation, which lies probably between -90.6 and -109 Cal. If silver vapour in oxygen is rapidly cooled traces of oxide can be detected in the condensed material. J. F. S.

Action of Light on Silver, Mercurous, Lead and Cuprous Azoimides; Basic Azoimides of Lead and Copper. LOTHAR WÖHLER and W. KRUPKO (*Ber.*, 1913, **46**, 2045—2057).—With the object of gaining further insight into the chemical condition of the photographic latent image, the authors have studied the action of light on the above azoimides. They find that decomposition occurs with immediate formation of the metal, and not of a sub-compound. Hence, by analogy, they are led to the conclusion that the photochemical alteration in the silver haloid of a photographic plate is due to an adsorption compound of finely-divided metal with unchanged haloid, and not to various subhaloids of different colours.

Silver azoimide is highly sensitive to light, decomposition occurring with evolution of nitrogen. In a specimen which had been exposed to light for such a period that decomposition had not occurred beyond the stage corresponding with the possible formation of a sub-azoimide, particles of metallic silver were visible under the microscope, and the residue behaved, when heated or subjected to percussion, in the same manner as silver azoimide. Full details of the precautions necessary in performing these tests are recorded.

Mercurous azoimide is more sensitive to light than the corresponding silver compound. In this case decomposition does not follow the same course as with calomel and other mercurous compounds, since mercuric azoimide is not formed. The percussion test points to immediate decomposition into mercury and nitrogen, and

the non-formation of a sub-azoimide is further confirmed by the absence of hydrazoic acid from the products of the decomposition of mercurous azoimide suspended in water.

Lead azoimide, which is extremely sensitive to light, decomposes according to percussion and temperature tests into metallic lead and nitrogen when the dry salt is illuminated. When exposed to air or placed under water, oxidation of the separated lead proceeds simultaneously, and the product consists of basic lead azoimide mixed with finely-divided lead hydroxide. The filtrate contains traces of lead, hydrazoic acid, and considerable quantities of ammonia. Reaction thus appears to proceed simultaneously according to the three equations: (i) $PbN_6 + 2H_2O = Pb(OH)_2 + 2N_3H$; (ii) PbN_6(in light) $= Pb + 3N_2$; (iii) $Pb + N_3H + 2H_2O = Pb(OH)_2 + N_2 + NH_3$. When preserved in the dark, lead azoimide is practically unaltered after twenty-four hours at 115°.

Cuprous azoimide, CuN_3, is obtained by the gradual addition of a solution of sodium azoimide to excess of a concentrated solution of copper sulphite to which potassium sulphite has been previously added, followed by acetic acid in quantity just sufficient to dissolve the precipitate formed. It forms a pale greenish-grey precipitate, which inflames at 220°. When exposed to light, it becomes deep red with a violet tint, and decomposes into copper and nitrogen.

Basic lead azoimide, PbO,PbN_6, has been prepared by three methods: (i) by heating the calculated quantities of lead azoimide and lead hydroxide under water in a sealed tube at 140° for twelve to fifteen hours, and separation of the basic azoimide from specifically heavier unchanged azoimide by elutriation. The method has the drawback that large spontaneously explosive crystals of lead azoimide are liable to separate during the slow cooling of the tube; (ii) by leading a current of carbon dioxide-free air through a boiling aqueous suspension of lead azoimide until the calculated amount of hydrazoic acid has been evolved; and (iii) by heating the requisite quantities of freshly precipitated lead hydroxide and lead azoimide under water on the water-bath for twenty hours. The two latter methods yield uniform products. The basic azoimide is less sensitive to percussion or temperature than lead azoimide, whilst an intimate mixture of lead azoimide and oxide in the proportions necessary to form the sub-azoimide shows the same sensitiveness as the pure azoimide. It is interesting to note that lead azoimide when mixed with 30% water has the same sensitiveness as the dry azoimide, whilst moist mercurous azoimide is scarcely less sensitive than the dry product.

Basic cupric azoimide, CuO,CuN_6, is obtained as a yellow substance which retains water when a suspension of the normal azoimide in water is heated at 70—80° in a current of air free from carbon dioxide until the calculated quantity of hydrazoic acid has been evolved. It inflames at 245°. When, however, cupric azoimide and cupric hydroxide are warmed under water, hydrazoic acid is evolved and cupric hydroxide alone remains.

Basic mercuric azoimide is not obtained when a solution of free hydrazoic acid is warmed with excess of mercuric oxide, whilst

mercuric azoimide is unchanged when air is passed through a suspension of it in water.

A series of experiments is described on the connexion between the size of crystals and the tendency towards spontaneous detonation, from which it appears that the size of the crystals has a far more pronounced influence on the percussion test than on the temperature test. H. W.

The Coupling of Metallic Silver and Copper with the Arsenic Haloids. SIEGFRIED HILPERT and FRITZ HERRMANN (*Ber*, 1913, **46**, 2218—2225).—When molecular silver, prepared either by the action of hydrazine sulphate on an ammoniacal silver nitrate solution or by the reduction of silver chloride with zinc, is well shaken in a sealed tube with molten arsenic tribromide, combination takes place with the formation of a *silver arsenic bromide*, Ag_3AsBr_3, which is readily freed from the excess of arsenic tribromide by washing with ether. After drying in a vacuum over phosphoric oxide, it forms an amorphous, black, odourless powder. That it is a chemical individual is shown by the following reactions: Cold water has very little action in the cold, but in the warm, grey, metallic silver is formed; this decomposition takes place readily in the cold with ammonium or potassium hydroxides. That the arsenic is directly linked with the bromine in the compound is shown by the fact that magnesium phenyl bromide gives a 70% yield of triphenylarsine. When the substance is digested with a concentrated solution of potassium cyanide, fission takes place in such a way that free arsenic is produced, the silver going into solution as a complex silver salt. A control experiment showed that molecular silver, potassium, cyanide, and arsenious acid react very slowly, giving arsenic, but this reaction could not account for the previous one. The compound is very stable, arsenic being volatilised only at a dark red heat. It is considered to have the constitution $\begin{array}{l}Ag\\Ag\\Ag\end{array}\!\!>\!As\!<\!\begin{array}{l}Br\\Br\\Br\end{array}$, the arsenic atom possessing the co-ordination number 6.

When arsenic trichloride is used instead of the tribromide, a *compound* is obtained which is similar in its properties to the silver arsenic bromide described. It has, however, the composition $7Ag,2AsCl_3$; with potassium cyanide a substance of the composition $AgAs_3$ is obtained (it is not certain whether this is a definite compound), as well as arsenic, which seems to indicate that one atom of silver is differently linked from the others, which give silver chloride. It may be that the compound is a solid solution of silver and the compound Ag_3AsCl_3, which would be the analogue of the bromine compound.

When copper is used instead of silver, the *compounds* $7Cu,2AsCl_3$ and $7Cu,2AsBr_3$ are obtained. They behave very similarly to the silver compounds, except that ammonium hydroxide, potassium hydroxide, and hydrochloric acid transform the copper into cuprous oxide or chloride; magnesium phenyl bromide gives triphenylarsine.

Substances of similar properties are obtained by the action of arsenic vapour at 500° on silver chloride or bromide and on cuprous chloride; it follows that the decomposition of these compounds at high temperatures, whereby arsenic is produced, is reversible.

T. S. P.

Calcium Hydride. WILHELM MOLDENHAUER and C. ROLL-HANSEN (*Zeitsch. anorg. Chem.*, 1913, **82**, 130—140).—Experiments to determine the dissociation pressure of calcium hydride, using a nickel boat in a porcelain tube, gave a marked dissociation from 600°, reaching one atmosphere below 800°. On the other hand, calcium hydride is readily prepared by heating calcium in hydrogen at 830°, so that the pressures measured above cannot be true dissociation pressures. The porcelain tube is attacked. If lined with iron, quite different results are obtained, the pressure being only 11 mm. at 780° and 705 mm. at 1027°. A second *hydride*, CaH, also exists, having its own dissociation pressure, and this compound appears to be volatile.

The heat of formation of CaH is calculated to be about 21,000 cal., and of CaH_2 from CaH and hydrogen also about 21,000 cal., making 42,000 cal. for the heat of formation of calcium hydride from liquid calcium and hydrogen, whilst Guntz and Bassett (A., 1905, ii, 300) found 46,200 cal. from solid calcium. C. H. D.

The Action of Calcium Hydride on Sulphates. ERICH EBLER and K. HERRDEGEN (*Ber.*, 1913, **46**, 2264—2267).—When a mixture of barium sulphate and calcium hydride is ignited by a fuse similar to that used in the thermit reaction, vigorous action takes place according to the equation:

$$BaSO_4 + 4CaH_2 = BaS + 4CaO + 4H_2.$$

The hydrogen apparently does not take part in the reduction, since water is not formed; of course, the reaction product may consist partly of barium oxide and calcium sulphide.

If the product of reaction is added to water in small portions at a time in order to decompose excess of calcium hydride, and then warmed with hydrochloric acid, complete solution is readily obtained; the barium may be quantitatively precipitated from solution by saturation with hydrogen chloride (compare Ebler, A., 1909, ii, 347).

The above reaction forms a ready method of getting insoluble sulphates into solution, a large number of sulphates reacting. Sulphates of the heavy metals sometimes give the metal itself; the reaction with lead sulphate proceeds with explosive violence.

Further experiments are being made with the sulphates of thorium and cerium and other rare earth metals. T. S. P.

Melting Points of Some Refractory Oxides. CLARENCE W. KANOLT (*J. Washington Acad. Sci.*, 1913, **3**, 315—318).—An Arsem graphite resistance furnace is used, the temperatures being determined by means of a Holborn-Kurlbaum optical pyrometer, sighted vertically downward through a glass window. Lime and

magnesia volatilise completely in a vacuum without melting, and in such cases an atmosphere of hydrogen is used.

Magnesia is melted in graphite crucibles, but lime forms carbide, and must be melted in a tungsten crucible, or by making a tube of lime, through which hydrogen is passed and down which the pyrometer is sighted. Alumina and chromium oxide are melted in tungsten crucibles in a vacuum.

The following results are obtained: MgO, 2800°; CaO, 2570°; Al_2O_3, 2050°; Cr_2O_3, 1990°. C. H. D.

Peroxide, Ozone, and Nitrous Acid in Calcium Hydroxide and Aragonite. WILHELM VAUBEL (*J. pr. Chem.*, 1913, [ii], **88**, 61—72. Compare A., 1912, ii, 1180).—According to Ditz (this vol., ii, 320), the starch–iodide reaction shown by calcium hydroxide and aragonite is due to the presence of small quantities of nitrites and of ferric compounds, and not to the presence of calcium peroxide, since neither aragonite nor calcium hydroxide give the usual peroxide reactions with titanic and vanadic acids.

The author points out, however, that the negative results obtained in the latter reactions furnish no criterion as to the absence of a peroxide, for calcium peroxide itself in the presence of an excess of calcium hydroxide does not react with either vanadic or titanic acids.

That the starch–iodide reaction is not due to the presence of nitrite is conclusively proved by the fact that a calcium hydroxide, which gave a distinct reaction with starch–potassium iodide, did not show the usual nitrite reactions with sulphanilic acid and phenol, resorcinol, pyrogallol, guaiacol, or brucine, although positive reactions were obtained at once on the addition of a trace of nitrite to the calcium hydroxide.

Further, it is improbable that the blue coloration is due to ferric compounds, for the latter react only slowly with starch–potassium iodide, whilst in many cases the blue coloration with calcium hydroxide develops instantly. Moreover, the estimation of the peroxide by titration of the liberated iodine with sodium thiosulphate is in good agreement with the results obtained by direct titration with permanganate, which would not be the case if the starch–iodide reaction were due to the presence of ferric compounds. Finally, although the peroxide in aragonite and calcium hydroxide cannot be detected by the uranyl nitrate, vanadic, titanic, and chromic acid reactions on account of the disturbing influence of the excess of calcium hydroxide, positive results have been obtained with the benzidine and *m*-phenylenediamine reactions.

The paper contains a summary in tabular form of thirty-eight reactions which may be used for the detection of ozone, nitrous acid, and hydrogen peroxide. F. B.

Reduction of Tricalcium Phosphate by Hydrogen. ARNOLD LASSIEUR (*Eighth. Inter. Cong. App. Chem.*, 1912, **2**, 171—174).—At 1300° calcium phosphate is reduced by hydrogen to a mixture of

calcium oxide and phosphorus. Only traces of phosphorus hydride and calcium phosphide are produced during the reaction. It is probable that a basic phosphate is produced as an intermediate product.

Carbon monoxide has no reducing properties towards calcium phosphate at 1300°. T. S. P.

Theory of Luminescent Stones and their Variously Coloured Phosphorescence. LUDWIG VANINO (*J. pr. Chem.*, 1913, [ii], **88**, 77—79. Compare this vol., ii, 591).—According to the author, luminescent sulphide stones on exposure to light become superficially transformed into modifications of higher energy content. The transformation is reversible, the phosphorescence after exposure to light representing the transformation into the original modification of lower energy content.

With respect to the effect of traces of impurities in modifying the colour of the phosphorescent light, the author considers that their action is not a chemical one, but is similar to that of the sensitisers in photochemical processes; the energy which becomes available during the transformation of the sulphides is converted by them into light energy.

The different phosphorescent colours exhibited by different parts of one and the same stone, is found to be due to a difference in the temperature to which the stones were exposed during their preparation; thus, a mixed calcium–strontium stone containing traces of rubidium showed, in its upper part, a light blue phosphorescence, whilst the lower part, which had been more strongly heated, exhibited a deep violet phosphorescence. F. B.

Glucinum Peroxide. A. S. KOMAROVSKI (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 608—613).—Attempts to prepare glucinum peroxide by the action of hydrogen peroxide on hydrated glucinum oxide resulted only in the formation of the compound $3GlO,4H_2O_2,8H_2O$, containing hydrogen peroxide of crystallisation.

With basic glucinum carbonate of the composition $GlCO_3,5GlO + 8H_2O$ hydrogen peroxide yields the *basic peroxide*, $2GlO_2,3GlO + 8\frac{1}{2}H_2O$, which is moderately stable, and exhibits all the usual properties of peroxides. T. H. P.

Glucinum Sulphide. K. MIELEITNER and HERMANN STEINMETZ (*Zeitsch. anorg. Chem.*, 1913, **82**, 92—96).—Glucinum sulphide may be prepared by heating glucinum chloride in hydrogen sulphide, previously purified by means of a chromous salt and phosphoric oxide. For analysis the product is heated in a sealed tube with nitric acid and silver nitrate. The silver chloride is collected, silver is removed from the filtrate by hydrochloric acid, and the sulphur is estimated as barium sulphate. Glucinum is estimated in the filtrate. The product contains 97—98% of sulphide.

Glucinum sulphide is a white, amorphous mass. It is little decomposed by water, even when boiling, but readily by acids, including atmospheric carbon dioxide. It burns with a bright

flame and separation of sulphur in contact with concentrated nitric acid. Dry hydrogen chloride at a red heat converts it into the chloride, and bromine vapour into the bromide. A polysulphide has not been obtained. C. H. D.

The Nature of Alkaline Glucinum Solutions. BENNO BLEYER and S. W. KAUFMANN (*Zeitsch. anorg. Chem.*, 1913, **82**, 71—91).—When a solution of glucinum sulphate is dropped into potassium hydroxide, a saturation point is reached, depending on the concentration of the hydroxide. From the solution saturated with the hydroxide *A* a second hydroxide, *B*, is obtained, and on collecting and drying *B* a third modification, *C*, which is still less soluble, is obtained. The solubility of the three modifications has been determined. When the relative concentrations of glucinum and potassium hydroxide are plotted against one another, *A* and *B* yield straight lines, whilst *C*, like the corresponding modification of zinc hydroxide, shows a marked curvature (compare Wood, T., 1910, **97**, 878). Analysis of the hydroxides, after washing with absolute alcohol, gives the compositions *A*, $H_2Gl_2O_3$; *B* and *C*, H_2GlO_2. The ionic products for *A*, *B*, and *C* respectively are K_1, $0{\cdot}73 \times 10^{-29}$; K_2, $0{\cdot}28 \times 10^{-29}$; K_3, $0{\cdot}144 \times 10^{-29}$, and the constants of acid dissociation are $1{\cdot}5 \times 10^{-12}$, $0{\cdot}56 \times 10^{-12}$, and $0{\cdot}29 \times 10^{-12}$. These are minimum values. Fresh glucinum hydroxide is a somewhat stronger acid than zinc hydroxide in the corresponding condition. C. H. D.

Thermal Dissociation of Magnesium Carbonate. ROBERT MARC and A. ŠIMEK (*Zeitsch. anorg. Chem.*, 1913, **82**, 17—49). Compare Grünberg, this vol., ii, 516).—According to Brill (A., 1905, ii, 522), the dissociation of magnesium carbonate by heat takes place in stages, seven basic carbonates being formed. Discontinuities were not observed by Friedrich and Smith (this vol., ii, 28). It is now shown that the dissociation proceeds very slowly in the dry substance, but is accelerated by the presence of moisture, this factor accounting for the divergent results.

Precipitated magnesium carbonate always contains water. Anhydrous rhombohedral artificial magnesite is obtained by heating 10 grams of precipitated carbonate with 300 c.c. of water and a few grams of solid carbon dioxide at 185° in an autoclave under 20 to 30 atmospheres pressure. Even this preparation retains water very obstinately. The dissociation at 350° is accelerated by mixing the carbonate with fused potassium nitrate. Manometric measurements with the dried carbonate give inconclusive results owing to the slowness with which equilibrium is reached.

Kinetic experiments have been made by heating the material in a platinum boat in a stream of dry or moist air. The latter accelerates the decomposition. The velocity of dissociation gradually diminishes with time.

The dissociation in presence of water-vapour has been determined. This is permissible, as the dissociation pressure of magnesium hydroxide is equal to one atmosphere at 180°, so that the hydroxide is

not formed during the experiments with carbonate. Heating in sealed tubes, and analysing the gaseous contents after removal from the furnace, does not yield satisfactory results, as re-combination takes place with appreciable velocity. This is avoided by mixing with potassium nitrate. A mixture of 1 part of magnesium carbonate and 3 parts of potassium nitrate allows of an accurate measurement of the dissociation. The pressure of one atmosphere is reached at 402°. The heat of dissociation is calculated to be −23,200 cal. C. H. D.

The Influence of Foreign Metals on the Rolling of Zinc. EUGÈNE PROST and A. VAN DE CASTEELE (*Bull. Soc. chim. Belg.*, 1913, **27**, 175—189).—The question of the influence of the presence of foreign metals on the rolling of zinc is little understood. The authors have taken for their experiments refined zinc (containing about 1% lead and a few hundredths % of cadmium and iron), and have added in various cases cadmium, tin, antimony, copper, arsenic, and iron. The results indicate that under the usual practical conditions of rolling the content of lead should not exceed 1·25%, and that of cadmium 0·2%; these limits are well above the quantities generally present in practice. The quantity of iron, arsenic, antimony, and tin (of which the last is most harmful) should be kept as low as possible, especially in view of the fact that the effect of these metals when present together is an additive one.
D. F. T.

A Process for Rendering Innocuous a Water Supply Contaminated with Lead. PAUL SCHMIDT (*Arch. Hygiene*, 1913, **80**, 70—73).—The colloidally dissolved lead hydroxide can be separated by filtration through a Berkfeld filter. S. B. S.

The Action of Potassium Amide on Thallium Nitrate in Liquid Ammonia Solutions. EDWARD C. FRANKLIN (*Eighth. Inter. Cong. App. Chem.*, 1912, **2**, 103).—When a solution of potassamide in liquid ammonia is added to a similar solution of thallium nitrate, a black precipitate of thallous nitride is formed in accordance with the reaction:

$$3TlNO_3 + 3KNH_2 = Tl_3N + 3KNO_3 + 2NH_3.$$

Thallium nitride dissolves readily in solutions of potassamide in liquid ammonia. When the ammono-base is used in limited quantity a yellow solution is formed, from which *potassium ammonothallite*, $TlNK_2,4NH_3$, may be obtained as beautiful, yellow crystals. This compound loses successive portions of its ammonia of crystallisation to form products represented by the respective formulæ: $TlNK_2,2NH_3$ and $TlNK_2,NH_3$.

When thallium nitride is dissolved in excess of potassamide, solutions are formed which give well-crystallised products, which are considered to be isomorphous mixtures either of potassium ammonothallite with potassamide or of potassamide and the unknown thallium amide. T. S. P.

Variation of Resilience in Copper and Some of its Alloys with Temperature. LÉON GUILLET and VICTOR BERNARD (*Compt. rend.*, 1913, **156**, 1899—1901).—The methods of examination used are those already published by Guillet and Révillon (*Rev. Metall.*, 1909, **6**, 94). The range of temperatures was from 0° to 1100°. Analyses of all the materials tested are quoted. With the exception of copper–nickel alloy (Cu, 77·9; Ni, 20·2; Zn, 1·7; Fe, 0·1%), all the alloys tested showed maximum fragility beginning at 300—400°, and disappearing at about 700°. In many cases the greatest resilience was exhibited at 100°.

Brass (Cu, 90·6; Zn, 9·3%) becomes less fragile between 700° and 900°, whilst the addition of lead (Cu, 90·3; Zn, 8·2; Pb, 1·3%) leads to the alloy showing maximum fragility up to 900°. Brasses containing 80·9 and 70% of copper respectively were fragile at 700° to 850°, whilst those with 61·8 and 61·3% of copper began to improve at 700°. Copper–nickel alloy begins to be fragile at 600°, but improves at 1000°. German silver (Cu, 54·1; Zn, 25·4; Ni, 19·7; Fe, 0·4%) begins to be fragile at 300°, and is less resilient all through than copper–nickel alloy. Aluminium–bronze (Cu, 90·0; Al, 9·8; Fe, 0·2%) showed discontinuity between 600° and 800°, and determinations could not be made between these temperatures. Addition of iron (Cu, 88·5; Al, 7·5; Fe, 3·7) caused fragility to lessen at 700°. The results of the investigation are shown graphically in the original. T. A. H.

Complex Copper Nitrites. ALBIN KURTENACKER (*Zeitsch. anorg. Chem.*, 1913, **82**, 204—215).—Potassium copper nitrite, $K_3Cu(NO_2)_5$, is obtained by mixing cold saturated solutions of copper sulphate and potassium nitrite, adding methyl alcohol, filtering, and adding ethyl acetate to the clear, green filtrate. Long crystals of the salt separate. The salt is stable when pure.

Rubidium copper nitrite, $Rb_3Cu(NO_2)_5$, closely resembles the potassium salt.

Barium copper nitrite, $Ba\left[Cu{(NO_2)_2 \atop OH}\right]_2$, from copper and barium nitrites, forms green double pyramids. Other compounds have not been obtained. Evaporating copper nitrite with zinc, nickel, or manganese nitrite yields a green, crystalline *compound*,

$$2CuO,N_2O_3,3H_2O,$$

which contains traces of the added metal. The presence of a complex anion in copper nitrite solution is shown qualitatively, but even concentrated solutions contain an excess of the normal ions. Two basic copper nitrites are also described: $3Cu(OH)_2, Cu(NO_2)_2$, and $2Cu(OH)_2,Cu(NO_2)_2$. C. H. D.

Thermal Analysis of Clays. RUBY-WALLACH (*Compt. rend.*, 1913, **157**, 48—50).—A comparative thermal study of kaolin, a pure clay, white mica, and some clays of known origin. The samples were heated in an electric furnace, and the temperatures of the furnace and substance noted. Curves are given showing the relationship between the furnace temperature and the temperature difference between furnace and substance. The results indicate no definite means of analysis. W. G.

The Reactions of Aluminium Nitride. FRITZ FICHTER and ADOLF SPENGEL (*Zeitsch. anorg. Chem.*, 1913, **82**, 192—203. Compare A., 1907, ii, 691).—Aluminium nitride is best prepared by passing nitrogen over aluminium powder at 800°. A reaction sets in, and the temperature rises to 1300°. Impurities are removed by treatment with dry hydrogen chloride at a red heat. The nitride may be decomposed by fusion with potassium hydroxide,

$$AlN + 3KOH = K_3AlO_3 + NH_3,$$

or by heating with a mixture of 10 c.c. of concentrated sulphuric acid with 40 c.c. of water. Dry halogens act slowly on the nitride; chlorine decomposes it at 760°: $2AlN + 3Cl_2 = 2AlCl_3 + N_2$. Sulphur chloride vapours act more rapidly. Hydrogen is without action.

Lead dichromate decomposes it completely, but the reaction with sodium peroxide remains incomplete, and nitrate is also formed. Sulphur, phosphorus, and carbon disulphide partly displace nitrogen, but phosphorus trichloride is without action. Carbon is without action at 1200°, and carbon dioxide merely oxidises, but a mixture of sodium and potassium carbonates with carbon converts a large part of the nitride into cyanide. Alcohol forms triethylamine at 230°. C. H. D.

The So-Called Manganese Trioxide. FREDERICK R. LANKSHEAR (*Zeitsch. anorg. Chem.*, 1913, **82**, 97—102. Compare P., 1912, 198).—A 6% solution of potassium permanganate is allowed to drop into a cooled mixture of one part of sodium hydrogen carbonate to four parts of anhydrous sodium carbonate. The gas is condensed in a flask cooled with liquid air. After evaporating the carbon dioxide, a dark red, amorphous solid, m. p. $-6°$, remains. The ratio of permanganate to manganese dioxide is about 4·8 : 1. The conclusion is confirmed that the gas is an impure hydrated permanganic acid. C. H. D.

The Critical Ranges, A_3 and A_2, of Pure Iron. GEORGE K. BURGESS and J. J. CROWE (*J. Washington Acad. Sci.*, 1913, **3**, 329—332).—Five separate preparations of electrolytic iron have been used, in quantities of from 21 to 31 grams. Both the inverse rate and differential methods have been employed. Ac_2 is as pronounced as Ar_2 for all the samples, and for metal re-melted in a vacuum the position of Ac_2 and Ar_2 is identical. A_2 and A_3 appear to be different in kind. C. H. D.

Formation of Rust under Protecting [Paint] Layers. GEORG PFLEIDERER (*Zeitsch. Elektrochem.*, 1913, **19**, 507—510).—Polemical. The author shows that the theory of Liebreich and Spitzer (A., 1912, ii, 259) with regard to the rusting of painted iron is unnecessary, and that their measurements will not bear the interpretation placed on them. J. F. S.

Formation of Rust under Protecting [Paint] Layers. ERIK LIEBREICH and FRITZ SPITZER (*Zeitsch. Elektrochem.* 1913, **19**, 510—513).—Polemical; an answer to Pfleiderer (preceding abstract). J. F. S.

The Absorption of Iron Pentacarbonyl by Iron. A. STOFFEL (*Eighth. Inter. Cong. App. Chem.*, 1912, **2**, 225—233).—The first part of the paper is a re-statement of results already published (A., 1912, ii, 986).

The author has devised a method by which he is able to estimate both the gaseous and adsorbed iron pentacarbonyl. The curves showing the relation between the concentration in the vapour and solid phases are exactly of the form of adsorption isotherms, from which the conclusion is drawn that the iron pentacarbonyl is adsorbed by the iron. This adsorption explains the slowness of the reaction between iron and carbon monoxide. T. S. P.

Neutralisation of Chromic Acid. RENÉ DUBRISAY (*Compt. rend.*, 1913, **156**, 1902—1904).—The method already described (this vol., ii, 388) has been applied to the investigation of the neutralisation of chromic acid by sodium hydroxide and by ammonia. The results show that chromic acid differs from a strong dibasic acid, such as sulphuric acid, in exhibiting a constant surface tension only until the first acid function is neutralised, after which the surface tension decreases gradually but slightly until the second is neutralised, when, as usual, a great decrease occurs. These results are in harmony with those recorded by Berthelot (A., 1883, 642, 707), Sabatier (A., 1886, 692), and Gröger (A., 1908, ii, 690) as a result of other methods of investigation. T. A. H.

Hydrates of Uranic Anhydride and Heat of Formation of Uranyl Nitrate. ROBERT DE FORCRAND (*Compt. rend.*, 1913, **156**, 1954—1958).—The uranic anhydride, UO_3, used by the author was prepared by heating uranyl nitrate at 290—300° for a considerable time, taking care to avoid fusion. If the heating takes place at 550—600° fusion occurs, and a polymeride of unknown molecular weight results. The dihydrate, $UO_3,2H_2O$, was obtained from the anhydride by the ordinary methods, and the monohydrate, UO_3,H_2O, by heating the dihydrate at 80° in dry air.

As the basis of his measurements the author assumes that the heat of formation of uranic anhydride from the oxide UO_2 and oxygen is the same, and has the heat of formation of the oxide U_3O_8 from UO_2 and oxygen, namely, 37·65 Cal. (compare Mixter, A., 1912, ii, 899). The following thermochemical values were obtained: Heats of solution in dilute nitric acid of: UO_3, 19·803 Cal.; UO_3,H_2O, 14·846 Cal.; $UO_3,2H_2O$, 12·375 Cal.; $UO_2+3O_2+N_2=UO_2(NO_3)_2(\text{solid})+67{\cdot}25$ Cal., or $UO_2(NO_3)_2\text{aq}+86{\cdot}25$ Cal.; $UO_2(NO_3)_2=N_2O_5(\text{gas})+UO_3-30{\cdot}60$ Cal.; $UO_3+H_2O(\text{gas})=H_2UO_4+14{\cdot}62$ Cal.; $UO_2(NO_3)_2,2H_2O=UO_2(NO_3)_2+2H_2O(\text{gas})-33{\cdot}27$ Cal.; $H_2UO_4+UO_2(NO_3)_2=$ basic nitrate $+4{\cdot}03$ Cal. T. S. P.

The Preparation of Thoria from Monazite Sand by means of Hypophosphoric Acid. Detection of Cerium with an Alkaline Solution of Ammonium Tartrate. FRITZ WIRTH (*Chem. Zeit.*, 1913, **37**, 773—774).—In the precipitation of thoria as

hypophosphate (compare A., 1912, ii, 948) difficulties may arise from the formation of sparingly soluble double sulphates of sodium and the cerium earths when sodium hypophosphate is added to the sulphuric acid solution of the monazite sand. These difficulties may be avoided if the anion of hypophosphoric acid is formed *in situ* in the acid solution. This may be accomplished either by direct oxidation of phosphorus in the solution, or by the anodic oxidation of copper phosphide, using the acid solution as electrolyte.

Thorium can be completely precipitated as hypophosphate by the addition of much sodium hypophosphate to a boiling, slightly ammoniacal solution of thorium tartrate if care is taken to keep the solution ammoniacal.

The formation of an intense, yellowish-brown colour on the oxidation of ammoniacal solutions of cerium tartrate is a very sensitive test for cerium. The oxidation takes place on exposing the solution to the air; if less than 0·1—0·5% of cerium is present it is necessary to boil the solution. If hydrogen peroxide is used as the oxidising agent, the test is sensitive to 0·0002 gm. of CeO_2 per 100 c.c. T. S. P.

Action of Boiling Sulphuric Acid on Platinum. LE ROY W. McCAY (*Eighth. Inter. Cong. App. Chem.*, 1912, **1**, 351—359).—Boiling sulphuric acid dissolves platinum in considerable amounts (in one experiment when boiling 10 c.c. of acid in a covered dish for one hour, 0·0038 gram of Pt was dissolved). The attack is not due to atmospheric oxygen, for the same thing happens when heating in a current of an inert gas. Excess of sulphur dioxide which may be conveniently generated by introducing a piece of sulphur into the hot acid, or else be passed in the form of a current, prevents almost entirely the solvent action.

If it is assumed that at the temperature of attack there is a slight dissociation of the acid, thus liberating oxygen which would cause the action; this would account for the protective power of such reducing substances as excess of sulphur dioxide, arsenious and antimonious oxides. L. DE K.

Alkali Osmibromides (Hexabromo-osmeates). ALEXANDER GUTBIER (*Ber.*, 1913. **46**, 2098—2103).—The observation of Moraht and Wischin (A., 1893, ii, 380) that finely-divided osmium does not enter into reaction with bromine was confirmed. It was found that the osmibromides could not be obtained from the osmichlorides in all cases by treatment with hydrobromic acid, owing to similar reactions occurring to those which take place with the corresponding iridium compounds (compare Gutbier and Riess, A., 1909, ii, 1025); only the ammonium and potassium osmibromides could be obtained in this way.

The most satisfactory method for obtaining sodium osmibromide was by the decomposition of sodium sulphito-osmiate (schwefligosmiumsaure Natrium), $3Na_2O,OsO_3,4SO_2,5H_2O$ (Rosenheim and Sasserath, A., 1899, ii, 664), with boiling concentrated hydrobromic acid, D 1·45. The other alkali salts were readily obtained from the

sodium salt by precipitation with the corresponding alkali bromides from not too concentrated solution. The sodium, ammonium, and potassium salts have already been described by Rosenheim and Sasserath (*loc. cit.*).

Rubidium osmibromide, Rb_2OsBr_6, forms a reddish-brown, fine-crystalline powder. *Caesium osmibromide*, Cs_2OsBr_6, is a dark reddish-brown, microcrystalline powder. T. S. P.

Mineralogical Chemistry.

Platinum Sands from New Zealand. R. A. FARQUHARSON (*Zeitsch. Kryst. Min.*, 1913, **52**, 419; from *Trans. New Zealand Inst.*, 1910, **43**, 448—482).—Platinum is found in several of the gold-fields of New Zealand. Near Orepuki, in Otago, it occurs in sands and shore deposits in the form of rounded scales; analysis gave:

Pt.	Ir.	Pd.	Rh.	Au.	Fe.	Cu.	Iridosmine.	Os.	Total.
74·61	1·30	1·36	3·52	0·39	5·08	0·15	14·32	trace	100·73

The gabbro of the neighbourhood contains no platinum, and the metal was probably derived from serpentine of the interior.

L. J. S.

Platiniferous Dunites. SANTIAGO PIÑA DE RUBIES and F. COMA Y ROCA (*Anal. Fis. Quim.*, 1913, **11**, 334—339).—Two specimens of dunite from Diudinsky had the compositions of olivines with 1·16% and 1·41% respectively of chromite. G. D. L.

Helium in Glucinum Minerals. II. ARNALDO PIUTTI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 671—672. Compare this vol., ii, 419).—The author has examined six further specimens of phenacite from different localities, and has been unable to detect helium in them. The minerals show no radioactivity. R. V. S.

Calcite Crystals from a Water-Tank. RUSSELL F. GWINNELL (*Min. Mag.*, 1913, **16**, 345—347).—The material consists of a glistening, white, crystalline powder, and it was deposited in a tank into which water was led from a spring rising from the ferruginous marlstone at Belton Park, near Grantham, Lincolnshire. It consists entirely of minute crystals having the form of the primary rhombohedron, $r(10\bar{1}1)$, of calcite. D 2·71. Analysis, by M. B. CHAPMAN, gave:

$CaCO_3$.	Al_2O_3.	Fe_2O_3.	SiO_2.	Insol.	Total.
95·65	0·93	0·21	3·14	0· 6	99·99

L. J. S.

Triplite from Eastern Nevada. FRANK L. HESS and W. F. HUNT (*Amer. J. Sci.*, 1913, [iv], **36**, 51—54).—Small, irregular masses of triplite occur with wolframite, bismuth minerals, etc., in quartz veins in the Reagan mining district, White Pine County. The material is light salmon-pink in colour with a vitreous lustre, and has cleavages in two directions. D 3·79, H 4—4½; refractive indices α 1·650, β 1·660, γ 1·672. Analysis gave the following results, agreeing with the formula $3MnO,P_2O_5,MnF_2$:

MnO.	FeO.	CaO.	MgO	P_2O_5.	F.	Total.
57·63	1·68	2·86	1·21	31·84	7·77	102·99

The mineral thus lies at the manganese end of the series, and it differs from those richer in iron in its colour. L. J. S.

Constitution and Genesis of Ferric Sulphates. VIII. Botryogen and Römerite; Copiapite. RUDOLF SCHARIZER (*Zeitsch. Kryst. Min.*, 1913, **52**, 372—398). —The formula of botryogen written in the form $(SO_4)_4(FeHO)_2(MgHO)_2H_2,12H_2O$ shows a relation to the römerite formula:

$$(SO_4)_4(FeHO)_2Fe''H_2,12H_2O.$$

Although botryogen is monoclinic and römerite is triclinic, the axial ratios can be so converted as to show a close relationship. The available crystallographic data of copiapite are also discussed, and a relation brought out between these and the data for botryogen. Copiapites fall chemically into two groups, namely, those without and those with bivalent oxides (RO = MgO, FeO, ZnO, MnO). Analyses of material belonging to the first group are: I, native copiapite from Sierra de l'Alcapa rossa, II, artificial copiapite, and of the second group: III–IV, copiapite from South America; and V–VI, from Rammelsberg, Harz:

	SO_3.	Fe_2O_3.	FeO.	ZnO.	MgO.	H_2O.	Insol.	Total.
I.	38·62	30·24	—	—	—	30·75	0·90	100·51
II.	38·72	30·68	—	—	—	30·60	—	100·00
III.	38·44	26·36	1·53	2·11	0·98	30·09	0·15	99·66
IV.	38·47	26·78	1·51	1·67	0·66	30·07	0·27	99·43
V.	38·27	26·39	0·33	1·45	1·73	30·60	0·79	99·56
VI.	38·22	26·19	0·45	2·47	0·85	31·33	0·40	99·91

For the first group the formula is $(HOFe)_4(HSO_4)_2(SO_4)_3,15H_2O$, and in the second group there is in addition the radicle $(RSO_4),xH_2O$. L. J. S.

Chemical Composition of Dysanalyte from Vogtsburg in Kaiserstuhl. WILHELM MEIGEN and E. HUGEL (*Zeitsch. anorg. Chem.*, 1913, **82**, 242—248. Compare Hauser, A., 1909, ii, 60).—Hauser's method of analysis gives low values for columbium. The powdered material is purified by treatment with hot dilute hydrochloric acid and potassium hydroxide, which are without action on dysanalyte. The mineral has D 4·26 and H 5·5. It is fused with potassium hydrogen sulphate, extracted with water containing sulphuric acid and hydrogen peroxide, and filtered. The residue, after ignition with hydrofluoric acid, is again fused with potassium hydrogen sulphate. The filtrates, after removal of hydrogen per-

oxide, are twice precipitated with ammonium carbonate. The precipitate is dissolved in sulphuric acid, neutralised carefully with ammonia, and mixed with sulphurous acid in large excess. Titanic and columbic acids are precipitated quantitatively on warming. The precipitate is dissolved in sulphuric acid and hydrogen peroxide, and again precipitated. Titanium and columbium are separated by Weiss and Landecker's method (A., 1909, ii, 942). Two specimens gave the following analyses (mean of several determinations):

	SiO_2.	TiO_2.	Cb_2O_5.	CaO.	Ce_2O_3 (La_2O_3).	FeO.	Al_2O_3.	K_2O.	Na_2O.	MnO.	MgO.	Total.
I.	0·29	48·31	16·12	21·63	3·32	5·35	1·25	0·39	4·20	0·02	—	100·88
II.	0·33	38·70	25·99	23·51	3·08	5·69	0·82	0·44	1·72	—	—	100·28

C. H. D.

Zirkelite from Ceylon. GEORGE S. BLAKE (*Min. Mag.*, 1913, **16**, 309—316).—The materials analysed were found as grains and small pebbles in the gem-gravels at various localities in the Sabaragamuwa province. They are brownish-black with sub-metallic lustre and sub-conchoidal fracture, and range in density from 4·72 to 5·22; hardness, 5½—6. Three varieties are distinguished according to the relative amounts of thorium and uranium oxides present; these are represented respectively by analyses I–III, IV and V, and VI. The material is slowly decomposed by hydrochloric acid, but readily by hydrofluoric. A 20-gram sample, heated with hydrogen potassium sulphate, yielded 134·9 c.c. of gas containing: CO_2, 40·2; H, 10·2; N, 34·9; He, 14·7%:

	ThO_2.	U_3O_8.	ZrO_2.	TiO_2.	(Ca,La,Di)$_2O_3$.	Y_2O_3.	FeO.	CaO.	MgO	PbO.	H_2O.	Total.	Sp. gr.
I.	20·17	—	—	—	3·61*	0·96	—	—	—	—	—	—	5·2
II.†	20·44	1·06	30·73	29·50	2·68	1·08	4·07	6·87	2·34	0·38	0·46	99·64	5·0–5·1
III.	18·78	0·65	32·56	30·95	1·40	0·40	4·42	6·78	3·04	—	1·05	100·03	4·72
IV.	8·33	4·66	34·19	36·26	0·32		4·72	8·55	1·33	—	1·70	100·06	4·47
V.‡	8·51	2·08	32·64	36·06	0·83		4·65	9·35	1·08	—	1·74	99·20	4·32
VI.	0·23	14·31	35·27	34·87	—	—	3·73	8·18	1·96	0·44	1·68	100·67	4·40

* Ce_2O_3, 1·44; (La,Di)$_2O_3$, 2·17. † Also MnO, 0·03. ‡ Also Al_2O_3, 2·26.

Material from the same samples as anal. IV–VI was examined crystallographically by G. F. H. SMITH. The rough crystals are hexagonal ($a:c=1:1·1647$) and twinned. It is suggested that the original zirkelite (A., 1895, ii, 508) may be rhombohedral or hexagonal rather than cubic. L. J. S.

Talc from Hozsuret, Hungary. H. MICHEL (*Tsch. Min. Petr. Mitt.*, 1912 [*i.e.* 1913], **31**, 331).—The following analysis is of a very pure sample of talc, which in thick pieces shows a blue or green colour. The material is optically negative, with 2V=7°, $\alpha=1·538$, $\gamma=1·588$:

SiO_2.	Al_2O_3.	FeO.	Cr_2O_3.	CaO.	MgO.	H_2O.	Hygrosc. H_2O.	Total.
61·75	3·52	1·13	trace	trace	28·28	5·05	0·23	99·96

L. J. S.

Solid Solution in Minerals: The Constant Composition of Albite. HARRY W. FOOTE and WALTER M. BRADLEY (*Amer. J. Sci.*, 1913, [iv], **36**, 47—50).—The variable compositions of nephelite, analcite, and pyrrhotite have recently been explained by the presence of other substances (not isomorphous) in solid solution (A., 1911, ii, 122; 1912, ii, 568, 354). It is found that nephelite contains more silica when it is intimately associated with albite; and if solid solutions of this kind were common amongst minerals it would be expected that their composition might vary according to their associations. In order to test this view, analyses are given of albite associated with quartz from Amelia Court House, Virginia (anal. I by Robertson in 1884; II by Musgrave, 1882), and of albite associated with corundum and nephelite in corundum-syenite from Brudenell, Renfrew Co., Ontario:

	SiO_2.	Al_2O_3.	CaO.	MgO.	Na_2O.	K_2O.	H_2O.	Total.
I.	67·06	21·72	1·59	0·03	10·01	0·39	—	100·80
II.	68·44	19·35	—	—	11·67	0·43	—	99·89
III.	63·86	23-32	3·76	—	9·20	0·16	0·24	100·54

Deducting anorthite, the ratios of $SiO_2 : Al_2O_3 : (Na_2O + K_2O)$ are respectively 6·00 : 1·04 : 0·93, 6·00 : 1·00 : 1·02, and 6·00 : 1·04 : 0·94. These slight variations may be explained by errors of analysis or the presence of impurities; and they do not support the view of any solid solution of quartz, nephelite, or corundum in albite.

L. J. S.

Nefedieffite from the Neighbourhood of Troickosavsk [Siberia]. ALEX. FERSMAN and L. CITLIADZEV (*Bull. Acad. Sci. St. Pétersbourg*, 1913, 677—687).—The authors describe a pale rose-coloured mineral found near Troickosavsk, and sold in large quantities in Irkutsk under the name of talc. It occurs in compact masses having a splintery fracture, and is fatty to the feel. Its hardness is about 1·5, and it cuts like hard soap. The intensity of its colour varies somewhat in different samples, and apparently depends on the presence of traces of manganese. Its composition is:

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	H_2O (below 100°).	H_2O (above 100°).	Loss on ignition.	Total.
51·33	17·75	0·62	2·83	4·61	9·51	13·66	23·17	100·31

These results are in close agreement with those obtained for nefedieffite, the formula of the latter being probably:
$1(MgO,CaO,FeO,K_2O,Na_2O),1(Al_2O_3,Fe_2O_3),5SiO_2,4H_2O + 3H_2O$, or $R''R_2'''Si_5O_{14},7H_2O$. It sometimes undergoes conversion into montmorillonite, from which it differs in fusibility and in its resistance to the action of acids.

Nefedieffite probably forms the chief constituent of Fuller's earth, and allied to it are the majority of the natural soaps, including keffekilite, confolensite, soapstone, saponite, pseudosteatite, etc., as well as the so-called "Basaltsteinmark." T. H. P.

Tourmaline Group. PAUL REINER (*Verh. naturhist.-med. Ver. Heidelberg*, 1913, **12**, 262—317; and *Diss. Heidelberg*, 1913, 1—57). —A detailed discussion of the formulæ proposed by Penfield and Foote (A., 1899, ii, 304), Tschermak (A., 1900, ii, 217), and Wülfing (A., 1901, ii, 65). Wülfing assumed the isomorphous mixing of the two molecules $Si_{12}B_6Al_{16}Na_4H_8O_{63}$ and

$$Si_{12}B_6Al_{10}Mg_{12}H_6O_{63},$$

and he now suggests to the author a third molecule,

$$Si_{12}B_6Al_{12}Fe_8H_8O_{63}.$$

Re-calculations of many previously-published analyses are given in support of these formulæ, and the percentage of each molecule present in the mixture is stated in each case. The following new analyses, by Dittrich and Noll, are given of tourmaline: I, bottle-green crystals from Brazil (D 3·064; $a:c=1:0·4480$; optical determinations are also given); II, black crystals from Pierrepont, New York (D 3·120); III, black crystals from Andreasberg, Harz (D 3·250; $a:c=1:0·4523$):

	SiO_2.	TiO_2.	B_2O_3.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.	CaO.	Na_2O.	Li_2O.	K_2O.	H_2O.	F.	Total.
I.	37·74	—	11·54	38·43	1·58	1·93	1·25	0·06	0·66	2·37	1·66	0·07	3·21	0·57	101·07
II.	35·86	0·70	11·46	22·91	2·56	6·08	—	11·06	3·04	1·19	—	0·20	2·99	0·72	99·77
III.	34·01	0·61	10·89	28·80	4·37	13·57	0·12	0·42	0·58	2·03	0·10	0·20	2·92	0·71	99·33

The material from Andreasberg is richer in iron than any other tourmaline (containing 54% of the iron molecule), and here the crystallographic axis *c* is slightly longer. L. J. S.

Ægirite-like Pyroxene and Crocidolite from Golling, Salzburg. RICHARD DOHT and CARL HLAWATSCH (*Verh. Geol. Reichsanst. Wien*, 1913, 79—95).—The well-known "sapphire-quartz" from Mooseck, near Golling, owes its blue colour to enclosed crocidolite. It is found in a gypsum quarry, and occurs in veins in a mixture of dolomite, chalybite, and steatite, with associated hæmatite, limonite, crocidolite, and an ægirite-like mineral. The last of these has the form of green radially-fibrous aggregates, and is shown by anal. I to contain much of the jadeite molecule, $NaAlSi_2O_6$, in addition to the ægirite molecule, $NaFeSi_2O_6$. The crocidolite forms loose, fibrous masses; D about 3·20; analysis II is near to that of "abriachanite" from Scotland:

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	Na_2O.	K_2O.	H_2O.	Total.
I.	52·61	8·51	22·22	1·47	trace	1·38	0·08	13·60	0·46	0·37	100·70
II.	56·71	2·38	14·70	7·60	—	—	9·62	5·42	0·57	3·69	100·49

L. J. S.

Composition and Origin of Alkaline Rocks. CHARLES H. SMYTH, jun. (*Amer. J. Sci.*, 1913, [iv], **36**, 33—46).—The average composition of all igneous rocks, as deduced by F. W. Clarke, is quoted under I, and the average of twenty-three analyses of alkaline syenites is given under II. The latter shows more alkalis and alumina and less lime and magnesia:

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.	CaO.	Na_2O.	K_2O.	P_2O_5.	Total.
I.	61·82	0·75	15·51	2·67	3·45	—	4·02	4·96	3·51	3·04	0·27	100·00
II.	62·46	0·56	18·07	2·24	2·31	0·08	0·97	2·57	5·58	5·02	0·14	100·00

The alkaline rocks are much rarer (less than 1% of the whole) and more local in their occurrence than the common type of sub-alkaline rocks. Further, they are characterised by the presence of the rarer elements lithium, glucinum, cerium, yttrium, zirconium, uranium, and thorium, and of the "mineralisers," fluorine, chlorine, and sulphur (as SO_3). It is maintained that these rocks have been derived from the more common magma by differentiation, and that this has been largely effected through the agency of the "mineralisers."
L. J. S.

The Meteorite of St. Michel, Finland. LEONHARD H. BORGSTRÖM (*Bull. Comm. Géol. Finlande*, 1912, No. **34**, 1—49).—Two stones weighing 10 kg. and 7 kg. fell on July 12th, 1910. Analyses of the metallic portion extracted by copper-ammonium chloride and of the stony portions soluble and insoluble in hydrochloric acid give the following as the bulk composition:

Fe.	Ni.	Co.	Cu.	P.	S.	SiO_2.	TiO_2.	Al_2O_3.
11·71	1·16	0·13	0·01	0·08	2·22	39·52	0·02	3·31

Cr_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.	Na_2O.	Total.
0·56	13·44	0·41	1·64	24·60	0·13	1·32	100·26

corresponding with the mineral composition: nickel-iron, 8·71; schreibersite, 0·51; troilite, 6·11; chromite, 0·82; olivine, 43·22; bronzite, 26·25; plagioclase, 14·63%.
L. J. S.

The Binda Meteorite. CHARLES ANDERSON and JOHN C. H. MINGAYE (*Records Australian Museum*, 1913, **10**, 49—52).—This stone was found near Binda, Georgiana Co., New South Wales, on June 5th, 1912, and, being perfectly fresh, it is probably connected with the meteor seen on May 25th. The weight was stated to be 12 lbs., and two fragments of 5 lbs. 13½ ozs. and 4 lbs. 6½ ozs. are preserved. The crust is in two layers: an outer brilliant black crust showing lines of flow, and readily detachable from the under dull, black layer. The material is friable and holocrystalline in structure, with no chondrules. Anorthite, hypersthene, chromite, and specks of nickel-iron were identified under the microscope. D 3·25. Analysis gave:

SiO_2.	Al_2O_3.	FeO.	Fe.	FeS.	MnO.	Cr_2O_3.	CaO.	MgO.	Na_2O.	K_2O.
50·50	8·84	15·29	0·45	0·96	0·51	0·75	6·15	16·15	0·28	0·13

CuO.	V_2O_3.	P_2O_5.	C.	H_2O (110°).	BaO. SrO. NiO. CoO. CO_2. Cl. SO_3. F.	Total.
trace	0·01	0·03	0·07	0·10	absent	100·22

L. J. S.

Analytical Chemistry.

Analysis of Combustible Gases by Explosion. ENRIQUE HAUSER (*Anal. Fis. Quim.*, 1913, **11**, 280—286).—A proportion of 8·33% of methane ensures that the combustion of nitrogen is too slight to cause an appreciable error. For exact work the oxides of nitrogen are absorbed by a known volume of water, the solubility of carbon dioxide being calculated and allowed for. G. D. L.

An Apparatus for Gas Analysis. T. S. AGRAZ (*Zeitsch. anal. Chem.*, 1913, **52**, 418—419).—The apparatus consists of a cylindrical tube. The tube has a capacity of 100 c.c., and is divided to 0·1 c.c. At the upper end the tube carries a stopcock, to which is sealed a tube bent downwards. For the passage of electric sparks platinum wires are fixed below this stopcock.

At the lower end of the tube two side-tubes with stopcocks are attached; one serves for the introduction or withdrawal of gases or liquids, the other is attached by caoutchouc tubing to a movable globular reservoir. The eudiometer is supported by a solid wooden foot loaded with lead. L. DE K.

A New Calorimeter Bomb. SAMUEL W. PARR (*Eighth. Inter. Cong. App. Chem.*, 1912, **1**, 389—393).—In this oxygen bomb for calorimetric use the platinum lining is replaced by an alloy composed of nickel, copper, tungsten, and chromium with smaller and more or less adventitious amounts of manganese, aluminium, titanium, boron, and silicon. This alloy is practically unaffected by the acids (nitric, sulphuric) which may form during the combustion.

A rubber gasket for sealing the bomb is substituted for the leaden one; in order to protect the rubber from being burnt a shoulder of massive metal is interposed between the rubber gasket and the inner chamber. The same principle is carried out in closing the main opening of the bomb and in closing the valve through which oxygen is admitted. L. DE K.

Some Tests on a New Calorimeter Bomb. RICHARD H. JESSE, jun. (*Eighth. Inter. Cong. App. Chem.*, 1912, **1**, 233—236).—The new alloy bomb devised by Parr (preceding abstract) has been successfully tried with sugar and benzoic acid. In these combustions the method of adiabatic calorimetry devised by Richards has been used (A., 1905, ii, 677; 1907, ii, 604). L. DE K.

Litmus Paper as a Quantitative Indicator of Reaction. GEORGE S. WALPOLE (*Biochem. J.*, 1913, **7**, 260—267).—The reaction of a solution is indicated by the colour of a piece of litmus paper immersed in excess of the fluid until no further change can be observed. The correction for neutral salts, if present, is a small

one. When, however, a drop of the fluid is placed on litmus paper, the colour changes are influenced by glazing of the paper, the actual effect of the reaction of the material in the paper on the solution used, the reaction inertia of the paper, the effect of exposure to air, and the liberation of indicator from the paper. Determinations of reaction when proteins and their decomposition products are present are very difficult with litmus paper. The same phenomena are even more marked with litmus tincture.

W. D. H.

Some Applications of the Hydrogen Electrode in Analysis, Research, and Teaching. JOEL H. HILDEBRAND (*J. Amer. Chem. Soc.*, 1913, **35**, 847—871).—An account of the value of the hydrogen electrode as an indicator in titrations. Curves are given representing the titration of a number of acids, bases, and salts, and attention is drawn to the fact that such curves supply the only generally trustworthy test as to the suitability of an indicator. It is also shown how magnesium may be rapidly estimated in the presence of calcium by following the hydroxyl ion concentration when sodium hydroxide solution is gradually added, and how, with an unattackable electrode in place of the hydrogen electrode, it is possible to follow the course of oxidation and reduction reactions.

D. F. T.

Electrometric Determination of the Concentration of Hydrogen Ions in Biological Fluids. KARL A. HASSELBALCH (*Biochem. Bull.*, 1913, **2**, 367—372).—In the electrometric method for the estimation of hydrogen ion concentration it is necessary that the electrode and the liquid should be saturated with hydrogen without any alteration in the hydrogen ion concentration of the liquid. In biological fluids containing volatile acids (or bases) this is a difficulty which can be overcome by leading a current of pure hydrogen saturated with moisture through the vessel containing the electrode until the latter is saturated with hydrogen. The liquid to be investigated is then led into the vessel, so that the electrode reaches into it for a certain depth. By shaking the vessel, the establishment of diffusion equilibrium between liquid and hydrogen, and attainment of constancy in the measured potential are accelerated. This constancy, however, is obtained by the loss of part of the volatile acid (or base) from the liquid to the hydrogen, and would therefore indicate an incorrect reaction. The liquid is next renewed without changing the gas mixture round the electrode, and shaking is repeated; electromotive constancy is thus reached without any appreciable alteration in the original fluid.

W. D. H.

Quantitative Relations in Capillary Analysis. HANS SCHMIDT (*Biochem. J.*, 1913, **7**, 231—248).—Diluted acids produce a ring system when dropped on blotting paper, the acid remaining behind the water. The radius of the coloured circle produced by

the acid is connected with the concentration by an exponential equation. Various other mathematical details are given.

W. D. H.

Use of Saponin [for Removing Precipitates]. C. BUNGE (*Pharm. Zentr.-h.*, 1913, **54**, 616).—In quantitative work it is often troublesome to remove the last traces of finely divided precipitates from the beaker. Addition of a drop of saponin solution to the rinsings overcomes this difficulty.

L. DE K.

Substitute for Platinum. LUD. KOPA (*Chem. Zeit.*, 1913, **37**, 754).—The author recommends rods made of quartz glass (2—3 mm. in diameter) as a substitute for platinum wire in the usual flame tests.

L. DE K.

Physiology of the Thyroid. I. Methods for Estimating Iodine in Organic Substances. F. BLUM and R. GRÜTZNER (*Zeitsch. physiol. Chem.*, 1913, **85**, 430—470).—In order to determine the question whether thyroid protein circulates in the blood, a certain method of detecting organically-bound iodine is necessary. A separation of these compounds from any potassium or other iodides can be accomplished by the use of acetone; it was found that 80% of acetone coagulates all proteins, and leaves alkaline iodine in solution. The estimation of very small quantities of iodine in the coagulum is not attended with any difficulty.

W. D. H.

Estimation of Sulphur in Pyrites. WALTER S. ALLEN and HOWARD B. BISHOP (*Eighth. Inter. Cong. App. Chem.*, 1912, **1**, 33—51).—1·3736 Gram of the ore is treated with 10 c.c. of a mixture of 2 parts of bromine and 3 parts of carbon tetrachloride. After fifteen minutes 15 c.c. of strong nitric acid are added, and after a while the whole is evaporated to dryness on a steam-bath. The residue is then again evaporated with 10 c.c. of hydrochloric acid to render silica insoluble. After moistening with 4 c.c. of hydrochloric acid and adding 100 c.c. of hot water, 0·2—0·3 gram of aluminium powder is added so as to reduce the ferric iron to the ferrous state, which is the chief feature in the process.

To the filtrate and washings are now added another 6 c.c. of hydrochloric acid (D 1·2), and then sufficient water to make up to 1 litre. The sulphuric acid is precipitated, in the cold, by adding at the rate of 5 c.c. per minute 125 c.c. of 5% barium chloride solution. The barium sulphate which is free from iron is then collected with the usual precautions.

L. DE K.

Estimation of [Combined] Sulphuric Acid in Wines. KARL VON DER HEIDE (*Zeitsch. anal. Chem.*, 1913, **52**, 440—451).—The author having noticed that the result of the estimation of sulphates in wines is always higher when the acid is estimated after burning off the organic matters, has carried out a large number of experiments in order to elucidate the matter. The conclusions arrived at

are as follows: The higher result obtained when testing the ash is due to an oxidation of sulphur dioxide during the ashing process or to the presence of organic sulphur compounds; there is no danger of sulphuric acid being absorbed from the gas employed. The matter is not without significance, and it is finally recommended to estimate the acid by direct precipitation with barium chloride, after boiling off any sulphur dioxide with hydrochloric acid in a current of carbon dioxide. L. DE K.

Apparatus for Nitrogen Estimation. O. WENTZKI (*Zeitsch. angew. Chem.*, 1913, **26**, 400).—Instead of measuring the nitrogen obtained in a nitrogen estimation in the azotometer itself, a special measuring tube is attached to the azotometer in such a way that the nitrogen can be readily transferred to it, and its volume measured over water. T. S. P.

Detection of Nitric Acid in Fruit Juices containing Added Water. ROBERT COHN (*Zeitsch. öffentl. Chem.*, 1913, **19**, 223—226. Compare this vol., ii, 528).—The author finds that the ordinary diphenylamine-sulphuric acid test is capable of detecting the presence of as little as 2 mg. of nitric acid (N_2O_5) in 1 litre of fruit juice; smaller quantities may be detected when the reagent contains sodium chloride, but in view of the fact that traces of nitric acid are found in pure fruit juices, this more sensitive test may be of some disadvantage in detecting the presence of nitric acid introduced with the added water. Of course, a negative reaction with the test does not definitely indicate the absence of added water. W. P. S.

Catalytic Acceleration of the Reduction of Nitrates by Schloesing's Method. RUDOLF HAC (*Eighth. Inter. Cong. App. Chem.*, 1912, **1**, 207—208).—In Schloesing's process (boiling the nitrate with ferrous chloride and hydrochloric acid and measuring the volume of nitric oxide evolved) the reaction may be much accelerated by addition of about 0·1 gram of molybdic acid before introducing the ferrous chloride and the acid. L. DE K.

Modification of Marsh's Process for the Estimation of Arsenic. ALEXANDRE HERBERT (*Eighth. Inter. Cong. App. Chem.*, 1912, **1**, 213—215).—The process is that of judging the amount of arsenic from the intensity of the arsenical mirror, but differs from the usual method in the way the hydrogen is generated. The author introduces into the generating flask a thin layer of pure mercury and 40 c.c. of dilute sulphuric acid (10 vol. %), also the liquid containing the arsenic (say, minute fractions of a mg.). The air having been displaced by a current of carbon dioxide, 100 grams of liquid sodium amalgam are introduced drop by drop, this operation occupying about half an hour. The slow but steady evolution of hydrogen then carries off the arsenic hydride, which is passed through a red-hot tube as usual. Finally, the flask is swept out by a very slow current of carbon dioxide. L. DE K.

Accurate Estimation of Arsenic Based on the Gutzeit Test. WALTER S. ALLEN and RALPH M. PALMER (*Eighth. Inter. Cong. App. Chem.*, 1912, **1**, 9—17).—In order to obtain accurate results with the well-known Gutzeit stain test, ferric chloride, reduced by means of stannous chloride, should be present. The standard stains should be made with ferrous and stannous chlorides present in the solution in approximately the same amounts as are found in the samples analysed. Iron should be added to all samples which do not contain it. L. DE K.

Volatility of Arsenious Chloride. JOHN T. D. HINDS (*Eighth. Inter. Cong. App. Chem.*, 1912, **1**, 227—231).—A series of experiments leading to the following conclusions:

The quantity of arsenious arsenic lost on boiling in hydrochloric acid solution is a function of the concentration both of the arsenic and of the acid. When the concentration of the acid exceeds that of the arsenic, the fraction of the arsenic volatilised approaches a constant value. With the concentrations usually employed in qualitative analysis, the loss of arsenic on boiling the solution to half its bulk may be disregarded. L. DE K.

Titration of Arsenic Acid. ALAN W. C. MENZIES and PAUL D. POTTER (*Eighth. Inter. Cong. App. Chem.*, 1912, **1**, 367—371).—Unsatisfactory results are obtained by direct titration of arsenic acid with standard alkali, but the process is much improved by adding barium chloride, thus liberating hydrogen chloride. A quantity of arsenic acid solution likely to require 30—40 c.c. of normal alkali is mixed with 15 c.c. of saturated barium chloride solution, and the whole is diluted to 250 c.c. and boiled for a few minutes. When cold, the liquid is titrated with *N*-sodium hydroxide (containing a little barium hydroxide). The alkali is added with stirring until the precipitate becomes slow in re-dissolving. After thorough stirring and removing any matter from the walls of the beaker, the liquid, which appears lustrous with fine crystals, is now titrated further, using phenolphthalein as indicator.

The alkali is preferably checked against pure arsenic acid in the manner described. L. DE K.

Detection of Infinitesimal Traces of Boron by means of Tincture of Mimosa Flowers. LUCIEN ROBIN (*Bull. Soc. chim.*, 1913, [iv], **13**, 602—606).—The principle of the method has already been described (A., 1904, ii, 445), and the present paper gives details for the use of the tincture instead of paper dyed with the tincture as a reagent for boron. By the method now described, as little as 0·00027 mg. of boric acid can be detected. The reaction is slightly affected by sodium phosphate, but not by other inorganic salts tried. In presence of organic salts, the latter must be removed by ignition before the reagent is applied. Directions for its use in the detection of boron in wines and milk are also given. T. A. H.

Estimation of the Organic Substance in Clays. F. EHRENBERG, C. DIEBEL, and H. VERKENSTEDT (*Zeitsch. anal. Chem.*, 1913, **52**, 408—418).—The authors come to the same conclusion as previous investigators, that the moist combustion methods (use of chromic acid or alkaline permanganate) are not so trustworthy in clay analysis as the combustion with copper oxide. L. DE K.

Apparatus for the Estimation of Air in Liquid Carbon Dioxide. O. WENTZKI (*Zeitsch. angew. Chem.*, 1913, **26**, 376).—The apparatus consists of a burette provided with a tap at the top and a three-way tap at its lower end. A side-tube above the three-way tap is connected with a reservoir containing potassium hydroxide solution. A measuring bulb is placed immediately below and in connection with the three-way tap, and is connected with a mercury reservoir. The carbon dioxide is admitted from the cylinder into the measuring bulb, and, when this is filled, the gas is shut off (a second three-way tap is provided between the apparatus and the cylinder, one arm of this tap being connected with a bubbling-flask, so that the rate of flow of the gas may be ascertained) and the gas is caused to pass slowly into the burette by raising the mercury reservoir, the burette having been filled previously with potassium hydroxide solution; the reservoir for the latter solution also serves as a levelling vessel when the volume of the residual air is read off. W. P. S.

Detection and Estimation of Exceedingly Minute Quantities of Carbon Dioxide. HERBERT N. MACCOY and SHIRO TASHIRO (*Eighth. Inter. Cong. App. Chem.*, 1912, **1**, 361—366; *Amer. J. Physiol.*, 1913, **32**, 137—145).—The gaseous mixture (air, for instance) is brought into contact with a drop of clear barium hydroxide solution in a special apparatus, and if a cloud should form, it is found by trial what volume of the gas is still capable of just showing the reaction within ten minutes. The minimum volume of carbon dioxide required must be determined by a previous experiment. L. DE K.

Estimation of Carbon Dioxide. LUDWIG W. WINKLER (*Zeitsch. anal. Chem.*, 1913, **52**, 421—446).—The author upholds the accuracy of his process published in 1903 (A., 1904, ii, 215), in which the expulsion of the carbon dioxide is much accelerated by the addition of zinc to the acid liquid; the gases evolved are first dried over calcium chloride, and then absorbed in a weighed Liebig's potash apparatus. The process is applicable to the analysis of carbonates as well as to natural waters.

For the estimation of carbon dioxide in the air, the time-honoured method of Pettenkofer is again recommended (action of lime water, titrating the excess with phenolphthalein as indicator). It is recommended that the bottle should be filled by applying suction, and not by blowing in the air by means of bellows. A convenient arrangement for this purpose is described. L. DE K.

The Use of the Fontactoscope for the Estimation of the Emanation Content of Spring Water. CARL ENGLER and HERM. SIEVEKING (*Physikal. Zeitsch.*, 1913, **14**, 658).—Polemical against Hammer and Vohsen (this vol., ii, 622). J. F. S.

Detection of Potassium with Tartaric Acid. HANS RECKLEBEN (*Zeitsch. angew. Chem.*, 1913, **26**, 375—376).—To the solution to be tested for potassium is added a moderately concentrated sodium hydrogen tartrate solution, and the mixture is stirred; if no crystals appear on the sides of the vessel containing the mixture, especially where the stirring rod has touched the side, a drop of the mixture is transferred to a watch-glass and stirred with a drop of 10% potassium chloride solution. A minute quantity of the crystals thus obtained is introduced into the original mixture, and stirred. A crystalline deposit will be obtained if potassium is present. A mixture of sodium acetate and tartaric acid may be used in place of sodium hydrogen tartrate, but the tartaric acid must be in excess, as potassium hydrogen tartrate is soluble in an excess of sodium acetate. W. P. S.

Rational Analysis of Sodium Nitrate. The Use of the Devarda Method versus the Misleading "Refraction" Method. WALTER S. ALLEN (*Eighth. Inter. Cong. App. Chem.*, 1912, **1**, 19—31).—The custom of estimating the moisture, sodium chloride, sodium sulphate, and insoluble matter, and then taking the sodium nitrate by difference ("refraction"), is shown to be quite erroneous, as they are by no means the only impurities (potassium, calcium, magnesium, perchlorate, etc.).

Hence, the estimation must be carried out by conversion of the nitric acid into ammonia and titrating the latter with methyl-red as indicator. For the conversion into ammonia, Devarda's alloy (aluminium, 45; copper, 50; zinc, 5 parts) is recommended in alkaline solution. L. DE K.

Spectroscopic Method for the Estimation of Lithium. W. W. SKINNER and W. D. COLLINS (*Eighth. Inter. Cong. App. Chem.*, 1912, **1**, 453—468).—The authors state that satisfactory spectroscopic estimations of lithium may be obtained according to the processes of Ballmann, Bell, or Foehr when applied to the alkalis extracted with amyl alcohol by the Gooch method.

Contrary to Ranzoli's statement, the quantitative spectroscopic estimation is not to be preferred to the gravimetric estimation (amyl alcohol process) if the lithium is present in weighable quantities. A rough spectroscopic examination is recommended in testing for alkalis, lithium, barium, strontium, and calcium, so as to serve as a guide to the proper procedure in analyses.

L. DE K.

Qualitative Analysis of the Calcium Group. RICHARD EDWIN LEE and F. L. MICKLE (*Eighth. Inter. Cong. App. Chem.*, 1912, **1**, 257—278).—Barium, calcium, and strontium may be separated

completely from magnesium by precipitation with ammonium carbonate (200 grams of the normal salt, 500 c.c. of ammonia, D 0·90, water up to a litre) in presence of a sufficiency of ammonium chloride in the cold and in slightly ammoniacal solution. Barium may then be separated from the other two metals by precipitating the hot acetic acid solution of the carbonates with potassium chromate. From the filtrate the strontium may then also be obtained as chromate on adding an equal volume of 95% alcohol. To the filtrate is added some more potassium chromate and also more alcohol to completely remove any strontium. The filtrate now containing only the calcium is diluted with twice its volume of water, and precipitated hot with ammonium oxalate. The precipitates may then be further identified in various ways, for instance, by means of the spectroscope. L. DE K.

Estimation of Magnesium by Precipitation as Magnesium Ammonium Phosphate or Arsenate. MAX WUNDER and C. SCHULLER (*Ann. Chim. anal.*, 1913, **18**, 221—222).—In order to obtain satisfactory results, the respective precipitates should be collected on a Gooch filter and washed with water containing 3·5% of ammonia; the precipitate is then dried at a temperature not exceeding 100°. For the conversion into the pyro-compounds the Gooch crucible is placed into a large porcelain crucible, the bottom of which is lined with asbestos. Heat is at first applied with a Bunsen burner for three-quarters to one hour, then the crucible is heated over a Teclu burner, and finally on the blowpipe. Both crucibles should be covered during the operation. L. DE K.

Rapid Estimation of Magnesia in Limestone by means of the Hydrogen Electrode. JOEL H. HILDEBRAND and HERBERT S. HARNED (*Eighth. Inter. Cong. App. Chem*, 1912, **1**, 217—225).—The process is based on the fact that if to a mixture of a neutralised solution of calcium and magnesium chlorides is added normal alkali the magnesium is precipitated first, the end-point being observed by a further rise in potential. The apparatus required, accompanied by a curve, is described and figured in the original paper. L. DE K.

The Roasting of Zinc Sulphide Precipitates and a New means of Rapid Coagulation of these Precipitates from Acid Solution. (Mutual Precipitation of Two Colloids, Applied to an Analytical Problem.) KARL BORNEMANN (*Zeitsch. anorg. Chem.*, 1913, **82**, 216—239).—Zinc sulphide may be directly ignited to oxide without separation from the filter paper if a shallow, open, porcelain crucible is used, ignited over a full Bunsen flame, or if, with a platinum crucible, the temperature does not exceed dull redness. When the filter paper is completely burnt, the precipitate must be heated strongly to decompose zinc sulphate. This must be above 935°, best in an electric furnace. Ignition in a well-closed crucible for fifteen to twenty minutes over a Teclu or Méker burner is sufficient.

The precipitation of zinc sulphide is greatly assisted by the presence of a second colloid, especially by sulphur. This is best carried out by precipitating in acetic or chloroacetic acid solution in presence of sodium hydrogen sulphite, passing hydrogen sulphide briskly. The precipitate coagulates well, and is washed on the filter with 0·5—1% ammonium nitrate. A slight turbidity remains in the solution, but this is due only to sulphur.

The presence of sulphur is without any harmful influence on the separation from iron, cobalt, or nickel. With strongly acid dilute solutions, the separation from iron is practically complete.

C. H. D.

Volumetric Estimation of Traces of Zinc. ANGEL DEL CAMPO Y CERDAN (*Anal. Fis. Quim.*, 1913, **11**, 287—293).—The blue coloration given by ammoniacal zinc solutions with resorcinol is discharged by alkali stannite, or, if acidified, by stannous chloride solution. A method of volumetric estimation is based on these facts. G. D. L.

Separation of Cadmium from Zinc. W. D. TREADWELL and K. S. GUITERMAN (*Zeitsch. anal. Chem.*, 1913, **52**, 459—469).—*By hydrogen sulphide.*—The solution should contain free sulphuric acid to the extent of ·4—5 normal. The cadmium is precipitated as sulphide in the hot solution, and the gas passed until the liquid is cold. If large excess of zinc is present, the precipitate is redissolved in hot dilute hydrochloric acid (1 : 1), evaporated with a slight excess of sulphuric acid, and reprecipitated with hydrogen sulphide.

By Electrolysis.—About 1 gram of the mixed chlorides or sulphates is mixed with 8 grams of potassium oxalate, 2 grams of ammonium oxalate, and 0·3—0·5 gram of oxalic acid, and the solution electrolysed with gauze electrodes at 70—80° for four to five hours for each 0·1 gram of cadmium present; current, 0·05 ampère; tension, 1·4—1·6 volt. From 0·04 to 0·20 gram of cadmium may be estimated in the presence of fifty times the amount of zinc by adding 5 grams of sodium hydrogen sulphate, and electrolysing in the cold with a quick rotating electrode; a gauze cathode is unsuitable here. 0·2 Gram of cadmium is deposited within thirty to sixty minutes. L. DE K.

Copper Content of Distilled Water. EMIL ABEL (*Zeitsch., Elektrochem.*, 1913, **19**, 477—480).—During studies on the velocity of the reaction between hydrogen peroxide and sodium thiosulphate (A., 1908, ii, 26) the author in one set of determinations obtained values for the velocity constant which were far higher than any previously obtained. Investigation showed that the high values were due to the presence of mere traces of copper in the distilled water which had catalysed the reaction. The author has devised a method, depending on the velocity of reaction between hydrogen peroxide and sodium thiosulphate, by which the amount of copper in distilled water can be estimated. In an experiment the author finds 0·000038% Cu present in the distilled water, whilst by

evaporating 80 litres of the water and weighing the residue the value 0·000040% Cu was obtained. J. F. S.

Estimation of Copper in Cupriferous Pastes. PHILIPPE MALVEZIN (*Ann. Chim. anal.*, 1913, **18**, 220).—0·1 Gram of the sample is calcined, the residue dissolved in nitric acid, and diluted to 20 c.c. Of the filtrate 10 c.c. are mixed with 2 c.c. of ammonia and made up to 20 c.c.; if necessary the solution is filtered, and to 10 c.c. of the filtrate another 1 c.c. of ammonia is added and the solution is now titrated with formaldehyde–sulphurous acid until colourless.

This reagent is prepared by passing sulphur dioxide through commercial "formalin." The solution is then standardised as follows: One gram of metallic copper is dissolved in nitric acid and diluted to 100 c.c.; 1 c.c. of this is then mixed with 2 c.c. of ammonia and 1 c.c. of water, and titrated. L. DE K.

Rapid Process for the Estimation of Copper in Roasted Pyrites. HERMANN KOELSCH (*Chem. Zeit.*, 1913, **37**, 753).—Ten grams of the finely powdered sample are heated to boiling with 6—7 grams of sodium hypophosphite and 40 c.c. of hydrochloric acid (D 1·16). Without filtering, the liquid is diluted with 100 c.c. of hot water, and then mixed with 50 c.c. of sodium sulphide solution (40 grams per litre). After shaking a few times the precipitate soon settles, and is then collected and washed with hot water. The filter and contents are treated in a porcelain crucible with nitric acid, which is then expelled by evaporation with sulphuric acid. After dissolving the residue in 100 c.c. of water, the copper is deposited electrolytically; or the precipitate may be dissolved in 10 c.c. of nitric acid, and heated until red fumes cease; the last traces of nitrous compounds are destroyed by addition of urea. The copper may then be estimated by first adding slight excess of ammonia and then a slight excess of acetic acid. Potassium iodide is added, and the iodine liberated (which represents the copper) titrated with thiosulphate. L. DE K.

Iodometric Estimation of Copper. M. EMMANUEL POZZI-ESCOTT (*Ann Chim. anal.*, 1913, **18**, 219).—In the analysis of copper products the iodometric estimation is interfered with by nitrous compounds, which also liberate iodine from potassium iodide. The author overcomes this difficulty by adding excess of urea. The liquid is then mixed with excess of ammonia, the residue freed from copper by redissolving in dilute sulphuric acid and reprecipitation with ammonia, the united liquids are acidified with acetic acid, and after adding potassium iodide, the iodine liberated is titrated as usual. L. DE K.

Detection and Separation of Aluminium and Glucinum by the Action of Amyl Alcohol on the Nitrates. PHILIP E. BROWNING and SIMON B. KUZIRIAN (*Eighth. Inter. Cong. App. Chem.*, 1912, **1**, 87—90).—The process is based on the solubility of

glucinum nitrate in amyl alcohol, when not more than 0·1 gram of the same dissolved in a few drops of water is boiled with 10 c.c. of amyl alcohol until the water has evaporated. In these circumstances aluminium nitrate is insoluble.

As a quantitative method the separation may be trusted to be accurate within about 1 mg. after a double treatment with amyl alcohol. In any case the process may be recommended for the preparation of glucinum nitrate free from aluminium. The nitrate may be recovered from its amyl alcohol solution by repeated shaking with water. L. DE K.

Influence of Hydrogen Sulphide on the Quantitative Precipitation of Certain Hydroxides by Sodium Thiosulphate. RUDOLF HAC (*Eighth Inter. Cong. App. Chem.*, 1912, **1**, 205—206).—An adverse criticism of Chancel's process for the separation of iron and aluminium by boiling the solution with sodium thiosulphate. The author states that the alumina is but imperfectly precipitated, although a complete precipitation will take place if a current of hydrogen sulphide is passed simultaneously. In that case, however, some ferrous iron is also thrown down.

Salts of glucinum are not precipitated on boiling with thiosulphate unless a current of hydrogen sulphide is passed for at least two hours. Thorium salts are quantitatively precipitated by simply boiling with thiosulphate. Ceric salts are not precipitated, not even by the simultaneous action of hydrogen sulphide.

L. DE K.

Reduction of Ferric Salts and Filtration by Potassium Permanganate. ANDRÉ LECLÈRE (*J. Pharm. Chim.*, 1913, [vii], **7**, 587—589).—The solution is acidified with 1 or 2 vols. % of sulphuric acid, a sufficiency of granulated zinc is added, also a piece of platinum wire. In order to render the ferrous sulphate formed more stable, 2—3 grams of ammonium sulphate are also added, and the whole is then heated in an Erlenmeyer flask, the neck of which is closed by a small funnel, for an hour at boiling heat. When all the iron has been reduced, the liquid is filtered through glass wool, and the residue is well washed. There is no fear of oxygen being absorbed, even if the filtration should have to be repeated before titrating with permanganate. L. DE K.

Detection and Estimation of Nickel by means of α-Benzildioxime. FREDERICK W. ATACK (*Analyst*, 1913, **38**, 316—321).—An alcoholic solution of α-benzildioxime, to which a little ammonia has been added, constitutes a delicate reagent for the detection of nickel owing to the formation of a red precipitate. When applying the reaction quantitatively, the solution, which should not contain more than 0·025 gram of the metal, is rendered alkaline with ammonia, an excess of the warm solution of the reagent is added with stirring, and the whole heated on the water-bath until the precipitate has coagulated After remaining for an hour in

a warm place, the precipitate is collected on counterpoised filters, washed with warm 50% alcohol, then with hot water, and finally dried at 110°. It contains 10·93% of nickel.

The detection and estimation is not affected by cobalt, ferric iron (to which sodium citrate has been added), manganese (in presence of a slight excess of acetic acid), zinc and magnesium (in presence of ammonium chloride), and chromium (in presence of ammonium tartrate).

The method is interfered with by the presence of nitrates, which should therefore be expelled by evaporation with sulphuric acid.

L. DE K.

Use of Hydrazine and Some of its Derivatives in the Gravimetric Estimation of Chromium. JOSEF HANŮS and T. LUKAS (*Eighth. Inter. Cong. App. Chem.*, 1912, **1**, 209—212).—Hydrazine, but preferably thiosemicarbazide, is stated to be a very suitable reagent for the estimation of chromium. To the neutral solution of the chromate is added an excess of ammonium chloride (at least 5 mols. to 1 mol. of chromate), then an excess of the reagent, and the whole is heated to boiling. The chromium is precipitated rapidly as hydroxide, which is then collected and treated as usual.

In the presence of iron and aluminium the mixture is oxidised with hydrogen peroxide in ammoniacal solution; sometimes it is advisable to redissolve the drained precipitate and repeat the operation. The mixed filtrates are then neutralised with hydrochloric acid, and precipitated as directed. L. DE K.

Volumetric Estimation of Chromium in the Presence of Iron. ALBIN KURTENACKER (*Zeitsch. anal. Chem.*, 1913, **52**, 401—407). —The solution of the mixed chlorides is introduced into a 250 c.c. flask, excess of bromine water is added, and then a large excess of aqueous potassium hydroxide. The mixture is now heated for half an hour on the water-bath with frequent shaking; by that time the iron has completely separated as hydroxide, whilst the chromium is converted into chromate. When cold, water is added to the mark, and, after shaking, the supernatant liquid is poured through a dry filter. One hundred c.c. of the filtrate are treated with dilute sulphuric acid until separation of bromine sets in, when 20 c.c. of 30% solution of potassium hydrogen sulphate are added, and the whole boiled for five minutes to expel the bromine. In case of doubt, another 10 c.c. of the hydrogen sulphate are added, and the boiling is repeated. When cold, the chromate is estimated iodometrically, as usual.

The iron precipitate is well washed, dissolved in dilute hydrochloric acid, and also titrated in the usual manner. L. DE K.

Assay of Tin, Solder, and Lead Dross by Electrolysis. L. BERTIAUX (*Ann. Chim. anal.*, 1913, **18**, 217—219).—Five grams of the tin or 1 gram of the solder dross are fused in a porcelain crucible with three parts of sodium carbonate and 3 parts of

sulphur, the mass is extracted with water, and the filtrate made up to a definite volume, of which is then taken an aliquot part representing 1 gram of material (in the case of solder the whole of the filtrate is used). The solution containing the tin sulphide is evaporated to dryness with addition of 15 grams of ammonium sulphate on a sand-bath, the residue is oxidised with nitric acid, and then evaporated with 5 c.c. of sulphuric acid until acid fumes cease. The residue is taken up with water, and boiled with 30 c.c. of hydrochloric acid and 30 grams of ammonium oxalate. The tin is then deposited electrolytically in the author's apparatus; temperature 40°, current 1—3 ampere.

In order to estimate the lead in the undissolved sulphide (tin material), this, after being washed with water containing hydrogen sulphide, is boiled for half an hour with a mixture of 100 c.c. of copper nitrate solution (? strength), 4 c.c. of ammonia, and 80 c.c. of nitric acid (D 1·33). The filtrate and washings are made up to 300 c.c., and the lead is then deposited as usual as peroxide; current, 0·3—1 ampere, finally 1—1 ampere, to deposit the last traces of lead. When estimating lead in solder dross, 1 gram is treated with 100 c.c. of copper nitrate and 25 c.c. of nitric acid, diluted to 300 c.c., and electrolysed; current 1—0·3 ampere. The same process is used for lead dross. L. de K.

Assay of Tin Ores. H. Milou and R. Fouret (*Eighth. Inter. Cong. App. Chem.*, 1912, **1**, 373—385).—The ore (2 grams) is fused in a steel crucible with 10 parts of sodium peroxide for twenty minutes, the mass is dissolved in water, and treated with 70 c.c. of hydrochloric acid, which should give a clear solution. After heating at 90°, 4 grams of iron wire are introduced, which precipitates any arsenic, antimony, and copper, and reduces the tin to the stannous state. After half an hour, the liquid is filtered, and the residue well washed. After again warming to about 95°, 10 grams of granulated zinc are added, so as to precipitate the tin.

After pouring off the liquid through a funnel containing a little glass wool, and washing the residue, the latter (to which the glass wool is then added) is dissolved in about 30 c.c. of hydrochloric acid in a flask fitted with a doubly perforated rubber cork, carrying an inlet tube connected with a carbon dioxide generator, and an exit-tube. When, after heating, all the metal has dissolved, the exit-tube is closed until the contents have cooled. Two hundred and fifty c.c. of water free from air are now introduced, and the tin titrated with standard iodine with starch as indicator.

L. de K.

Volumetric Estimation of Titanium. Porter W. Shimer and Edward B. Shimer (*Eighth. Inter. Cong. App. Chem.*, 1912, **1**, 445—451).—Reduction of titanium dioxide to sesquioxide by means of dilute sulphuric acid and zinc rods is very slow and often imperfect, but according to the authors complete reduction takes place within fifteen minutes by using a very long reductor filled with amalgamated zinc. This also reduces any iron present, so that the titanium cannot then be estimated with permanganate; a

standard solution of ferric ammonium sulphate is, therefore, used with potassium thiocyanate as indicator. The operations should be carried out in an atmosphere of carbon dioxide. Titanium may be separated from vanadium by fusion with sodium carbonate and sulphur; from the fused mass the vanadium may be extracted with water. When testing pig-iron for titanium a large quantity may be dissolved in hydrochloric acid, when all the titanium will be found in the insoluble residue. L. DE K.

Antimony Pentachloride as a Reagent for the Examination of Aromatic Hydrocarbons. SIEGFRIED HILPERT and LUDWIG WOLF (*Ber.*, 1913, **46**, 2215—2218).—Antimony pentachloride dissolved in carbon tetrachloride gives characteristic reactions with many aromatic hydrocarbons. About 0·1 gram of the hydrocarbon is dissolved in 1 or 2 c.c. of the solvent, and a 30% solution of the reagent is added drop by drop. Pure benzene gives a yellow to orange coloration, but concentrated solutions deposit a pale additive compound. Commercial benzene, however, gives a dirty green colour and a dark precipitate, 0·3 mg. of thiophen per c.c. still responding to the test. Condensed hydrocarbons produce deeper colours. Naphthalene gives, in a few seconds, a dark lilac precipitate, indene gives a bluish dark-red precipitate at once, and anthracene forms an intense green precipitate. Phenanthrene gives a brown precipitate, but 8 mg. of anthracene in 1 gram of phenanthrene can be detected by the formation of the above green precipitate. Carbazole gives a light green precipitate, and may thus be distinguished from thiophen.

The detection of impurities in anthraquinone may be carried out by extracting a sample with a small volume of hot carbon tetrachloride and testing the extract for anthracene or carbazole in the above manner, and then applying the reagent to a solution of the less soluble quinone. Anthraquinone forms a cinnabar-red precipitate, whilst phenanthraquinone gives a deep red coloration, and traces of the latter may thus be detected. Diphenyl- and triphenyl-methane and fluorene also yield green additive compounds. The presence of methyl groups renders the colour more and more dark red. Nitro-, amino-, and carboxyl groups, however, have the opposite influence.

Carbon tetrachloride must be used as the solvent, for in chloroform solution less characteristic and even colourless products are obtained. J. C. W.

Volumetric Estimation of Methoxy- and Ethoxy-groups. ALFONS KLEMENC (*Monatsh.*, 1913, **34**, 901—912).—Zeisel's method of estimating alkoxy-groups has not found technical application, since alcoholic silver nitrate solutions must be employed, and the determination requires considerable time. The author has endeavoured to overcome these difficulties by leading the alkyl iodide, evolved in the usual manner, through a heated tube packed with a suitable material, the liberated iodine being subsequently titrated by means of sodium thiosulphate solution.

The apparatus consists of a small flask in which the decomposi

tion is effected, and from which the alkyl iodide is driven by a current of carbon dioxide-free air through a reflux condenser, and thence through a small bubbler containing a suspension of red phosphorus in water. Thence the vapours pass into a hard glass decomposition tube about 25 to 28 cm. long and 1·2 cm. external diameter. The tube is drawn out at either end. The front end of the tube is packed with about 1 gram of 25% platinised asbestos, behind which is a roll of platinum foil formed by making a number of parallel cuts in a piece of foil and rolling it round an axis parallel with the line of the incisions. The remainder of the tube is filled with pumice held in position by a wad of asbestos. The narrowed end of the decomposition tube is connected by a ground joint with a tube which dips into a small vessel containing concentrated potassium iodide solution. The latter vessel is contained in an Erlenmeyer flask, on the bottom of which is a layer of water; this communicates with the air through a Peligot tube.

In the actual determination it is important that the alkyl iodide should be driven into the decomposition tube mixed with as much air as possible. In normal cases, decomposition is complete in one-half to three-quarters of an hour.

At the conclusion of the decomposition, the liberated iodine is titrated in the ordinary manner. To determine the small quantity of iodine which is evolved in the form of hydrogen iodide, a considerable excess of potassium iodate is added; the solutions are allowed to remain for fifteen to thirty minutes, and the liberated iodine estimated with sodium thiosulphate. Since, however, small quantities of carbon dioxide are always present, partly dissolved in the water and partly obtained by the combustion of the alkyl iodide, it is necessary to carry out a blank experiment for this stage, and to deduct the iodine thus found from that obtained as above.

From a large number of experiments the author is led to the conclusion that the errors of his method are slightly greater than those of Zeisel's gravimetric estimation, and lie generally between +0·5% and −1·0%.

For the determination of the methoxy-group it is sufficient to fill the decomposition tube solely with pumice; with a tube filled in this manner, however, the values found in estimating ethoxy-groups are very low. The error is due to decomposition of ethyl iodide into ethylene and hydrogen iodide, and subsequent partial combination of the former with the liberated iodine with production of di-iodoethane. This error can be minimised, but not completely abolished, by packing the tube with platinum and platinised asbestos as described above, so that the hydrocarbon is completely oxidised. H. W.

The Effect of Nitrotoluenes on the Determination of Glyceryl Trinitrate by means of the Nitrometer. C. G. STORM (*Eighth. Inter. Cong. App. Chem.*, 1912, **4**, 117—125).—The determination of glyceryl trinitrate by the nitrometer is not

affected by the presence of pure di- or tri-nitrotoluenes; in the process, however, any mononitrotoluene becomes quantitatively converted into dinitrotoluene by the nitric acid liberated from the glyceryl trinitrate, thus decreasing the volume of gas produced. Analysis of unknown mixtures of glyceryl trinitrate with nitrotoluenes will therefore be trustworthy only if the amount of mononitrotoluene present is too small to cause an appreciable effect.

D. F. T.

Behaviour of Sugars with Diphenylamine and Hydrochloric Acid. H. T. B. RASMUSSEN (*Ber. deut. pharm. Ges.*, 1913, **23**, 379—382).—The author has applied the reaction described by Jolles for the detection of lævulose in urine (A., 1909, ii, 1057) to a number of sugars, and finds that the ketoses give a deeper colour and in a shorter time than the aldoses. Furfuraldehyde gives a brownish-red coloration with diphenylamine and hydrochloric acid, which becomes dark green on shaking with ether. When hydrochloric acid is replaced by sulphuric acid, a gooseberry-red tint is produced. A table showing the colours given by solutions of various sugars at different concentrations and after various times of warming, is given in the original. The test is suitable for the detection of lævulose in urine, but not for finding lævulose or sucrose in presence of other sugars. For the detection of lævulose in presence of dextrose by this means, the quantity of the latter must be known.

T. A. H.

Ivar Bang's Method for the Estimation of Sugar. ZENNOSHIN HATTA (*Biochem. Zeitsch.*, 1913, **52**, 1—43).—As a result of detailed experimental investigation in each stage of Bang's method for the estimation of sugar, the author draws the conclusion that the deviations from the correct result may be influenced by three principal factors, namely, (1) the rate of titration; (2) the temperature of the copper solution at the time of reduction; (3) the auto-reduction of the sugar solution. It is not difficult to obtain fairly constant results by titrating at constant rate and at the same temperature. The deviations from constant results due to the first two factors are therefore not of great moment. The error due to the third factor will, however, vary with the amount of sugar in the solution, and tables are given showing corrections for this factor obtained by two different methods of calculation. The results thus obtained still show deviations from the correct values.

S. B. S.

Influence of Urea and Betaine on the Velocity of Hydrolysis of Sucrose by Hydrochloric Acid. WILLIAM E. CROSS and W. G. TAGGART (*Zeitsch. ver deut. Zuckerind*, 1913, 560—565).—It is proved that both urea and betaine have very little effect in retarding the velocity of hydrolysis of sucrose by hydrochloric acid at 28° or even at 20°. Consequently the use of these substances in analytical methods, which aim at determining the rotatory power of sucrose in acid solution, is unsafe, and the method is inapplicable for the analysis of molasses.

E. F. A.

New Test for the Detection of Saccharine Substances in Urine. ARDESHIR K. TURNER (*Chem. World*, 1913, **2**, 202—203).—The test depends on the rise in temperature which takes place when urine is mixed with sodium hypobromite solution. If 5 c.c. of normal urine are added to 25 c.c. of hypobromite solution (2 c.c. of bromine dissolved in 23 c.c. of sodium hydroxide solution prepared by mixing 100 grams of sodium hydroxide with 250 c.c. of water) the increase in temperature of the mixture will be from 4° to 13·5°. Should the urine contain a sugar or glycerol, the rise in temperature may amount to 40°, this result being obtained in the case of a urine containing 10% of added dextrose. On keeping, the mixture deposits characteristic crystals, which appear to be sodium oxalate resulting from the oxidation of sugar or glycerol. Sugars, starch, and glycerol yield the same kind of crystals.

W. P. S.

The Hydrolysis of Levulosans and its Application to Plant Analysis. PH. L. DE VILMORIN and FERDINAND LEVALLOIS (*Bull. Soc. chim.*, 1913, [iv], **13**, 684—691).—An examination of the behaviour of inulin towards various hydrolysing agents. The authors recommend the use of 5-sulphosalicylic acid at a concentration of 0·72 to 4·3 grams per litre, and at a temperature of from 80° to 100°, the results obtained being constant over a sufficiently wide period of time to avoid risk of error, and, furthermore, this acid has no effect on the subsequent estimation of the reducing sugars by Fehling's solution. Sulphuric and oxalic acids give figures which are too variable to serve as a basis for analysis. Acetic acid at a temperature of 80° and a concentration of 3—10% gives fairly concordant results, but this acid and its salts interfere with the subsequent determination of the sugars. W. G.

Estimation of Crude Fibre and Cellulose. HERMANN MATTHES and F. KÖNIG (*Arch. Pharm.*, 1913, **251**, 223—245).—The authors have compared the "crude fibre" isolated from cinchona bark by the Henneberg-Weende, König, and Cross and Bevan processes, and find that of the three products that afforded by the Cross and Bevan process is the most satisfactory, and they describe in detail a modification of this process for general use. Full details are given in the original of the yields of "crude fibre" and "cellulose" obtained by these three processes, and of the behaviour of these products with various reagents (compare A., 1907, ii, 991).

T. A. H.

Volatility of Lactic Acid. EDWIN B. HART and J. J. WILLAMAN (*J. Amer. Chem. Soc.*, 1913, **35**, 919—923).—In reply to Dox and Neidig (this vol., i, 236), who have criticised the authors' methods for the determination of the volatile acids of silage, the results of experiments are described which indicate that lactic acid is so little volatile in steam at 100° that the amount which passes over in the distillation of volatile acids from silage is insignificant. The higher results of Dox and Neidig in their experiments on the

volatility of lactic acid, may have been due to carbon dioxide in the water used or to volatile impurities in the lactic acid.

D. F. T.

Application of the Method of Estimating Tartaric Acid as Calcium Racemate to Solutions of Tartaric Esters. ANDRE KLING and E. GELIN (*Eighth. Inter. Cong. App. Chem.*, 1912, **1**, 251—256).—For the estimation of tartaric acid, the process by precipitation as calcium racemate (Abstr., 1911, ii, 666) is again recommended. If tartaric esters are also present, the total amount of the tartaric acid may be estimated after saponification.

If ethyl hydrogen tartrate is present, the tartaric acid contained therein may be estimated by titration, allowance being made for any free tartaric acid. The result must then be multiplied by two.

L. DE K.

Detection and Estimation of Salicylic Acid in Fruit Juices. WALTER HEINTZ and R. LIMPRICH (*Zeitsch. Nahr. Genussm.*, 1913, **25**, 706—717).—The method depends on the fact that, under given conditions, light petroleum extracts a definite proportion of salicylic acid from its aqueous solution, and that on shaking the petroleum solution with dilute ferric chloride solution, the salicylic acid is obtained in the aqueous layer in the form of its violet-coloured iron compound. Twenty-five grams of the fruit juice are diluted with water to 50 c.c., acidified with a few drops of concentrated sulphuric acid, and shaken with 100 c.c. of light petroleum. Fifty c.c. of alcohol are then added, the mixture is again shaken, and allowed to separate. Ten c.c. of the light petroleum layer are now transferred to a tube, mixed with 10 c.c. of a 0·1% ferric chloride solution, and the coloration obtained is compared with that produced by known quantities of salicylic acid. These comparison solutions are prepared by shaking 50 c.c. of a 0·1% salicylic acid solution with a few drops of sulphuric acid, 100 c.c. of light petroleum, and 50 c.c. of alcohol; quantities of 0·5, 1·0, 1·5, 2·0, etc., c.c. of the light petroleum layer are then transferred to separate tubes and mixed with 10 c.c. of the ferric chloride solution. The method may also be applied to the estimation of salicylic acid in jams, beer, and wine, but any alcohol present in the substances must be removed previously by evaporation in the presence of an alkali. The process described by Vierhout (Abstr., 1911, ii, 775) was found to be untrustworthy. W. P. S.

A Colour Reaction of Gallic Acid and of Tannin (Tannic Acid) and its Application. O. SCHEWKET (*Biochem. Zeitsch.*, 1913, **52**, 271—274).—When 3 c.c. of a 1% solution of iodine in potassium iodide are mixed with 2 c.c. of a 1% solution of gallic or tannic acids, and the mixture is diluted to 300—500 c.c. with tap-water, a reddish-violet colour is produced. This is due to the alkaline constituents of the water, and the same colour is produced when dilute solutions of carbonates of alkali metals or other alkaline reacting salts and alkali salts of organic acids are substi-

tuted for tap-water. The reaction can be applied to the detection of gallic acid in plant materials and in pharmaceutical preparations, and also to the detection of alkalis. With more concentrated alkali carbonate solutions, or with alkali hydroxides, the colour is dirty brown. S. B. S.

An Examination of the Kumagawa-Suto Fat Estimation Method, as Regards the Oxidation of the Fatty Acids and Unsaponifiable Substances during the Process. MUNEMICHI TAMURA (*Biochem. Zeitsch.*, 1913, **151**, 463—483).—No change in either the weight or iodine number of the fatty acids is caused in the saponification of animal tissues in the Kumagawa-Suto process. Neither is any change produced in the acids during the course of the evaporation of the petroleum, as the same results were obtained when the solvent was distilled off in the presence of oxygen, hydrogen, and carbon dioxide. In drying at 50° in air, there is an increase in weight and a diminution of the iodine number after prolonged heating. In one or two hours, the time required by the Kumagawa and Suto process, the change is, however, so small that any error due to this factor can be neglected. The unsaponifiable substances also undergo changes when heated in air at 50°, but here again the change is so small during the time required for drying in the Kumagawa-Suto process that it may be neglected. The modifications proposed by Mottram for this process are therefore necessary.
S. B. S

The Action of Milk on Certain Reagents. FRED. BORDAS (*Eighth. Inter. Cong. App. Chem.*, 1912, **18**, 69—72).—Since *p*-phenylenediamine in the presence of an oxidising agent yields a blue coloration when brought into contact with a calcium salt, the author argues that the peroxydase reaction of milk is due to the presence of calcium salts in milk. The fact that boiled milk does not give the reaction is due to coagulation caused by the heating; when heated milk is homogenised or shaken with pure silica, it regains its power of giving the peroxydase reaction.
W. P. S.

Reactions of Digitoxin. C. REICHARD (*Pharm. Zentr.-h.*, 1913, **54**, 687—692).—A large number of tests are given, of which the following seem the most characteristic. Sulphuric acid does not dissolve digitoxin, and is in the cold apparently without action, but on warming darkening sets in. Glacial acetic acid is a good solvent. If a little digitoxin is triturated with some ammonium molybdate, or potassium dichromate, and a drop of water, no action takes place on evaporation, not even on again evaporating with glacial acetic acid. If now sulphuric acid is added a clear solution is gradually obtained, which does not change in the cold, but gives on warming intense colorations, an azure-blue in the case of the molybdate and a nickel-green in the case of the chromate. These colours gradually fade, but return on warming, and this may be shown over and over again.

Digotoxin may be distinguished from a number of similar substances by not liberating iodine from a mixture of sodium iodate and sulphuric acid. It is not coloured red by bromine water, as stated in the literature, unless it contains impurities. If a drop of cobalt nitrate solution is evaporated and the residue mixed with a little digitoxin and then warmed with glacial acetic acid, the liquid on exposure to the air will turn yellowish-green. L. DE K.

Estimation of Tannin in Tea. HENRY L. SMITH (*Analyst*, 1913, **38**, 312—316).—An application of Chapman's "cinchonine method" for the estimation of tannin in hops to the estimation of tannin in tea. Good results may be obtained when the caffeine is removed from the solution previously.

Ten grams of tea are boiled with 800 c.c. of water for half an hour, the liquid filtered hot, and the leaves washed with 200 c.c. of boiling water. When cold, the volume is made up exactly to 1000 c.c.; 50 c.c. of the liquid are then shaken four times in succession with 30 c.c. of chloroform, which completely removes the caffeine. After concentrating the liquid to one-half, 30 c.c. of saturated solution of cinchonine sulphate are added at once, and after a few hours the precipitate is collected on a Gooch filter, which is previously washed with a half-saturated solution of the reagent, dried, and weighed. After washing with a half-saturated solution of cinchonine sulphate, the precipitate is drained by suction, and, so as to prevent melting on warming, first dried over sulphuric acid in a vacuum desiccator and then dried at 100°. It may be taken to contain 55% of tannin. L. DE K.

Estimation of Urea by Hypobromite. LÉON GRIMBERT and M. LAUDAT (*J. Pharm. Chim.*, 1913, [vii], **7**, 569—574).—The authors, who use a nitrometer filled with mercury, noticed that on shaking the hypobromite solution a small but decided quantity of free oxygen is given off. This, however, is not due to any action on the part of the mercury.

In order to get correct results in the estimation of urea, by observing the volume of gas given off on adding hypobromite, it is necessary to conduct a blank experiment with a solution of pure urea of about the same strength. In both experiments the volume of gas should be corrected for temperature and pressure before comparing the results. L. DE K.

Value of the Guaiacum Test for Blood-stains. HERBERT S. SHREWSBURY (*Analyst*, 1913, **38**, 186—189).—When properly carried out, the guaiacum test is of value in detecting the presence of blood in stains on linen, etc., but must, however, be regarded as a sorting test, and the indications it affords confirmed by supplementary tests. The guaiacum tincture employed must be prepared freshly, as when even only twenty-four hours old, it gives poor results. The fabric to be tested is moistened, and a few drops of guaiacum tincture are added; if no coloration is produced within a few seconds, a few drops of hydrogen peroxide solution (20 vols.) are

added. When blood only is present, a blue coloration develops within one second after the addition of the peroxide. Blood never reacts with guaiacum alone, but certain substances, such as oxydases, oxidising agents, etc., yield a coloration with the reagent before the peroxide is added. The presence of urine or sweat does not vitiate the test under the conditions given. The guaiacum test will readily reveal the presence of a blood-stain that has been washed thoroughly.

W. P. S.

Micro-chemical Estimation of Certain Blood Constituents. IVAR BANG and K. O. LARSSON (*Biochem. Zeitsch.*, 1913, **51**, 193—199).—A description of the microchemical method for estimating total nitrogen and the nitrogen of extractives is given. The blood is taken upon filter paper, weighed on a micro-torsion balance, and the total nitrogen is estimated by Kjeldahl's method adapted for microchemical estimations, for which the apparatus is figured and described. The ammonia is collected in excess of standard hydrochloric acid, the excess being estimated after the distillation, by addition of potassium iodate and iodide, and titration of the iodine set free by $N/100$-thiosulphate solution. For estimation of extractives the blood on the filter paper is coagulated in acid potassium chloride, the extractives removed, and the nitrogen estimated microchemically in the residue. S. B. S.

The Employment of Neutral-red Paper for Estimation of the Alkali of Serum. J. SNAPPER (*Biochem. Zeitsch.*, 1913, **51**, 88—90).—Attention is called to the advantages of using neutral-red paper instead of lacmoid paper when estimating the alkalinity of the serum by titration. Details as to the method of preparing this paper are given. S. B. S.

Method of Analysis of Brain Lipoids. J. LORRAIN SMITH and WILLIAM MAIR (*J. Path. Bact.*, 1913, **17**, 609—618).—A full account with certain modifications of the methods already described (A., 1911, ii, 1006). W. D. H.

The Bacterial Testing of Disinfectants. CHARLES T. KINGZETT and REGINALD C. WOODCOCK (*Analyst*, 1913, **38**, 190—197).—The authors have determined the Rideal-Walker coefficients of a large number of chemical substances, all of which are known to possess either oxidising, antiseptic, disinfectant, preservative, corrosive, or lethal properties, and the results obtained lead them to the conclusion that the Rideal-Walker test is untrustworthy for ascertaining the real disinfectant value of sanitary preparations. They are of opinion that the only gauge of utility of the various disinfectants is the extent to which, as shown by experience, they may be employed satisfactorily for the particular purposes for which they are intended. W. P. S.

General and Physical Chemistry.

Refractive Power of Liquid Hydrogen. WALTHER MEISSNER (*Ber. Deut. physikal. Ges.*, 1913, **15**, 540—554).—Liquid hydrogen was produced by means of a Nernst liquefaction apparatus, which is described in the paper. The refractive index was determined by Wiedemann's method. The following refraction quotients, between liquid hydrogen and the gas between the suspended parallel plates, are found: white light, 1·1087, $\lambda=0·656\mu$, 1·1098, $\lambda=0·589\mu$, 1·1096 and $\lambda=0·491\mu$, 1·1101. The relationship between the refractions of liquid and gaseous hydrogen is considered, and the values of liquid hydrogen are calculated. The calculated values agree with the observed values within the limits of experimental error. Liquid hydrogen is shown to possess no dispersion of magnitude greater than the experimental error. J. F. S.

Double Spectrum of Sodium Chloride. WILDER D. BANCROFT (*Eighth Inter. Cong. App. Chem.*, 1912, **20**, 37—43).—The author considers the causes of the differently coloured luminescence of sodium salts under different conditions. It is shown that when sodium burns slowly in chlorine or oxygen a blue light is emitted; the same light is emitted when sodium chloride is fused, when sodium chloride is placed in the layer separating the oxidising and reducing zones of a Bunsen flame, when sodium chloride is precipitated by alcohol or hydrochloric acid, and when sodium chloride crystals are crushed. The light in all these cases is produced by the change from sodium ion to undissociated sodium chloride. Cathode rays excite the blue luminescence in sodium chloride, whilst canal rays excite a yellow luminescence. The blue luminescence in the Bunsen flame is found where the rate of oxidation of the reduced sodium is slowest, at the surface between the oxidising and reducing zones. The yellow luminescence is observed where the rate of oxidation is higher, that is, in the oxidising zone. The simplest assumption in regard to the reaction producing the yellow sodium flame is that it is due to the change from sodium to sodium ion. This assumption is inadequate because it does not take into account the other spectra of sodium observed by Lenard (*Ann. Physik*, 1903, [iv], **11**, 636) and Wood (*Astrophys. Journ.*, 1911, 72). Under the influence of cathode rays potassium iodide emits green light. Part of this light is probably due to the iodine, and it seems possible that the chlorine may be responsible for some of the white light observed with many chlorides. Whilst it is probable that the crystalloluminescence and the triboluminescence of potassium iodide are the same as the cathodoluminescence of this salt, the experimental evidence is insufficient definitely to decide the question. J. F. S.

Vapours and Band Absorption [Spectra]. F. BURGER and JOHANNES KOENIGSBERGER (*Physikal. Zeitsch.*, 1913, **14**, 725—726. Compare this vol., ii, 85).—An answer to Stark (this vol., ii, 539)
J. F. S.

Absorption Spectra in the Red and Near Infra-red. AUGUST H. PFUND (*Eighth Inter. Cong. App. Chem.*, 1912, **20**, 279—287). —The author has examined the absorption in the region $0{\cdot}55\mu$—$1{\cdot}5\mu$ of ruby glass, cobalt glass, and chromium glass, also aqueous solutions of soluble Prussian-blue, sodium chromate mixed with cyanin, naphthol-green, naphthol-green mixed with cyanin, neodymium nitrate and distilled water. Absorption curves are given for all the substances. J. F. S.

Visible and Ultra-violet [Absorption] Spectra of Orange and Yellow Dyes Authorised for Use in Confectionery. GUSTAVE MASSOL and A. FAUCON (*Bull. Soc. chim.*, 1913, [iv], **13**, 700—704. Compare this vol., ii, 264, 542).—Solutions of orange I, chrysoine, naphthol-yellow S, and auramine O in solutions of the concentration 1:10,000 were examined by the method previously described. Orange I allows all visible light up to the *D*-line to pass through; chrysoine allows a small amount of the green to pass; naphthol-yellow S rather more of the green; and auramine O transmits the whole of the green. In the invisible spectrum, chrysoine has no absorption bands. Orange I and naphthol-yellow S have each one band in the ultra-violet; the latter about $\lambda = 285$, the former about 260. Auramine O has three bands in the ultra-violet at $\lambda = 350$, 310, and 265. J. F. S.

Absorption of Ultra-violet Rays by Some Organic Colouring Matters in Aqueous Solution. GUSTAVE MASSOL and A. FAUCON (*Compt. rend.*, 1913, **157**, 206—209).—The authors have studied the absorption of ultra-violet rays by aqueous solutions of the twenty-one colouring matters authorised for use in confectionery. These colours divide into two groups:

1. Those which absorb only the radiations of short wave-length.
2. Those which absorb both radiations of short and long wave-length, whilst allowing the intermediate ones to pass.

The rays used were between λ 2200 and 4045.

Group 1 comprises three pinks, eight reds, one blue, and two violets; whilst group 2 contains one orange, three yellows, two greens, and one blue.

Some of the colours possess distinctive absorption bands, which are of use in characterising them. These are set out in detail.
W. G.

Valency Electrons, Colour and Fluorescence. HANS VON LIEBIG (*Zeitsch. Elektrochem.*, 1913, **19**, 559—570).—Polemical against Stark (this vol., ii, 456). A long criticism of Stark's views with regard to the constitution of organic substances and their fluorescence. J. F. S.

Connexion between Fluorescence and Ionisation. JOHANNES STARK (*Ann. Physik*, 1913, [iv], **41**, 728—738).—Polemical against Volmer (this vol., ii, 456) and Pauli (this vol., ii, 456). The author also considers theoretically the relationship between fluorescence and ionisation of benzene, naphthalene and anthracene vapours.

J. F. S.

Oxidation and Luminescence. BLANCHETIÈRE (*Compt. rend.*, 1913, **157**, 118—121. Compare Ville and Derrien, this vol., ii, 654). —On oxidation by a mixture of hydrogen peroxide and sodium hypochlorite, certain glyoxaline derivatives, 2 : 4 : 5-triphenylglyoxaline (lophine), amarine, and hydrobenzamide, show marked luminescence. The examination, under similar conditions, of a large number of organic compounds, having no chemical relation with glyoxaline, has never given luminescence. Certain natural products, such as urine, infusion of tea, and extract of meat, and many other substances, exhibit marked luminescence, but the author is as yet unable definitely to fix on any organic complex the oxidation of which results in luminescence. W. G.

A New Luminescence of Calcium Compounds in the Hydrogen Flame, particularly those containing Bismuth or Manganese, and a Method of Detecting Traces of These Metals. JULIUS DONAU (*Monatsh.*, 1913, **34**, 949—955).—The author shows that when calcium compounds are drawn through a non-luminous hydrogen flame, a bluish-green luminescence is produced. This is not produced by all calcium compounds, but only by those which contain traces of manganese. When a trace of a bismuth salt was placed on a piece of chalk and drawn through a hydrogen flame, a brilliant blue luminescence was produced. It is shown that, by taking pure chalk or gypsum and placing a drop of a solution containing a bismuth or manganese compound and then heating this on the lower edge of a hydrogen flame, traces of these metals may be readily detected. The reaction can be obtained for one ten-millionth of a milligram of bismuth and a millionth of a milligram of manganese. The luminescence is not affected by the presence of other metals. Barium and strontium compounds show similar but much less marked reactions.

J. F. S.

Experiments on Crystalloluminescence. EARL F. FARNAU (*Eighth Inter. Cong. App. Chem.*, 1912, **20**, 127—128).—The author has noted the colour of the light emitted when sodium chloride, sodium bromide, sodium iodide, potassium chloride, potassium bromide, and potassium iodide were respectively precipitated from solution by alcohol, subjected to cathode rays, and formed from their elements. It is shown that the colour of the light emitted in the chemical reaction is the same as that produced during precipitation and during exposure to cathode rays. J. F. S.

The Walden Reaction. CECIL L. HORTON (*Chem. News*, 1913, **108**, 37).—Of the various reagents which have been employed to

effect substitutions and replacements in the study of the Walden inversion, only phosphorus pentachloride exhibits a constant behaviour, its action always being accompanied by a change in the sign of the rotation. With all other reagents the direction of the action is apparently dependent on the number of free carboxyl groups present in the parent substance. When the number of free carboxyl groups is even, the influence on the sign of the rotation is the reverse of that if the number of free carboxyls is odd. Thus the action of thionyl chloride, sodium hydroxide, potassium hydroxide, sodium methoxide, and ammonia on an active monocarboxylic acid gives rise to an active product having the same sign as that of the parent substance, whereas, if the latter contains no free carboxyl group or an odd number of carboxyl groups, the product has the opposite sign. The action of silver oxide, water, nitrous acid, nitrosyl chloride, and nitrosyl bromide is the reverse of that of the reagents last mentioned. Of the twenty-six examples quoted, only one forms an exception to the above rule, namely, *d*-*a*-bromo*iso*valeric acid, which, under the influence of ammonia, gives rise to *l*-valine, whereas the *d*-isomeride would be expected.

F. B.

Action of Light on Water Vapour and Electrolytic Gas. IVAN I. ANDRÉEV (*Zeitsch. Elektrochem.*, 1913, **19**, 551—552).—Polemical against Coehn and Grote (A., 1912, ii, 1118). The author answers the criticism against his work (A., 1912, ii, 112).

J. F. S.

Action of Ultra-violet Rays on Solutions of Hydrogen Peroxide. VICTOR HENRI and RENÉ WURMSER (*Compt. rend.*, 1913, **157**, 126—128).—A study of the photochemical decomposition of hydrogen peroxide by monochromatic light from the ultra-violet portion of the spectrum. The results confirm those of Tian for total light (compare A., 1911, ii, 35) that the reaction is unimolecular, and that the velocity of decomposition is proportional to the concentration. For each wave-length the velocity is proportional to the incident energy. It is further proportional to the absorbed energy, the factor being a constant for wave-lengths between λ 2800 and 2060, the photochemical susceptibility varying proportionately with the absorption. Einstein's law of photochemical equivalence does not apply to the decomposition of hydrogen peroxide. The energy which must be absorbed for the decomposition of one gram-molecule of hydrogen peroxide is practically equal to the energy given out by the decomposition of the same amount of hydrogen peroxide in the dark. W. G.

Additive Reactions between Carbon Monoxide and Other Gases under the Influence of Ultra-violet Rays. DANIEL BERTHELOT and HENRY GAUDECHON (*Compt. rend.*, 1913, **157**, 129—131).—The aptitude of carbon monoxide to form additive products is shown by its behaviour towards certain gases under the influence of ultra-violet light. In the presence of nitric oxide, a

small proportion of the carbon monoxide is oxidised by the oxygen set free from the decomposition of the nitric oxide. With water the reaction is more complex, one part of the carbon monoxide combining directly with the water, yielding formic acid, whilst the rest combines with the hydrogen and oxygen, resulting from the dissociation of the water, to give formaldehyde and carbon dioxide respectively (compare A., 1910, ii, 564, 606). Of the halogens, chlorine combines with carbon monoxide, but bromine and iodine are without action even in the ultra-violet light. Whilst combining with ammonia, it is without action on hydrogen phosphide or arsenide, and it does not react with hydrogen sulphide or free sulphur. W. G.

Influence of the Wave-length on the Velocity of a Photochemical Reaction. MARCEL BOLL (*Compt. rend.*, 1913, **157**, 115—118. Compare this vol., ii, 265).—From a study of the photochemical hydrolysis of the hydrochloroplatinic acids, the author has deduced the following formula governing the reaction: $m = \psi\epsilon^{av}P_0stc(1-e^{-xlc})/x$, where m is the weight of substance destroyed in a given time t; ψ is a constant for each substance considered being its "photochemical lability"; ν is the frequency, and P_0 the power of the incident radiation; s is the surface area irradiated; c the concentration of the solution; l the thickness of the layer; and x the coefficient of absorption. The constant ψ depends on the temperature and the nature of the reaction. W. G.

Wave-length and Velocity of Reaction. LUDWIK BRUNER (*Zeitsch. Elektrochem.*, 1913, **19**, 555—558).—The author considers and criticises the work of Winther (this vol., ii, 458) and Plotnikov (A., 1911, ii, 4, 452), and draws the conclusion that up to the present there is no evidence that photochemical reactions are influenced by the wave-length of the acting light, but rather that every kind of absorbed light energy plays an equal part in the velocity of the change. J. F. S.

A Simple Method of Counting α- and β-Rays. HANS GEIGER (*Ber. Deut. physikal. Ges.*, 1913, **15**, 534—539).—An apparatus consisting of a brass cylindrical box of 2 cm. diameter, fitted with an ebonite cover through which a metal rod passes, is described for the purpose of counting the α- and β-particles emitted by a radioactive substance. The bottom of the box is perforated by a round hole, and the rod is sharpened to a fine point. The box is raised to a potential of 1200 volts, and the rod is connected to an electrometer. The radioactive substance is placed at a short distance from the hole, the entrance of α- or β-particles into the chamber causes a passage of electricity to the electrometer, and from the amount of deflexion the number of particles can be calculated. By covering the opening by a piece of lead, the apparatus may also be used for counting γ-rays, although in this case the deflexion of the electrometer is due to secondary β-rays

(compare also Rutherford and Geiger (A., 1908, ii, 794; 1912, ii, 1021). J. F. S.

A Method of Determining the Number of Ions Produced by an α-Particle of Polonium. RENÉ GIRARD (*Le Radium*, 1913, **10**, 195—198).—The method consists (1) in determining in absolute measure the saturation current I given by a film of polonium, supposed to be infinitely thin; (2) in counting the number of α-particles given in a known time in a small solid angle, and calculating N the total number given per second, supposing the emission is uniform in all directions. If e is the charge on an ion, and X the required number of ions produced per α-particle, $X = I/Ne$. The film of polonium was deposited from hydrochloric acid on a silver plate, which retained its brilliance and polish. The saturation current was measured by means of the quartz electric balance, and the α-particles were enumerated by means of a zinc sulphide screen in a vacuum. The mean value found for X was 116,000, the accuracy being estimated at 10%. This number is very much inferior to that found by Geiger (162,000) and by Taylor (164,000). The difference is ascribed to the fact that the ionisation current was measured for all the α-rays emitted over a hemisphere rather than for a narrow parallel pencil, and that some of the more oblique α-rays suffer appreciable absorption in the film of polonium. F. S.

Effect of Temperature on Cathodoluminescence. EARL F. FARNAU (*Eighth Inter. Cong. App. Chem.*, 1912, **20**, 133—135).—Starting from the assumption that all forms of luminescence are due to chemical reaction, the author draws the conclusion that those conditions which increase the velocity of chemical reaction will increase the intensity of the luminescence. Cadmium sulphate and potassium bromide were placed in cathode tubes and cooled with liquid air, and as the salts cooled the luminescences decreased in intensity and finally vanished, the luminescence reappearing when the cooling agent was removed, thus confirming the author's initial assumption. J. F. S.

Radiation of Radium at the Temperature of Liquid Hydrogen. (Mme.) P. CURIE and H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 1430—1441, and *Le Radium*, 1913, **10**, 181—186. Compare P. Curie, A., 1903, ii, 50, 255).—The ionisation produced by the γ-rays of radium at the temperature of liquid hydrogen, 20·3° Abs. has been compared with the ionisation at the ordinary temperature. The measurements were made in hydrogen. It is shown that no change of radiation occurs which has a greater value than 0·1%, and probably not even of 0·02%. Preliminary experiments were also made with polonium, and the same results indicated. J. F. S.

Radium Content of Some Alabama Coals. STEWART J. LLOYD and JOHN CUNNINGHAM (*Amer. Chem. J.*, 1913, **50**, 47—51).—An examination of representative samples of various coals of Alabama

has shown that the amount of radium present ranges from $0{\cdot}028 \times 10^{-12}$ to $0{\cdot}37 \times 10^{-12}$, with an average of $0{\cdot}166 \times 10^{-12}$ per gram of coal, or from $0{\cdot}51 \times 10^{-12}$ to $7{\cdot}05 \times 10^{-12}$, with an average of $2{\cdot}15 \times 10^{-12}$ per gram of ash. The wide variation in the amount of radium per gram of ash is probably due to a specific tendency of certain plants to secrete exceptionally large quantities. E. G.

Colloidal Solutions of Radioactive Substances. FRITZ PANETH (*Kolloid Zeitsch.*, 1913, **13**, 1—4).—It is shown that the separation of radium-*E* and polonium from radioactive lead (Paneth, *Sitzungsber. K. Akad. Wiss. Wien*, 1912, **121**, 2193) by dialysis is due to the fact that radium-*E* and polonium are both easily hydrolysed in aqueous solution. The basic salts or hydroxides thus formed remain in solution as colloids, and consequently do not pass through the membrane with lead and radium-*D*. If, on the other hand, a nitric acid solution of radioactive lead is dialysed, there is no separation. J. F. S.

Electric Conductivity of Thin Liquid Layers. A. UNGERER (*Physikal. Zeitsch.*, 1913, **14**, 685—688).—The electro-conductivity of silver nitrate and sodium chloride solutions of varying concentrations has been compared with the conductivity of similar solutions in thin layers of the order 10^{-4} mm. The thin layers were obtained by pressing two plane glass plates together and regulating the thickness of the layer by means of the number and colour of the Newton rings visible. The conductivity was determined by means of a telephone arrangement, and also by direct current and a galvanometer. It is shown that conductivity ratio of the thin layer to the ordinary solution is independent of the concentration, that is, the conductivity of thin layers is relatively the same as that of solutions of ordinary dimensions. J. F. S.

Conductivity, Temperature-coefficients of Conductivity, Dissociation and Dissociation Constants of Certain Organic Acids between 0° and 65°. LESLIE D. SMITH and HARRY C. JONES (*Amer. Chem. J.*, 1913, **50**, 1—46).—In continuation of earlier work on the conductivity and dissociation of organic acids (White and Jones, A., 1910, ii, 13, 821; Wightman and Jones, A., 1911, ii, 689; 1912, ii, 1035), a study has been made of a large number of acids, and the molecular conductivities, temperature-coefficients, limiting conductivities, percentage dissociation, and dissociation constants at various temperatures between 0° and 65° are recorded.

The results confirm most of the relations established previously. With regard to isomeric acids, it has been found that the ortho- and *cis*-forms are the stronger, that is, have the larger dissociation constants. It is also shown that the migration velocities of the anions are functions of the number of atoms they contain, and that most dibasic acids dissociate like monobasic acids. E. G.

Electric Conductivity of Salt Vapours. II. GERHARD C. SCHMIDT (*Ann. Physik*, 1913, [iv], **41**, 673—708. Compare A., 1911, ii, 788).—A continuation of previous work on the conductivity of

salt vapours. It is shown that the conductivity of the halogen salts of zinc and cadmium is independent of the time, when a concentration change is not brought about by the current and when the surface of the solid is kept constant. The fall in the conductivity, which is often observed as the measurements proceed, is due to a migration of the salt to the central electrode, with consequent change of concentration, and also to the change in the surface of the solid. The increase which is observed at the commencement of the measurements is due to the fact that the vapour only slowly reaches the electrode. The hypothesis previously stated by the author (*loc. cit.*) does not coincide with facts. With a constant surface, the concentration being kept constant, the conductivity first increases with increasing pressure, and then falls. The conductivity increases with increasing temperature.

J. F. S.

Liquid Helium. II. The Electrical Resistance of Pure Metals, etc. VII. The Potential Difference Necessary for the Electric Current Through Mercury Below 4·19°*K*. H. Kamerlingh Onnes (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 1406—1430).—The resistance of mercury at helium temperatures has been determined. It is shown that when a definite current strength known as the "threshold value" has been reached, the resistance practically disappears when the temperature 4·19°*K* is reached. The ratio of the value at 2·45°*K* to that at 273°*K* is expressed by 2×10^{-10} ohm. This represents the lowest value. It is shown that as the current strength is increased, the resistance rises due to heating effects occurring in the mercury thread itself, and not in any way due to conduction from the leads. The residual resistance of the mercury is evidently due to the mercury itself, and not to impurities, for mercury artificially amalgamated with traces of gold and cadmium lost its resistance at 4·19°*K*. Even mercury used for mirror preparation lost its resistance in the same way.

J. F. S.

Conductivity and Ionisation of Sodium Ethoxide, Potassium Ethoxide, Lithium Ethoxide, Sodium Phenoxide, Potassium Phenoxide, Lithium Phenoxide, Sodium Phenylthiourazole, Sodium Iodide, Sodium Bromide, and of Mixtures of these Electrolytes in Absolute Ethyl Alcohol at 0°, 25°, and 35°. H. C. Robertson and Solomon F. Acree (*Eighth Inter. Cong. App. Chem.*, 1912, **26**, 609).—The conductivities of these compounds in alcohol at 0°, 25°, and 35° have been determined in concentrations ranging from *N* to *N*/256,000. The percentage ionisation is much lower in concentrated alcoholic solutions than in the corresponding aqueous solutions, the ionisation of *N*-solutions of sodium ethoxide and sodium phenoxide, for example, being 14·8% and 12·2% respectively at 25°. The decrease in ionisation with rise of temperature is about 0·4—0·5% per degree. The maximum molecular conductivity is attained in concentrations between *N*/2000 and *N*/8000. The molecular conductivities of *N*, *N*/2, *N*/4, *N*/8, *N*/16, *N*/32, and

$N/8000$ solutions of sodium ethoxide at 25° are 4·93, 7·78, 10·37, 13·04, 15·98, 19·16, and 33·2 respectively. E. G.

Electromotive Behaviour of Some Cadmium Elements. L. WILLIAM ÖHOLM (*Chem. Zentr.*, 1913, i, 1853; from *Acta Soc. Sci. Fennicae*, 1912, **41**, No. 1).—The element Cd | $CdCl_2$ | Hg_2Cl_2 | Hg has an *E.M.F.* of 0·6717—0·6718 volt at 18° in saturated solutions. The variation with the temperature from 10° to 30° is given by the equation $E_t = 0{\cdot}67179 - 0{\cdot}000074(t - 18°) - 0{\cdot}0000015(t - 18°)^2$. The *E.M.F.* increases on dilution, reaching in $N/10$-$CdCl_2$ solution a value of 0·7447 volt at 18°. The temperature-coefficients of cells with dilute solutions are positive, and increase with the dilution. For the same current, elements with concentrated solutions are more polarised than elements with more dilute solutions. In the former, however, the depolarisation is much more rapid. The cells are constant in value, and not altered by shaking.

When cadmium bromide replaces the chloride, the *E.M.F.* falls to 0·5592 volt, and the temperature-coefficient becomes five times as great. The cadmium iodide cell has E_{18} 0·4147 volt. Cadmium sulphate cells have an *E.M.F.* of 1·0186 volts at 20° and the lowest temperature-coefficient of any cadmium cell.

There is very close agreement between the thermodynamical calculation of the heat liberation in these cells and the values determined calorimetrically. For cadmium chloride they are respectively 31,993 cal. (calculated), 31,984 cal. (found). E. F. A.

Gas-Electrode for General Use. GEORGE S. WALPOLE (*Biochem. J.*, 1913, **7**, 410—428).—The apparatus and technique are described of an electrode for determining the hydrogen-ion concentration of protein solutions often containing dissolved carbon dioxide, within a few minutes and correct to 1 millivolt with 1 or 2 c.c. of fluid without loss or contamination. Sörensen titrations of 4% Witte peptone both colorimetrically and electrometrically are described.

E. F. A.

Mineral Electrodes. ROGER C. WELLS (*Eighth Inter. Cong. App. Chem.*, 1912, **21**, 149—154).—Although it is known that pyrolusite, magnetite, and pyrite are conductors of electricity, it does not seem to have been recognised that some other sulphides are even better conductors than pyrite, and can therefore serve as electrodes. An account is now given of certain phenomena which have been observed when conducting minerals function as electrodes in aqueous solutions. The minerals studied, in the approximate order of their conductivity, are galena, pyrrhotite, magnetite, chalcopyrite, and pyrite. Some of these develop potentials comparable with those shown by metals in contact with solutions of their salts. The potential is considerably affected by a change in the acidity or alkalinity of the solutions. Pyrite and marcasite are most positive in acid solutions; the potential falls as the solution becomes alkaline, and may even become negative in alkali sulphide solutions.

E. G.

The Product of an Electrolytically Disintegrated Carbon Anode, and the Existence of Colloidal Carbon. BARTOLO L. VANZETTI (*Kolloid. Zeitsch.*, 1913, **13**, 6—9).—The author has prepared a quantity of the disintegration product by passing a current of 4 amps. per sq. dcm. through a dilute solution of sulphuric acid by means of carbon poles, which had been previously heated to 1000° in chlorine. On heating, the substance gives rise to water, carbon dioxide, and carbon monoxide. It is soluble in alkaline solutions, producing stable suspensoids which are precipitated by acids. The colloid wanders to the negative electrode when electrolysed between platinum electrodes. The author discusses the evidence for and against the product being colloidal carbon or an organic substance of acid or phenolic nature. It is shown that there is not sufficient evidence to warrant a conclusion, but that there is no evidence which makes the idea of a colloidal solution of carbon impossible. J. F. S.

The Hall Effect in Liquid Electrolytes. A. E. OXLEY (*Proc. Roy. Soc.*, 1913, *A*, **88**, 588—604).—The author has examined solutions of copper sulphate, silver nitrate, and cadmium sulphate, and a gelatin solution of copper sulphate under the influence of direct and reversed magnetic fields. The method adopted differs from that usually employed in the facts that the cells were very small in comparison with the pole pieces of the magnet, and a very sensitive Paschen galvanometer was employed. It is shown that in the experiments the effect observed is due largely to the Hall concentration effect, and that only a small portion is due to the true Hall effect. The potential differences in all the experiments are of the calculated order; they reverse with the magnetic field, and act in the same direction when the experimental conditions vary widely. The results are regarded as establishing the existence of a Hall effect in liquid electrolytes. J. F. S.

Co-precipitation of Copper and Carbon by Electrolysis: Oxidation at the Cathode. ELLWOOD B. SPEAR, C. CHOW, and A. L. CHESLEY (*Eighth Inter. Cong. App. Chem.*, 1912, **21**, 93—97).—Lambris (A., 1910, ii, 131) has demonstrated the presence of carbon in the deposits obtained by the electrolysis of iron and nickel solutions, but has stated that, in the case of copper solutions, carbon is not precipitated under the same experimental conditions.

In the present paper, experiments are described which show that carbon is precipitated at the cathode during the electrolysis of a copper sulphate solution containing a little nitric acid and a small quantity of gelatin, and that some of the carbon is in the free state. It is considered that an oxidising action takes place at the cathode, and is doubtless due to secondary reactions. E. G.

Function of Inorganic Additive Agents in the Electrolytic Deposition of Copper. ELLWOOD B. SPEAR (*Eighth Inter. Cong. App. Chem.*, 1912, **21**, 99—103).—In the electrolysis of copper solutions, the addition of certain inorganic substances under suit-

able conditions produces a beneficial effect on the deposition of the metal. The substances which have the greatest influence are nitric, hydrochloric, and sulphuric acids, and the nitrates and chlorides of ammonium and the alkali and alkali earth metals. It is suggested that the function of such agents is to keep the copper in solution. This theory is based on the assumptions that some particles of copper may assume the colloidal form at the moment of giving up their electric charges at the cathode, and that oxidation may take place on the cathode during the passage of the current. Experiments are described which show that copper is continuously dissolved and reprecipitated at the cathode during the electrolysis. The theory affords an explanation of the fact that good deposits of copper become loose and worthless if the electrolysis is continued too long. E. G.

Present Theory of Magnetism and the Periodic System of Chemical Elements. JAKOB KUNZ (*Eighth. Inter. Cong. App. Chem.*, 1912, **22**, 187—203).—A discussion of the electron theory of magnetism with special reference to Langevin's kinetic hypothesis of dia- and para-magnetism. It is shown that the phenomena are more complicated than Langevin's theory indicates, and that certain elements seem to exist in both the diamagnetic and paramagnetic state. A certain periodicity is pointed out between the atomic weights of the elements and their magnetic properties. A modification of the theory with regard to the difference between diamagnetic and paramagnetic properties is proposed. Ferromagnetism is discussed chiefly on the basis of Weiss's work, and particular attention is devoted to Weiss's magneton (A., 1911, ii, 183, 367, 694). E. G.

Magnetic Researches. VIII. The Susceptibility of Gaseous Oxygen at Low Temperatures. H. KAMERLINGH ONNES and E. OOSTERHUIS (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 1404—1406).—The magnetic susceptibility of gaseous oxygen is determined between the temperatures of 17° and −126·7° at 100 times the normal density. It is shown that a Δ does not appear in oxygen above the critical temperature when the densities are 100 times the normal value. From this it appears probable that a Δ only appears for oxygen at great densities, and that in liquid oxygen it can rise to 71° as the density approaches 1000 times the normal value. J. F. S.

Magnetic Investigation of Some Iron Compounds. W. HAGEN (*Kolloid Zeitsch.*, 1913, **13**, 4—6).—The magnetic susceptibilities of a number of iron compounds have been determined, and the following relative values obtained: Ferric chloride, 1·000; ferric oxide, 0·116; iron formate, 0·784; iron acetate, 0·553; basic iron acetate, 0·540; iron valerate, 0·459; iron lactate, 0·810; iron malate, 0·675; iron tartrate, 0·634; iron citrate, 0·493; and iron saccharate, 1·010. Solutions of these compounds have been examined in the same way, and it is shown that they are mostly hydrolysed in solution, the

formate most strongly, and the citrate and malate only to the smallest extent. The formate and acetate contain all the iron in a colloidal condition in solution, and from the magnetic susceptibility it is shown that, in addition to colloidal hydroxide, another colloidal iron compound is present. The susceptibility of iron acetate and formate solutions increases with time, and eventually reaches a constant value, whilst the electric conductivity decreases to a constant value. On diluting ferric chloride with water, the hydrolysis increases with tho dilution; sucrose solution and glycerol have the same effect, but dextrose and lævulose solutions decrease the hydrolysis. J. F. S.

Decomposition of Complicated Chemical Compounds in a Variable Magnetic Field. ROMAN CEGIELSKIJ and, in part, E. L. LEDERER (*Ber, Deut. physikal. Ges.*, 1913, **15**, 566—570).—Rosenthal (A., 1908, ii, 152) has shown that starch, sucrose, and certain proteins can be hydrolysed when a solution is placed in a continuously varying magnetic field. The authors have repeated these experiments, taking care to sterilise the solutions and containing vessels before the experiments. In no single case when the solutions were sterilised could hydrolysis be observed. In two cases, however, the solutions were not sterilised, and in these cases starch solutions were hydrolysed. J. F. S.

The Heat Theorem of Nernst. HENDRIK A. LORENTZ (*Chem. Weekblad*, 1913, **10**, 621—627).—A theoretical paper embodying applications of Nernst's theorem. A. J. W.

Allotropy of Iron and Silver Iodide. CARL BENEDICKS (*Eighth Inter. Cong. App. Chem.*, 1912, **22**, 13—27).—An allotropic change is not necessarily a sudden transformation of one modification into another, since there is always the possibility that one or both forms may have a certain solubility in the other, and in such cases the transformation in part takes place continuously.

Determinations of the dilatation of silver iodide from $-180°$ to $+200°$ have shown that the transformation point of this substance at about $+147°$ affords an illustration of this fact. At low temperatures the dilatation is positive, but at 0° or the ordinary temperature it is negative. The dilatation must be ascribed to a solubility of the regular modification, stable above the transition point, in the hexagonal modification; this solubility increases with the temperature, and according to the curve of dilatation is probably very limited.

Consideration of the critical transformation point, A_3, of iron at about 890°, and of the lower more undecided transformation range, A_2, shows that the transformation at 890° is of the same type as that of silver iodide. According to this view, the so-called β-iron is really α-iron (stable at low temperatures), containing in solution a limited amount of γ-iron, increasing with the temperature (stable at temperatures above 890°). This conception greatly simplifies certain questions relating to the metallography of iron.

For example, the three most probable theories for the constitution of martensite when regarded from this point of view become identical. E. G.

Contractive Volume- and Surface-Energy and Thermal Condition of Matter. PETR. P. VON WEIMARN (*Kolloid. Zeitsch.*, 1913, **13**, 16—19).—A theoretical paper in which the author advances the view that the thermal condition of a substance is dependent on its dispersity. In considering the thermal condition of a solid substance, three surfaces have to be considered: (1) The outside surface, which bounds the substance from the surrounding objects; (2) the inner surface of contact of the crystalline particles; and (3) the inner pulsating surface of the crystalline particles. J. F. S.

Thermal Properties of Carbonic Acid at Low Temperatures. C. FREWEN JENKIN and D. R. PYE (*Phil. Trans.*, 1913, *A*, **213**, 67—117).—The thermal properties of carbon dioxide, liquid and gaseous, have been determined over the temperature range $-50°$ to $+20°$. The thermal quantities determined include: latent heat, total heat of the liquid, specific heat of the gas, dilation and elasticity of the liquid, and the Joule-Thomson effect for the liquid. From the experimental quantities, the specific volume and density of the saturated vapour and the specific heat of the liquid at constant pressure have been calculated. The pressure-temperature curve for the saturated vapour, and the entropy-temperature curve for the range $+20°$ to $-50°$ have been constructed. The following values of the specific heat of the gas have been obtained over the temperature ranges indicated, the former temperature being that at the commencement of the experiment, and the latter at the end of the experiment: $-30·4°$ to $+7·8°$, 0·22; $-22·4°$ to $+8·6°$, 0·25; $-13·0°$ to $+11·2°$, 0·275; $-1·9°$ to $+9·1°$, 0·32; $+8·3°$ to 19·5°, 0·41; 14·9° to 25·6°, 0·435; 20·4° to 30·5°, 0·495; 24·6° to 35·4°, 0·55. The latent heat has a value 81·2 at $-53·4°$, which decreases to 36·56 at $+20·05°$. The specific heat of the liquid at constant pressure has the value 0·47 at $-50°$, and 0·68 at $+20°$. The value of the Joule-Thomson temperature change alters its sign at about $-30°$, being negative from 10° to $-30°$, and becoming positive at this point. J. F. S.

Capacity for Heat of Metals at Different Temperatures. ERNEST H. GRIFFITHS and EZER GRIFFITHS (*Proc. Roy. Soc.*, 1913, *A*, **88**, 549—560 *).—The authors have determined the specific heats of copper, aluminium, iron, zinc, silver, cadmium, tin, and lead at temperatures from 0° to 100°. The experiments were carried out with large quantities of the metals (1—3 kilos.), and the temperature differences never amounted to more than 1·4°. The temperature readings were made by means of platinum resistance thermometers. The specific heat of the metals examined at 0° bear the relationship to their atomic weights represented by $S = 4·804 \times a^{-0·95}$, in which S represents the specific heat, and a the

* and *Phil. Trans.*, 1913, *A*, **213**, 119—185.

atomic weight. By extrapolation the authors deduce that the atomic heat of the metals at absolute zero has a mean value of 4·813. J. F. S.

New Method of Measuring the Pressure of Corrosive Gases at Constant Volume. GEORGE S. FORBES and LESLIE BRIGGS COOMBS (*Eighth Inter. Cong. App. Chem.*, 1912, **22**, 79—85).—The determination of the pressure of corrosive gases at constant volume and high temperatures presents considerable difficulty, and the methods described hitherto are not satisfactory. Apparatus has therefore been devised which can be readily constructed. The pressure gauge is outside the oven, and is easily manipulated, and does not require calibration.

The apparatus consists of a glass bulb of about 250 c.c. capacity which has a small closed tube at the bottom and a tube at the top which carries a side-tube bent so as to emerge from the electric oven in which the bulb is heated. The tube, after leaving the oven, is bent horizontally and wound closely with fine nichrome ribbon to a point a little beyond the second of two depressions it bears. The first of these depressions is filled before the determination with a mixture of powdered fused lead and silver chlorides in molecular proportions. This mixture melts at about 350°. The tube is constricted at a point a little beyond the second depression, and the volume of the further portion is reduced by the introduction of a piece of glass rod. A piece of vacuum tubing connects the end of the tube with a section of thermometer tubing, and contains a smooth glass bead, which acts as an airtight seal unless the tubing is pinched at this point. By this means any rapid flow of air in either direction is prevented. At the end of the thermometer tubing where it is joined to the manometer is a fine capillary, which can be broken and re-sealed in order to admit air or to expel it from this part of the apparatus. The manometer is provided with a flexible tube, which enables the open arm to be raised or lowered at will to adjust the pressure.

If the pressure of the vapour of a liquid, such as phosphoryl chloride, or of a solid, such as iodine, is to be measured, a weighed quantity is sealed in a capsule of glass tubing provided with a very fine, closed capillary, and this capsule is inserted into the small closed tube at the bottom of the bulb. The bulb is then rendered nearly vacuous, and the upper end of the tube at the top of the bulb is sealed off. The mixed chlorides in the depression in the horizontal tube are fused by means of a small flame, and the tube is inclined by raising the bulb. The liquid flows towards the second depression, and forms a drop about 1 cm. long. A current just sufficient to keep it fused is passed through the nichrome ribbon. The drop readily responds to pressure changes of 0·1—0·2 mm. in the manometer, and thus enables the pressure in the bulb to be equated exactly to that in the manometer. The capsule is broken by means of gentle shaking at a temperature at which its vapour pressure does not exceed the pressure of the residual air in the bulb.

If a gas is to be investigated, it is admitted slowly into the vacuous bulb through a well-ground stopcock, and the drop is kept stationary in the tube by forcing in the requisite amount of air through the vacuum tubing.

The mode of calculating the results is explained, and experiments are described which demonstrate the practicability of the method.

E. G.

Vapour Pressure of Zinc Amalgams. JOEL H. HILDEBRAND (*Eighth Inter. Cong. App. Chem.*, 1912, **22**, 147—156).—A study of the vapour pressure of amalgams has been undertaken with the object of testing the vapour pressure law on solutions differing widely in physical nature from the organic mixtures to which it has hitherto been applied, and also of investigating the general problem of metal compounds from a new point of view.

The results of some measurements of the vapour pressure of zinc amalgams are recorded. The values of the relative vapour pressures, P, of the amalgam and, P_0, of mercury are plotted against $N/N+1$, where N represents the number of mols. of mercury per mol. of zinc. If the amalgams were perfect solutions and obeyed the law $P/P_0=N/N+1$, the curve should be a straight line, and the values $N/N+1$ and P/P_0 should agree. The results show, however, that the pressures are considerably higher than they should be for a simple solution. This divergence is explained by assuming that the solute is associated to some extent, and hence the number of mols. of zinc is less than is assumed in the simple formula. If the zinc was partly associated thus, $2Zn=Zn_2$, and α represents the number of mols. of Zn_2 formed from 1 mol. of Zn, there would remain $1-2\alpha$ mols. of Zn, and the total number of mols. present in the mixture would be $N+1-\alpha$. The values of $N/N+1-\alpha$, calculated from the law of mass action, agree closely with the observed values of P/P_0, and thus indicate that the assumptions involved are correct. The extent of the association at various concentrations has been calculated, and it is shown that if zinc could exist in the liquid state at 300°, it would be associated to Zn_2 to an extent of two-thirds.

E. G.

Vapour Pressures of Some Concentrated Zinc Chloride Solutions. ALAN W. C. MENZIES and HENRIK BOVING (*Eighth Inter. Cong. App. Chem.*, 1912, **22**, 219—220).—Determinations of the vapour pressures of zinc chloride solutions have given the following results, expressed in mm. of mercury at 0°: 60% solution, 4·4 at 14·64°, 8·1 at 24·64°, and 10·8 at 29·60°; 65% solution, 2·5 at 14·64°, 5·0 at 24·64°, and 6·9 at 29·60°; 70% solution, 1·4 at 14·64°, 2·9 at 24·64°, and 4·1 at 29·60°.

E. G.

The Rate of Evaporation of Liquids. PAUL DE HEEN (*J. Chim. phys.*, 1913, **11**, 205—213. Compare Jablczynski and Przemyski, A., 1912, ii, 908).—In the author's measurements (1891) a stream of gas was allowed to impinge normally on the surface of a liquid, and the rate of evaporation was proportional to the product of the vapour tension and the internal friction of the gas. In Jablczynski

and Przemyski's recent experiments, the stream of gas was practically tangential to the surface of the liquid. Under these conditions a stationary saturated gaseous diffusion layer is formed, and the laws of evaporation are profoundly modified. Thus the relative rates of evaporation of water in hydrogen and in air are opposite in the two kinds of experiment.

Both normal and tangential gas streams were employed by the author in 1891, and Jablczyński and Przemyski's results are in better accord with the laws then established the more nearly their experimental conditions approximate to his. R. J. C.

Thermal Analysis. FRANCESCO OLIVARI (*Chem. Zentr.*, 1913, i, 2001; from *Rendiconti Soc. Chim. Ital.*, 1911, **5**).—Rudolfi (A., 1909, ii, 536) found no halt points in certain binary mixtures of organic compounds, and inferred partial isomorphism. Such points are now shown to exist in some of his cases. In the case of the system *m*-dinitrobenzene-naphthalene, an equimolecular compound exists which is strongly dissociated in the fused mass. A mathematical consideration is elaborated for the existence of compounds in the liquid phase which cannot be separated in the solid state. E. F. A.

Heat of Formation of the Oxides and Sulphides of Iron, Zinc, and Cadmium. Heat of Combination of Acidic Oxides with Sodium Oxide. IX. WILLIAM G. MIXTER (*Amer. J. Sci.*, 1913, [iv], **36**, 55—69. Compare A., 1912, ii, 899, and earlier abstracts).—The results of this work may be summarised as follows: $Fe + O = FeO + 64,300$ cal.; $2Fe + 3O = Fe_2O_3$ (faint red) $+ 192,200$ cal.; $3Fe + 4O = Fe_3O_4$ (magnetite) $+ 265,700$ cal.; $3Fe + 4O = Fe_3O_4$ (fused) $+ 265,200$ cal.; $2FeO + O = Fe_2O_3 + 63,700$ cal.; $2Fe_3O_4 + O = 3Fe_2O_3 + 54,500$ cal.; $FeO + Fe_2O_3 = Fe_3O_4$ (magnetite) $+ 9200$ cal.; $Fe_2O_3 + xNa_2O = Fe_2O_3,xNa_2O + 58,000$ cal.; $Fe + S = FeS$ (amorph.) $+ 18,800$ cal.; FeS (amorph.) $+ S = FeS_2$ (cryst.) $+ 16,700$ cal.; $Zn + S$ (rhombic) $= ZnS$ (cryst.) $+ 41,300$ cal.; $CdO + Na_2O = Na_2CdO_2 + 6500$ cal. (approx.); $Cd + O = CdO$ (amorph.) $+ 57,000$ cal.; $Cd + O = CdO$ (mostly cryst.) $+ 63,000$ cal.; $Cd + S$ (rhombic) $=$ CdS(cryst.) $+ 34,000$ cal.

Ferrous oxide can be obtained free from carbon or iron carbide by heating ferrous oxalate in a current of dry nitrogen. The temperature is gradually raised, until after four hours it is about 520° and carbon dioxide has ceased to be evolved. The temperature is then raised to 900°, and maintained at this point for an hour. The product thus obtained appears to be a mixture of FeO (4 mols.) and Fe (1 atom).

Reddish-brown, amorphous cadmium oxide volatilises or dissociates slowly at 900—1000°, but the rate of loss diminishes as the oxide becomes denser and crystalline. E. G.

The Heats of Formation of Some Silicates of Iron and Manganese. S. WOLOGDINE (*Compt. rend.*, 1913, **157**, 121—123).—The author has determined the heats of formation of silicates of

iron and manganese, starting with pure quartz and ferrous oxide and manganous carbonate respectively. The figures he obtained for the molecular heats of formation are, for FeO,SiO_2, 5905 cals., and for MnO,SiO_2, 7725 cals., allowance being made in the latter case for the heat of dissociation of the manganous carbonate with formation of the oxide. W. G.

Relation Between the Thermal Effect which Accompanies the Immersion of Dry, Powdered Substances in Liquid Substances and the Aptitude of the Latter to Form Associated Molecules. HENRY GAUDECHON (*Compt. rend.*, 1913, **157**, 209—211).—The author has determined the amount of heat evolved per gram of dry powder on plunging a dried, powdered substance into a liquid without action on it. Four powders were used, and numerous liquids were examined. From the results the liquids arrange themselves in much the same order as from a study of the Pictet-Trouton coefficient LM/T, or the Ramsay-Shields coefficient K. The more abnormal the liquid with respect to these two laws, the more heat is evolved in the experiment. With normal liquids, the thermal effect is practically zero. From the results, it appears that the thermal effect depends principally (1) on the abnormal nature of the liquid; (2) on the area of the solid surface with respect to the weight of the solid, the greater part of the thermal effect being attributable to the aggregation or polymerisation of the molecules of the liquid at the surface of the solid. W. G.

Characterisation of Flame. NICOLAE TECLU (*J. pr. Chem.*, 1913, [ii], **88**, 189—192).—The author criticises the use of the term "flameless combustion" in connexion with the surface combustion of inflammable gaseous mixtures, and maintains that the combustion of the latter is invariably accompanied by the production of flame.

The invisibility of the flame in the surface combustion of inflammable gas mixtures is due to the luminosity of the flame being very feeble in comparison with that of the heated surface at which the combustion occurs. F. B.

Two Small Corrections to be Applied to Densities of Gases Determined at Geneva. PHILIPPE A. GUYE (*J. Chim. phys.*, 1913, **11**, 319—326).—Recent measurements of gaseous densities at Geneva by the bulb method have shown a variation of less than 1 in 10,000. In reducing the weighings to vacuum standard at sea level in latitude 45° the normal weight of 1 c.c. of air has been assumed to be 0·00117 gram, and the gravity constant 980·616, and the platinum fractions have been corrected to vacuum standard independently of the brass gram weights. The first correction is not justified without taking into account the pressure, temperature, and humidity of the air at the time of weighing, and as the platinum fractions are standardised in air against brass, the whole of the weights should be considered as brass in applying vacuum corrections. The necessity for vacuum corrections is largely avoided

if the uncorrected tare of the bulb under similar meteorological conditions is known.

The most recent determinations of the gravity constant at Geneva, made in 1894 by Messerschmitt, gave $g = 980 \cdot 600$, corresponding with an error in the previous corrected values of 16/1,000,000. A table is given of the total correction to be applied to various weights of gas on account of these considerations. The correction on 1 gram of gas, for instance, is 0·000068 gram, but there are other sources of error in bulb measurements which render these small corrections to some extent illusory. R. J. C.

Specific Gravity and Displacement of Some Saline Solutions. JOHN Y. BUCHANAN (*Trans. Roy. Soc. Edin.*, 1912, **49**, 1—225).—An account is given of the determination of the specific gravity of solutions of the iodides, bromides, chlorides, nitrates, iodates, bromates, and chlorates of potassium, rubidium, and cæsium at temperatures 15·0°, 19·5°, 23·0°, and 26·0°, the values being referred to water at the same temperatures as unit. Determinations were also made with solutions of sodium chloride, calcium chloride, magnesium chloride, and glucinum chloride. The concentrations of the solutions varied from solutions containing 1/1024 of the gram-molecular weight in 1000 grams of water to those containing 9 gram-molecular weights in the same weight of water. In the case of the calcium chloride determinations, measurements were made with supersaturated solutions. All the determinations of solutions containing less than half molecular weight were made by specially prepared hydrometers, the more concentrated solutions were determined by means of a pyknometer, and for the supersaturated solutions the hydrometer was again used. A long description of the preparation of the hydrometer and its standardisation is given; this instrument resembles that used by the author on the *Challenger* Expedition. A description is also given of an open hydrometer for use with solutions of high specific gravity. The author considers the relationships between the displacement increments of analogous salts with change of concentration and the specific gravity of salts of nearly the same molecular weight, for example, RbCl, KBr, and K(Cl + I)/2, which are generally found to be very much alike. The specific gravity of solid potassium chloride, bromide and iodide, rubidium chloride, bromide and iodide, cæsium chloride, bromide and iodide, potassium chlorate, bromate and iodate, rubidium chlorate, bromate and iodate, and cæsium chlorate, bromate and iodate are also determined. This is effected by weighing the crystals in their own saturated mother liquor at the saturation temperature in a specific gravity bottle. The following values, compared with water at the same temperature, are obtained at temperatures 24·3—22·8°: KCl, 1·951; KBr, 2·679; KI, 3·043; RbCl, 2·706; RbBr, 3·210; RbI, 3·428; CsCl, 3·982; CsBr, 4·455; CsI, 4·508; $KClO_3$, 2·319; $KBrO_3$, 3·219; KIO_3, 3·924; $RbClO_3$, 3·176; $RbBrO_3$, 3·681; $RbIO_3$, 4·336; $CsClO_3$, 3·582; $CsBrO_3$, 4·109; and CsI, 4·849. The specific gravities of the solutions are given to six places of decimals,

and it is shown that in many cases there is a probable error of only one or two units in the sixth place. Finally a series of factors is given for converting the values of ${}_tS_t$ to ${}_{4^\circ}S_t$. In the determination of the specific gravity of supersaturated solutions of calcium chloride, the values fluctuated a great deal owing to rapid internal changes of temperature, from which it is deduced that the solution is internally in a state of unrest, which the author compares to the state of a gas or liquid at the critical temperature when under a pressure greater than the critical pressure. J. F. S.

Viscosity of Gases at Low Temperatures. I. Hydrogen. H. KAMERLINGH ONNES, C. DORSMAN, and SOPHUS WEBER (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 1386—1396).—The viscosity of hydrogen has been determined by the transpiration method from the temperature of solid carbon dioxide down to that of liquid hydrogen. The results are calculated on the basis of O. E. Meyer and Knudsen's formula. The results are recorded in a table along with those of Markowski and Kopsch (A., 1904, ii, 652). The value of $\eta \times 10^7$ is compared with the value calculated from Sutherland's formula, using the values $\eta_0 = 841{\cdot}10$ and $C = 83$. It is shown that there is a very great divergence at the lower temperatures between the observed and calculated values, which amounts to more than 100% at the temperature of liquid hydrogen. The authors deduce the formula $\eta = \eta_0(T/273)^{0{\cdot}695}$ to represent the relationship between viscosity and temperature. This formula is applied to the present results and to those of Markowski and Kopsch (*loc. cit.*), and gives good agreement over the whole range of temperature. J. F. S.

Viscosity of Gases at Low Temperatures. II. Helium. H. KAMERLINGH ONNES and SOPHUS WEBER (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 1396—1399. Compare preceding abstract).—The viscosity of helium is determined at temperatures from that of solid carbon dioxide to that of liquid helium by the transpiration method. The values of $\eta \times 10^7$ are given, and diverge widely from those calculated by the Sutherland formula. The relationship between viscosity and temperature is expressed by the formula $\eta/\eta_0 = (T/273{\cdot}1)^{0{\cdot}647}$, which gives calculated values agreeing over the whole temperature range with the experimental values.

J. F. S.

Viscosity of Gases at Low Temperatures. III. Comparison of the Results Obtained with the Law of Corresponding States. H. KAMERLINGH ONNES and SOPHUS WEBER (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 1399—1403. Compare preceding abstracts).—A theoretical paper, in which the dependence of viscosity on temperature is discussed. The viscosities of two mechanically similar systems are shown to give a constant ratio, which can be calculated from the expression $-\frac{1}{2}\log \eta/\sqrt{T\sqrt{M}} = \log \sigma - \log c$, in which M is the molecular weight, σ the mean radius of a molecule, and c a constant which is the same for all substances.

J. F. S.

Method of Measuring the Viscosities of Vapours of Volatile Liquids, with an Application to Bromine. ALEXANDER O. RANKINE (*Proc. Roy. Soc.*, 1913, *A*, **88**, 575—588).—The author, making use of O. E. Meyer's transpiration formula, has devised a method of determining the viscosity of vapours of volatile liquids. The apparatus consists of two U-tubes of about 2 mm. internal diameter connected at one end to a capillary tube of 0·018 cm. diameter and 39 cm. long. One U-tube is filled with the liquid under examination, and the apparatus is exhausted and sealed. The U-tubes are placed in baths at known temperatures, one to evaporate the liquid, and the other to condense it. The capillary is placed in a third bath, which represents the experimental temperature. Experiments were carried out with bromine at temperatures from 13° to 220°, and the viscosity was determined; this quantity increases with temperature, and has the values in C.G.S. units at 12·9°, $1·511 \times 10^{-4}$; 65·8°, $1·705 \times 10^{-4}$; 99·8°, $1·885 \times 10^{-4}$; 139·8°, $2·079 \times 10^{-4}$; 179·8°, $2·273 \times 10^{-4}$; and 220·4°, $2·480 \times 10^{-4}$. The author is able to calculate his values from Sutherland's equation, and with the exception of two values at the lowest temperatures, to obtain very good agreement. The values agree well with those obtained by the author by another method (A., 1912, ii, 332). J. F. S.

Determination of the Viscosity of Caoutchouc Solutions. PHILIP SCHIDROWITZ and H. A. GOLDSBROUGH (*Kolloid. Zeitsch.*, 1913, **13**, 46—48).—Polemical. The authors criticise changes made in their method of viscosity determination by Fol (this vol., ii, 301). J. F. S.

Stalagmometric Studies of Solutions of Colloids and Crystalloids. I. L. BERCZELLER (*Biochem. Zeitsch.*, 1913, **53**, 215—231). —The surface tensions of protein solutions which are sufficiently free from salts not to coagulate on heating, diminish strongly on boiling. On keeping, however, the surface tension increases again. The phenomenon can be explained on the assumption that a change in the size of the particles takes place. The surface tension of water is diminished by albumoses (Witte's or Grübler's peptone). These substances diminish the surface tension of a trypsin solution less than they do that of distilled water. The surface tension of a trypsin-albumose solution is not constant, but progressively increases on keeping, at first rapidly, then more slowly. The trypsin appears to form an unstable compound with the albumose, which is then hydrolysed. Pepsin acts in a manner similar to trypsin. During hydrolysis with trypsin and pepsin, the surface tension strongly diminishes, the amount of diminution running parallel with the amount of albumose formed. S. B. S.

Stalagmometric Studies of Solutions of Colloids and Crystalloids. III. L. BERCZELLER and L. CSÁKI (*Biochem. Zeitsch.*, 1913, **53**, 238—255).—The authors confirm generally the results of Traube, who has shown that the addition of small quantities of

alkali to solutions of salts of alkaloids diminishes the surface tensions of the solutions, increasing at the same time the toxicities. With the aggregation of the alkaloid in colloidal solution, which takes place on keeping, and more rapidly on warming than in the cold, the surface tensions again increase, whilst the toxicity diminishes. The alkaloids of the morphine series are an exception to this rule, as this is probably due to the chemical constitution of the substance, which has some relation to the surface-tension effects. A similar effect to the majority of alkaloids is observed when salicylic acid is separated from its salts by means of acids. This, again, is probably due to the existence of the free acid in colloidal solution. The adsorption of alkaloids by various adsorbents from alkaline solutions was also studied. By adsorption of the colloidal substance, the surface tension of the solutions was increased. S. B. S.

Stalagmometric Studies of Solutions of Colloids and Crystalloids. II. L. Berczeller (*Biochem. Zeitsch.*, 1913, **53**, 232—237).—Pure caseinogen has no marked action on the surface tension of water. On boiling, however, the surface tension of water is diminished, and apparently a certain amount of hydrolysis takes place. If the caseinogen is dissolved in acids or alkalis, the surface tension of water is diminished considerably; the stronger the acid or alkali, the greater being the amount of diminution. S. B. S.

Adsorption in Solutions, and the Chemical Processes Brought About Thereby. Adsorption in Aqueous Solutions of Potassium Dichromate and Potassium Chromate by Animal Charcoal. Tadeusz Oryng (*Kolloid. Zeitsch.*, 1913, **13**, 9—14. Compare A., 1912, ii, 1145).—It is shown that potassium dichromate is strongly absorbed by animal charcoal, and that the absorption consists mainly in the absorption of $H_2Cr_2O_7$, which is probably converted into chromic hydroxide by reaction with the charcoal. It is found that after shaking for five minutes the Cr_2O_7'' concentration has decreased by 17·99%, and the $K^{\cdot}$ concentration by 3·2%. The adsorption is much increased by the presence of 0·1*N*-hydrochloric acid, and in this process chromic ions are found in the solution. Sodium hydroxide retards the adsorption, and when the concentration 0·3*N* is reached entirely prevents it. This is attributed to the conversion of the dichromate into chromate, which, the author shows, is not adsorbed at all.
J. F. S.

Negative Adsorption. Tadeusz Oryng (*Kolloid. Zeitsch.*, 1913, **13**, 14—16. Compare preceding abstract).—It is shown that on shaking potassium dichromate containing 0·3NaOH with purified animal charcoal, an increase in the concentration amounting to 6·5% occurs. This increase is independent of the time of shaking, and is uninfluenced by the addition of 1·2—0·15 molar sodium hydroxide, but more dilute solutions cause a positive adsorption. The amount of negative adsorption increased in proportion to the

amount of charcoal used. The change is explained by the assumption that there is an increased water concentration on the surface layer. J. F. S.

Colloidal Constituents of Clay. PAUL ROHLAND (*Kolloid. Zeitsch.*, 1913, **13**, 62—63).—The author advances evidence to show that the absorption of organic colouring matters is dependent on their structure. Those dyes derived from azo- or diazo-compounds are but slightly adsorbed by alumina. Thus it is shown that to absorb 0·003 gram of the following dyes, different quantities of alumina are required. Aniline-blue, victoria-blue, violet, and diamond-green require 5 grams; orange and vesuvine, 10 grams; and metanil-yellow, 30 grams. The yellow dye substance contained in the wash water of the sulphite cellulose manufacture is not absorbed at all. J. F. S.

Kinetic Theory of Osmotic Pressure. GUSTAV JÄGER (*Ann. Physik*, 1913, [iv], **41**, 854—865).—The author has deduced from the analogy between a gaseous mixture of a compressed gas containing a small quantity of a second gas, and a solution, a kinetic theory of osmotic pressure, and from this developed mathematically the usual expressions for osmotic pressure and lowering of the freezing point of solutions. J. F. S.

The Strenuous Period in the Development of the Theories of Solution. SVANTE ARRHENIUS (*Chem. Weekblad*, 1913, **10**, 584—599).—An interesting autobiographical sketch, including an account of the evolution of the ionic theory, and of the criticism it evoked. A. J. W.

Classification of the Colloids. RICHARD ZSIGMONDY (*Eighth Inter. Cong. App. Chem.*, 1912, **22**, 263—274).—The various ways which have been proposed for classifying the colloids are reviewed, and a new scheme is put forward based on the behaviour of the colloid solutions on evaporation to dryness. The colloids are divided into (1) "resoluble" colloids, which, on evaporation of their solutions, yield a residue completely soluble in the dispersion medium, and (2) "irresoluble" colloids, which furnish a partly or completely insoluble residue owing to the occurrence of irreversible changes of state during the drying process. The first class is subdivided into (*a*) those which require the application of heat for the preparation of solutions, such as gelatin, starches, agar-agar, and many soaps, and (*b*) those which do not require to be heated, such as dextrin, gum arabic, Paal's colloidal metals, Graham's tungstic and molybdic acids, molybdenum-blue, and albumin. The irresoluble colloids are also of two kinds: (*a*) those which during drying yield pulverulent precipitates which are no longer peptisable, including pure metal colloids, certain sulphides, and salts, such as silver bromide and chloride, and (*b*) those which suffer an irreversible transformation on drying, and give peptisable jellies, such as stannic acid, silicic acid, and ferric oxide.

The classification of dispersed systems is also discussed. E. G.

Influence of Surface-active Substances on the Stability of Suspensoids. HUGO R. KRUYT (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 1344—1349).—The influence of *iso*amyl alcohol, *iso*butyl alcohol, propyl alcohol, and ethyl alcohol on the limitation value of the absorption value of arsenic sulphide sols for barium chloride is investigated. The sol is shaken with the organic solvent, and then with sufficient barium chloride solution, so that the sol shall not be completely coagulated. The concentrations are found to increase with increasing concentration of the alcohol, that is, the limitation value is increased. The greatest increase is observed in the case of *iso*amyl alcohol, the others being, in decreasing order, *iso*butyl alcohol, propyl alcohol, and ethyl alcohol. This order is the same as that in which the substances reduce the surface tension of water. Some preliminary experiments with phenol are described which comes between *iso*butyl alcohol and propyl alcohol in its action. J. F. S.

The Formula Expressing the Reduction in the Value of the Quantity *b* in the Equilibrium Equation with Diminution of Volume. JOHANNES D. VAN DER WAALS (*Chem. Weekblad*, 1913, **10**, 628—634).—A theoretical paper. A. J. W.

Equilibria in Ternary Systems. VI. FRANS A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 1298—1312).—A theoretical paper, in which the considerations of the previous papers are continued for the complex, solid–gas. The various transformations of the system are considered. J. F. S.

Equilibria in Ternary Systems. VII. FRANS A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 1313—1326. See preceding abstract).—A theoretical paper, in which the behaviour of the systems containing two solid phases is considered under various changes of external conditions. J. F. S.

Equilibria in Quaternary Systems. IX. Quaternary Systems with Ternary Mixed Crystals with a Gap of Miscibility. NICOLA PARRAVANO (*Gazzetta*, 1913, **43**, i, 594—608. Compare this vol., ii, 571).—A mathematical discussion of this subject. R. V. S.

Intramolecular Transformations. VI. Influence of the Solvent on the Equilibrium and the Velocity of Transformation. OTTO DIMROTH (*Annalen*, 1913, **399**, 91—119).—The author has previously shown, by experiments on the methyl and ethyl esters of 5-amino-1-phenyl-1 : 2 : 3-triazole-4-carboxylic acid and their intramolecular transformation products, methyl and ethyl 5-anilino-1 : 2 : 3-triazole-4-carboxylates, that the displacement of the state of equilibrium, which a chemical system experiences through the influence of the solvent, is not dependent on any physical constant of the solvent, but is related to the solubilities of the reacting molecules. This relation is expressed by the

equation $c_A/c_B = Kl_A/l_B$, where c_A and c_B are the concentrations of the two modifications in the state of equilibrium, l_A and l_B are the solubilities, and K is a constant which is independent of the nature of the solvent

In order to verify this important relation and to widen the region of its applicability, two other pairs of structural isomerides have been examined, namely, methyl 5-hydroxy-1-methyl-1 : 2 : 3-triazole-4-carboxylate and methyl diazomalonmethylamide, and the ketonic and enolic modifications of benzoylcamphor. In the former pair of isomerides, in methyl alcohol, benzyl alcohol, acetone, ethyl acetate, ethyl nitrate, and nitrobenzene at 18°, although c_A/c_B (where A denotes the neutral isomeride, methyl diazomalonmethylamide) varies between 3·27 and 99 and l_A/l_B between 6·29 and 171·3, the value of K only varies between 0·52 and 0·68. This variation from constancy is attributed to the errors unavoidably introduced, partly by the enormously great solubility of the neutral isomeride as compared with that of the acidic form, partly by the fact that the value of c_A/c_B at 18° can only be obtained by extrapolation, the time required to attain equilibrium being thirty to forty days even at a temperature as high as 50°.

Similarly with the two forms of benzoylcamphor at 0° in ether, ethyl acetate, ethyl alcohol, methyl alcohol, and acetone, c_A/c_B (where A denotes the enolic modification) varies between 0·852 and 6·81, l_A/l_B between 0·748 and 6·39, and K between 1·06 and 1·15. The two varieties of benzoylcamphor are obtained by modifications of Forster's method (T., 1901, **79**, 987); the ketonic form has m. p. 112° (Forster, 87—88°), and the enolic form, 90—91° (Forster, 89°).

Since $c_A/c_B > l_A/l_B$ at 0°, it follows that enolic modification of benzoylcamphor is stable in the crystalline state. This is verified experimentally by dilatometric method, whereby it is shown that the ketonic form changes to the enolic by long keeping. The transition temperature at which $c_A/c_B = l_A/l_B$, and therefore $K = 1$, in other words, the temperature at which both forms can co-exist in the crystalline state, cannot be determined experimentally, but lies below $-10°$.

The author offers some interesting remarks concerning the relations between the solubilities and the constitutions of organic substances. These remarks can only be mainly speculations in the present state of our knowledge, but the author suggests that the solubility is a constitutive property in the sense that it is the product of factors each of which corresponds with each of the atomic groupings of which the molecule is composed. C. S.

System Oxalic Acid, Ammonium Oxalate, and Water at 30° and 45°. HERMAN W. WOUDSTRA (*Eighth Inter. Cong. App. Chem.*, 1912, **22**, 251—257).—Three well-defined ammonium oxalates are known, namely, the normal oxalate, $C_2O_4(NH_4)_2,H_2O$, the hydrogen oxalate, $CO_2H{\cdot}CO_2{\cdot}NH_4,H_2O$, and the tetroxalate, $C_2O_4H_2,CO_2H{\cdot}CO_2{\cdot}NH_4,2H_2O$. The equilibria have been studied which occur when mixtures of oxalic acid and ammonium oxalate

in different proportions are shaken with water at constant temperatures.

The isotherms of the system ammonium oxalate, oxalic acid, and water have been determined at 30° and 45°. The solubilities of oxalic acid at these temperatures are 12·59 and 21·015 grams respectively in 100 grams of solution, and those of normal ammonium oxalate are 5·53 and 8·3 grams respectively in 100 grams of solution. A saturated solution of normal ammonium oxalate deposits the tetroxalate both at 30° and at 45°. Graphical determinations of the solubility of the tetroxalate have shown that it is soluble to the extent of 7·21 grams in 100 grams of solution at 30°, and 11·12 grams at 45°. E. G.

Applications of the Partition Law. WALTHER HERZ and W. RATHMANN (*Zeitsch. Elektrochem.*, 1913, **19**, 552—555).—The partition coefficient of bromine, iodine, phenol, and acetone is determined between water and a number of aliphatic chlorinated hydrocarbons. From the results of the experiments at 25°, it is shown that bromine and iodine have normal molecular weights in tetrachloroethane, pentachloroethane, trichloroethylene, and tetrachloroethylene. Phenol is bimolecular in chloroform, tetrachloroethane, pentachloroethane, trichloroethylene, and tetrachloroethylene, and exists as bi- and ter-molecular complexes in carbon tetrachloride. Acetone is bimolecular in carbon tetrachloride and tetrachloroethylene, unimolecular in trichloroethylene, and forms complexes with chloroform pentachloroethane and tetrachloroethane. J. F. S.

Gradual Hydrolysis. II. CARL L. WAGNER (*Monatsh.*, 1913, **34**, 931—948. Compare this vol., ii, 200).—The author has examined dilute solutions of ferric chloride by means of an ultramicroscope, with and without the presence of potassium sulphate. It is shown that the gradual hydrolysis, as followed under the microscope, confirms the hypothesis put forward (*loc. cit.*) with regard to the gradual increase in the electric conductivity of ferric chloride solutions. The ratio between the surface of the colloidal particles at $t=0$ and $t=15$ is calculated, and this value agrees well with the corresponding ratio obtained from the electric conductivity. Similar experiments were carried out with zirconium nitrate, and the results obtained were found to be analogous to those obtained for ferric chloride. J. F. S.

Studies in the Speed of Reduction. MORRIS LOEB (*Eighth Inter. Cong. App. Chem.*, 1912, **26**, 601—604).—A study has been made of the effect of aluminium chloride on the behaviour of ferric chloride towards stannous chloride by a method similar to that employed by Noyes (A., 1895, ii, 257; 1897, ii, 17) in his investigation of the rate of reaction between ferric chloride and stannous chloride, and has shown that the rate of reaction between the two salts in $N/20$-concentration is more than doubled when aluminium chloride is present in $N/20$-concentration, whilst in presence of $N/10$-aluminium chloride the rate is quadrupled. Manganous

chloride and glucinum chloride in $N/20$-concentration also double the speed of the reaction, whilst a $N/20$-quadrivalent thorium solution does not cause so great an acceleration.

When a solution of ceric sulphate is left under ordinary conditions, it gradually undergoes reduction to the cerous state. The rate of reduction is increased by dextrose, but the reaction does not follow a logarithmic law, the amount of cerium reduced being simply proportional to the time. When lanthanum sulphate or thorium sulphate is added to the ceric solutions, they exert an unmistakable influence on the rate of reduction by dextrose.

The variation in the velocity of these reactions seems to be due to a specific influence of the metals concerned, and probably indicates the formation of complex bases. E. G.

Contributions to the Chemical Kinetics of Enzymes. Kikunaë Ikeda (*Eighth Inter. Cong. App. Chem.*, 1912, **22**, 157—167).—The exact study of enzyme actions is rendered difficult owing to the gradual decay of the enzyme during the course of the experiments. Certain problems relating to the decay of the enzyme in the presence of the substratum are now discussed from a theoretical point of view. The case in which the velocity of the destruction of the enzyme is proportional to that of the transformation of the substratum is considered in detail, and certain deductions are made which are confirmed by Yamasaki's work on catalase.

The problem of the optimum temperature is also dealt with, and the relation between this temperature and the temperature-coefficient of the decay of the enzyme is elucidated. E. G.

Catalytic Studies. IV. H'-ion Catalysis and Autocatalysis of the Modified Hydrogen Peroxide–Thiosulphate Reaction. Emil Abel (*Monatsh.*, 1913, **34**, 821—881. Compare this vol., ii, 399).—It is shown that the reaction between hydrogen peroxide and sodium thiosulphate in the presence of molybdic acid yields sulphate instead of tetrathionate according to the equation $4H_2O_2 + S_2O_3'' \longrightarrow 2SO_4'' + 2H^{\cdot} + 3H_2O$. This reaction is accelerated by $H^{\cdot}$ ions in proportion to their concentration. The coefficient of acceleration is given by $3{\cdot}5 \times 10^7$ at 25°, when the units are, time in minutes, and weights in gram-equivalents. The velocity of the sulphate formation is expressed by the equation $-d[H_2O_2]/dt = (1{\cdot}5 \times 10^3 + 3{\cdot}5 \times 10^7[H^{\cdot}])[MoO_3][Na_2S_2O_3]$. Since this reaction itself furnishes $H^{\cdot}$ ions, the change becomes autocatalytic. The velocity of the reaction in the presence of acetic acid and sodium acetate, added to define the $H^{\cdot}$-ion concentration, is given by the expression:

$$-d[H_2O_2]/dt = dy/dt = \{1{\cdot}5 \times 10^3 + 3{\cdot}5 \times 10^7 k((CH_3{\cdot}CO_2H) + y/4)/\alpha[(CH_3{\cdot}CO_2Na) - y/4]\}{\cdot}[MoO_3][(Na_2S_2O_3) - y/8],$$

in which the quantities in round brackets represent initial concentrations, α the degree of dissociation of the acetate, and k the dissociation constant of the acetic acid. This equation admits of values being calculated which are in close agreement with the experimentally determined values. When the conditions of the

reaction are so chosen that the formation of both sulphate and tetrathionate occur simultaneously, the hydrogen-ion concentration is affected by both, the former producing hydrogen ions, and the latter removing them. The effect of the tetrathionate formation is consequently to retard the autocatalytic action of the hydrogen ion, and this can proceed so far as to convert a positive autocatalysis into a negative autocatalysis. With respect to the mechanism of the reaction, it is suggested that the catalysis is brought about by an oxidation, and that a highly dissociated permolybdic acid is produced as an intermediate product.

J. F. S.

The Intervention of the Number π in the Relationships between Atomic Weights. P. DAMBIER (*J. Chim. phys.*, 1913, **11**, 260—266).—Two types of arithmetical relationship involving the number π exist between atomic weights. The first type, $R_1/R_2=\pi/n$, where n is an integer, is exemplified in the ratio $3I/(Cl+Br+I)=3{\cdot}1417/2$, using Stas's atomic weights. The second type is $(M\pm n\pi)/(M'\pm n'\pi)=a/b$, where M and M' are molecular weights, and n, n', a, b simple integers. An example is $(HCl+2\pi)/(NH_3-2\pi)=4$, which leads to a value $\pi=3{\cdot}1416$ when the Geneva atomic weights are used instead of Stas's. It is urged that the intervention of π in these relationships is significant of some general connexion between the elements, but it must be assumed that atomic weights vary according as the atoms are neutral or ionised.

R. J. C.

The Intervention of the Number π in the Relationships Between Atomic Weights. PHILIPPE A. GUYE (*J. Chim. phys.*, 1913, **11**, 267—268).—Such considerations as those put forward by Dambier (preceding abstract) and by Nicholson (A., 1912, ii, 35) must certainly be taken account of in the study of atomic relationships.

R. J. C.

Theory of Electrical and Chemical Atomic Forces. ALFRED BYK (*Ber. Deut. physikal. Ges.*, 1913, **15**, 524—533).—A mathematical paper in which the author propounds a theory of the atom in which no structural hypotheses are contained. The applications of the theory to the physics and chemistry of the atom are indicated. The heat of dissociation of the chemical molecules and their cross section are calculated on the theory and compared with experimental results.

J. F. S.

Molecular Compounds as Primary Stages of Chemical Reactions. CARL ENGLER (*Eighth. Inter. Cong. App. Chem.*, 1912, **25**, 131—140).—Evidence is adduced in support of the view that in many chemical reactions the reacting molecules first unite to form molecular compounds. Attention is directed particularly to the question of oxidation, and the author's theory expressed in his papers on autoxidation is emphasised, namely, that oxidation generally takes place by direct attachment of a molecule of oxygen

leading to the formation of a peroxide. This theory is confirmed by a series of investigations carried out by the author and his co-workers on the oxidation of organic compounds, such as the fulvenes and ketens. The course of the reaction in the formation of peroxides can be represented by the three following stages: (1) M:O:O (asymmetrical), (2) $M<\overset{O}{\underset{O}{|}}$ (symmetrical), and (3) $M\ll\overset{O\cdot}{\underset{O}{}}$

The asymmetrical oxide passes spontaneously, as a rule, into the symmetrical form, which is but rarely transformed into the stable modification (3). Hydrogen peroxide and ozone are quoted as examples of the first form, and barium peroxide and lead peroxide as examples of the second and third respectively. The second (and first) form corresponds with Schönbein's "autozonides" and the third form with his "ozonides." E. G.

Electron Conception of Valence. III. Oxygen Compounds. JOHN M. NELSON and K. GEORGE FALK (*Eighth Inter. Cong. App. Chem.*, 1912, **6**, 212—221. Compare A., 1911, ii, 104, 711).—The consideration of the direction of the valencies is extended to oxygen compounds. Owing to the pronounced electronegative character of oxygen, the problem is simpler than in the case of carbon, for in most cases the valencies can be assumed to be directed toward the oxygen atom, this having taken up two electrons, either from the same atom or two similar or different atoms. Tautomerism is due to the replacement of a hydrogen atom and the redistribution of the valencies of the other atoms, the oxygen atom always having two valencies directed towards it. The isomerism of the benzopinacolins should also be regarded as a case of tautomerism, the only difference being that a phenyl group migrates.

In the case of isomeric ketones, however, it is necessary to assume that the valencies in the carbonyl group are not both directed towards the oxygen atom. The symbol $C \rightrightarrows O$ is assigned to the more stable form, and $C \rightleftarrows O$ to the unstable.

The tautomeric forms of hydrogen peroxide are represented by the formulæ $H \rightarrow O \rightarrow O \leftarrow H$ and $\begin{matrix} H \searrow \\ H \nearrow \end{matrix} O \rightrightarrows O$. The formulation of hydrates is exemplified with nickel chloride as type. J. C. W.

The Conception of Valency as an Electronic Action. K. GEORGE FALK and JOHN M. NELSON (*J. pr. Chem.*, 1913, [ii], **88**, 97—128).—The views expressed in this paper have already been published (A., 1911, ii, 104, 711, and preceding abstract). F. B.

Reminiscences of R. W. Bunsen. WILLEM A. VAN DORP (*Chem. Weekblad*, 1913, **10**, 600—603).—An account of the author's personal experiences as a student in the Heidelberg laboratories under Bunsen in 1869. A. J. W.

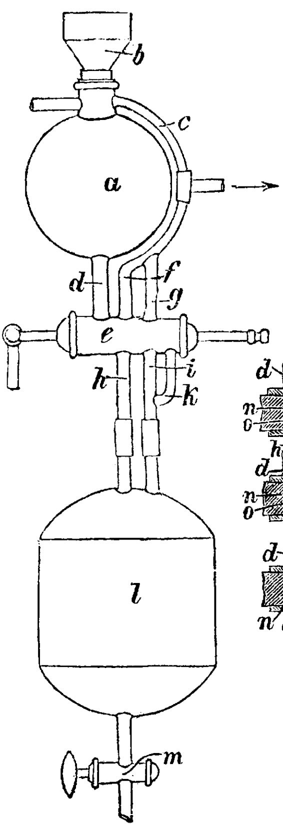
The Ring Figures in Frozen Gelatin. HUGO ROHONYI (*Biochem. Zeitsch.*, 1913, **52**, 210—214).—If solutions of gelatin are poured into

a test-tube and then poured out again, and the thin layers of the solutions adhering to the glass are then frozen by the method described by the author, characteristic ring figures are formed, which are illustrated in the text. These are similar to Liesegang's figures obtained when silver nitrate is dropped into a film of potassium dichromate solution in gelatin. Ostwald's explanation of the Liesegang figures is quoted, and it is assumed that this also explains the phenomena with frozen gelatin recorded by the author.

S. B. S.

Combined Distillation Apparatus. LENHARD (*Zeitsch. angew. Chem.*, 1913, **26**, 431).—A piece of apparatus is described which may be used for reflux and condensing operations. In the first case, the condenser is arranged vertically, and its lower end is attached to the flask by means of a short length of tube the ends of which form ground-in joints with the condenser tube and a tube sealed into the glass stopper of the flask; a tapped funnel is also sealed into the stopper. When required for distillation, the condenser is inclined and attached to the flask by means of a bent tube, the ends of which also form ground-in joints with the flask and condenser. W. P. S.

Fig 1



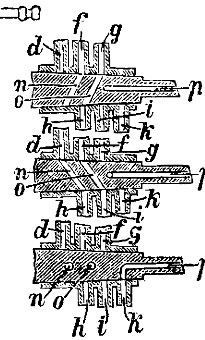


Fig. 2

Fig. 3

Fig. 4

New Vacuum Filtering Apparatus for Continuous Filtration. WALTER DECKERT (*Zeitsch. anal. Chem.*, 1913, **52**, 547—548).—The apparatus (see Fig. 1) consists of two reservoirs *a* and *l*, which are connected by means of a multiple-way stopcock *e*. On the reservoir *a* is placed the funnel *b*. The stopcock has three channels, of which two, *n* and *o*, run in an oblique direction parallel to each other (Figs. 2 and 3), whilst the third, *p*, terminates in an axial tube

giving communication with the outer air (Fig. 4). When the stopcock is placed in the position indicated in Fig. 2, the reservoir *l* is exhausted during the filtration in the passage *c g h l*; in the position in Fig. 3, the vacuum in reservoir *l* is obtained in the passage *c f i l*, whilst the filtrate runs through the passage *d h l* into the reservoir *l*. On placing the stopcock in the position indicated by Fig. 4, the outer air enters through the passage *p k l* into the lower reservoir, from which the liquid may then be run into a vessel by opening tap *m*. The bores in the stopcock are so arranged that in order to carry out the required manipulations, the stopcock has only to be turned like the hands of a clock; twice in succession 90°, once 180°.

The chief advantage of the apparatus is the withdrawal of filtrate without disturbing the filtering process. L. DE K.

Universal Extraction Apparatus. HAHN (*Chem. Zeit.*, 1913, **37**, 880).—A modified form of apparatus serving for the extraction of solid matters as well as for heavy or light liquids, and requiring but little solvent. L. DE K.

Lecture Experiment. An Apparatus for the Volumetric Synthesis of Water. MILAN J. STRITAR (*Chem. Zeit.*, 1913, **37**, 860).—The author describes a modified Hofmann apparatus for demonstrating the volumetric composition of water. It is claimed that the apparatus can be filled with mercury by one person without assistance, that it is easily obtained free from air, and that a comparatively small quantity of mercury (1·5 kilo.) is required to fill it. J. F. S.

Inorganic Chemistry.

Review of the Determinations of the Atomic Weight of Chlorine. The Atomic Weight of Silver. General Considerations on the Determination of Atomic Weights. PHILIPPE A. GUYE (*J. Chim. phys.*, 1913, **11**, 275—318).—Since the international atomic weight of chlorine was fixed at 35·460, important determinations by Dixon and Edgar, Gray and Burt, Scheuer, Baume and Perrot, and Wourtzel have been described.

Recent determinations at Harvard of the atomic weight of chlorine by the two classic methods of Stas and Marignac lead to a value 35·454 when the atomic weight of silver lies between 107·87 and 107·88. Nine series of experiments by five different modern methods depending on gaseous interactions, such as the syntheses of nitrosyl chloride and ammonia, lead to a value Cl = 35·461 when H = 1·00762 and N = 14·008.

The difference between 35·454 and 35·461 corresponds with the presence of 0·02% of bromine in the chlorine, a quantity outside

the range of possibility. If the weight of an electron is 0·00054 atomic units, the difference between gaseous and combined chlorine might be as much as 0·003, but as this hypothesis cannot be verified, it is more profitable to regard the difference as due to experimental error. The modern methods are less circuitous than those based on the atomic weight of silver, and on account of the great variety of reactions used and the close agreement between different experimenters, the value 35·461 must be admitted to be correct. A slight impurity in the silver or the formation of a sub-chloride would vitiate the results obtained at Harvard.

If the atomic weight of chlorine is 35·461, the corresponding value for silver, namely, 107·89, must be considered possible. This value is arrived at directly from the ratio Ag : Cl (Richards and Wells), indirectly from the ratios Na : Cl (Smith) and Ag : NaCl (Richards and Wells), and also indirectly from the ratios Cl : Na, Na : Br, Br : Ag, and corresponds with any value for chlorine between 35·459 and 35·461. Further work is necessary to dispel the uncertainty as to the atomic weight of silver. A slight alteration in the accepted value for silver will lead to a wholesale revision of the values for phosphorus, the platinum metals, and many other elements.

The necessity for a concerted international scheme of atomic weight research is again urged. R. J. C.

New Revision of the Atomic Weights of Chlorine and Nitrogen. EUGÈNE WOURTZEL (*J. Chim. Phys.*, 1913, **11**, 214—248). Compare Boubnoff and Guye, A., 1911, ii, 599).—The experimental conditions necessary for a quantitative synthesis of nitrosyl chloride (A., 1912, ii, 934) are described. In Boubnoff and Guye's product an excess of chlorine was present because the temperature employed was below the solidifying point of the nitrosyl chloride, and some uncombined chlorine remained entrapped in the solid. In the author's experiments an excess of nitric oxide was used, and the reaction tube was shaken for fifteen minutes at room temperature under pressure to complete the reaction. No chlorine could remain uncombined, as nitrosyl chloride is stable up to $+700°$, and any molecular compound, such as $NOCl_3$, would be relatively unstable. When the nitrosyl chloride is solidified, the nitric oxide comes out of solution, and may be pumped off at $-160°$ to $-135°$, the vapour pressure of nitrosyl chloride being practically zero at that temperature. The nitrosyl chloride was successively re-melted, frozen, and exhausted three times to remove the last traces of nitric oxide before weighing. The mean atomic weight of chlorine was found to be 35·460.

Five determinations of the atomic weight of nitrogen were made by the synthesis of nitrogen peroxide from nitric oxide and oxygen. For convenience in weighing, the nitric oxide was dissolved in purified peroxide, but in less amount than that required for the complete conversion of the latter into trioxide. Excess of oxygen was passed in at $-15°$, and the excess removed by successively boiling the product at the temperature of solid carbon dioxide

and exhausting at $-180°$. The atomic weight of nitrogen was found to lie between 14·006 and 14·009, the mean value being 14·0075.

A method is described for the synthesis of pure nitrosyl chloride in quantity embodying the principles used by the author in his quantitative experiments. R. J. C.

Weight of a Normal Litre of Gaseous Chlorine and Silicon Tetrafluoride. Determination of the Atomic Weights of Chlorine and Fluorine. ADRIEN JAQUEROD and MELCON TOURPAIAN (*J. Chim. phys.*, 1913, **11**, 269—274. Compare this vol., ii, 401).—Some unpublished determinations by Pellaton giving $+143·9°$ and 79·6 atmospheres as the critical constants of chlorine are considered to be more trustworthy than the previous estimates by Ladenburg, Dewar, and Knietsch, and are utilised in the calculation of the compressibility of chlorine by comparison with the data for sulphur dioxide and ammonia. The atomic weight of chlorine deduced from its density as determined by the authors is 35·296 with sulphur dioxide and 35·263 with ammonia as basis of comparison. The error in these values indicates that the physico-chemical methods are inapplicable to chlorine, or that gaseous chlorine is partly monatomic. The compressibility of silicon tetrafluoride directly adduced from Moissan's critical data or by comparison with the data for oxygen leads to a value 19·09 as the mean atomic weight of fluorine. It is suggested that the international atomic weight of fluorine, namely, 19·0, is too low. R. J. C.

The Spontaneous Transformation of Hypochlorites into Chlorates and of Hypobromites into Bromates. J. CLARENS (*Compt. rend.*, 1913, **157**, 216—219).—The spontaneous transformation of hypochlorites into chlorates takes place through the intermediate formation of chlorites, but the latter cannot be detected, since in strongly alkaline media they disappear progressively without affecting the hypochlorite content. In old, commercial solutions of hypochlorites almost entirely converted into chlorates, chlorites are present in notable quantities.

The author has made a detailed study of this transformation in the case of hypobromites, which are converted into bromates, with the intermediate formation of bromites, and has determined the amounts of hypobromite and bromite present at different stages in the reaction. A theoretical discussion of his results shows that the bromate, the ultimate term in the evolution, is produced by the oxidation of the bromite existing in the liquid by the unchanged hypobromite. W. G.

Is the Proportion of Oxygen in Air Constant? OLIN F. TOWER (*J. Chim. phys.*, 1913, **11**, 249—259).—According to Loomis (1875), a cold wave, accompanied by a high barometric pressure, corresponds with a low proportion of oxygen in the air which has descended from high altitudes, whereas Vogler (1882) suggested that a high barometer coinciding with a minimum of atmospheric

disturbance should lead to a concentration of oxygen at sea level. Jolly (1879) supposed that he had detected a diminished proportion of oxygen in wind blowing from equatorial regions where oxidation processes are rapid, and analyses by Hempel (1886) of air from Tromsoe, Dresden, and Para seem to support this view.

More recent work by Durius and Zuntz (1894), Watson (T., 1911, **99**, 1460), and Benedict (*Carnegie Inst. Report*, 166) indicate, however, that such small variations as occur in the proportion of oxygen are not traceable to meteorological conditions. The mean percentage of oxygen (20·952) found by Benedict from 1909 to 1912 corresponds very closely with the mean percentage (20·955) found by Morley in 1881. R. J. C.

Reaction Between Ozone and Hydrogen Peroxide. VICTOR ROTHMUND (*Eighth Inter. Cong. App. Chem.*, 1912, **26**, 611—615).—The estimation of ozone in presence of hydrogen peroxide can be effected iodometrically if potassium bromide is added to the weakly acid mixture before treating it with potassium iodide.

A study of the reaction between ozone and hydrogen peroxide in $N/100$-sulphuric acid solution has shown that when the peroxide is present in very large excess of the ozone (about 30 : 1), approximately equal numbers of mols. of the two substances are decomposed, but if more dilute peroxide is used, much more ozone is decomposed than peroxide. In alkaline solutions, however, the reaction takes place much more rapidly, and in the presence of excess of hydrogen peroxide, approximately equal numbers of mols. of the two substances suffer decomposition. These observations indicate that the reaction with the peroxide is accompanied by a spontaneous decomposition of the ozone, which is greatly accelerated by the presence of the peroxide. E. G.

Sulphuric Acid and its Anhydride. HENRI GIRAN (*Compt. rend.*, 1913, **157**, 221—223. Compare Pickering, T., 1890, **57**, 338).—The author has confirmed Pickering's work on the solidification points of mixtures of sulphuric acid and water, and has completed his curve in the region between 68 and 76% H_2SO_4, at which stage crystallisation is difficult to produce. The curve at this portion presents a maximum corresponding with the hydrate $H_2SO_4,2H_2O$. To complete the curve, the author has studied mixtures of sulphuric acid and its anhydride, the curve showing only one maximum at 35° corresponding with pyrosulphuric acid. The last portion of the curve confirms the existence of the α- and β-modifications of sulphuric anhydride. W. G.

Preparation of Telluric Acid and a Test for Associated Tellurous Acid. PHILIP E. BROWNING and H. D. MINNIG (*Amer. J. Sci.*, 1913, [iv], **36**, 72—73).—The methods usually adopted for the preparation of telluric acid are not altogether satisfactory. Pure telluric acid can, however, be obtained by the following process. Powdered amorphous tellurium is suspended in water, and chlorine is passed into the mixture. About an hour after the tellurium

has dissolved, a portion of the solution is rendered alkaline, and afterwards acidified with acetic acid. If the solution remains clear, the tellurium has been oxidised completely to telluric acid. Experiments have shown that this test is capable of detecting 1 mg. of tellurous acid in presence of 0·1—0·2 gram of telluric acid in a volume of 5 c.c. When it is found that oxidation is complete, the solution is evaporated to a small volume, tested to ensure that reduction has not taken place, and again treated with chlorine if necessary. Acetone or alcohol is now added to the concentrated solution, and telluric acid is obtained as a crystalline precipitate. E. G.

Constitution of Carbon. OTTO DIMROTH and BERTHOLD KERKOVIUS (*Annalen*, 1913, **399**, 120—123).—By boiling wood charcoal with nitric acid, D 1·5, the authors have obtained, in addition to mellitic acid, a yellow, amorphous, very hygroscopic product, which has a strongly acid reaction, develops a black coloration with alkalis, dissolves easily in alcohol and ether, and by distillation of the barium salts, produced from it, with an excess of barium oxide yields benzene, naphthalene, and fluorene. Had fluorenone been obtained, there could be little doubt that this ring system was produced during the distillation. The production of fluorene itself, however, indicates that the yellow mass contains a carboxylic acid derived from fluorene, and, therefore, that the molecule of carbon contains C_5-rings as well as benzene rings.

The research is being continued and extended to include graphitic acid. C. S.

A Remarkable Condition for the Attack of Quartz by Gaseous Hydrogen Fluoride. ARMAND GAUTIER and PAUL CLAUSMANN (*Compt. rend.*, 1913, **157**, 176—179. Compare A., 1912, ii, 806).—The attack of gaseous hydrogen fluoride on a polished surface of quartz is dependent on the inclination of the surface to the axis of the crystal from which it was cleaved. Quartz cut parallel to the axis and the facets at the point of a crystal corresponding with the inverse rhombohedron are moderately attacked, whilst a surface cut perpendicularly to the axis or the facets corresponding with the direct rhombohedron are hardly marked. The attack on a polished surface of previously melted quartz is much more vigorous, but even this is only about one-tenth of the action on glass. W. G.

Density and Atomic Weight of Helium. WILHELM HEUSE (*Ber. Deut. physikal. Ges.*, 1913, **15**, 518—523).—The atomic weight of helium has been determined from density determinations. The gas was purified by the usual method, and weighed against a glass counterpoise of about the same weight and volume as the vessel containing the gas. The weight of a normal litre of helium, as a mean of seven experiments, is found to be $0·17856 \pm 0·00008$ gram, from which the atomic weight is calculated as 4·002. J. F. S.

Nomenclature of the Complex Salts of Mineral Chemistry. GEORGES URBAIN (*Eighth Inter. Cong. App. Chem.*, 1912, **25**, 177—183).—Considerations are advanced which serve to justify the system of nomenclature of complex salts proposed by the French Commission of Nomenclature for Mineral Chemistry, in which carnallite, for example, is regarded as a double salt, $MgCl_2,KCl,6H_2O$, and potassium platinocyanide as a perfect complex salt, $K_2[Pt(CN)_4]$. E. G.

The Solubility Scheme $KCl,MgCl_2,H_2O$ (Carnallite Scheme), at 50°. JOHANNES UHLIG (*Centr. Min.*, 1913, 417—422).—A saturated solution in contact with solid potassium chloride and carnallite at 50° contains per 1000 mol. H_2O, 79·5 mol. $MgCl_2$ and 14·9 mol. KCl; and when in contact with solid magnesium chloride hexahydrate and carnallite the solution contains 111·9 mol. $MgCl_2$ and 1·2 mol. KCl. Interpolating these values between van't Hoff's corresponding values for 25° and 83°, a slight error is noted in his values at 25°, for which a correction is made. L. J. S.

The System Sodium Sulphate, Manganous Sulphate, and Water at 35°. FRANS A. H. SCHREINEMAKERS and D. J. VAN PROOIJE (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 1326—1328). —It is shown that at equilibrium at 35° four solid phases are to be found: anhydrous sodium sulphate, $MnSO_4,H_2O$, $9MnSO_4,10Na_2SO_4$, and $MnSO_4,3Na_2SO_4$. The authors are unable to detect the presence of the double salts, $Na_2SO_4,MnSO_4,2H_2O$ and $Na_2SO_4,MnSO_4,4H_2O$, which have been previously described, whilst the double salts found have not been previously observed. It is thought that the two previously described salts are metastable under the conditions of the present experiments. J. F. S.

Hardening of Gypsum. PAUL ROHLAND (*Kolloid. Zeitsch.*, 1913, **13**, 61—62).—The author indicates that the hardening of burnt calcium sulphate with water is a colloidal process. The same applies to cadmium sulphate, copper sulphate, ferrous sulphate, and magnesium sulphate, which have been similarly treated. It is shown that only those sulphates harden, which in the crystallised condition contain several molecules of water of crystallisation. It is also pointed out that a strict division between crystal and colloidal water cannot be maintained. J. F. S.

Borates. System $CaO-B_2O_3-H_2O$ at 30°. III. UMBERTO SBORGI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 798—801. Compare this vol., ii, 700).—In this paper the author discusses the results published in the two preceding papers on this system. The borates stable in contact with water at 30° are those containing the constituents in the proportions 1 : 1 : 6 and 2 : 3 : 9. R. V. S.

Marls of Umbria. DANTE BACHILLI (*Gazzetta*, 1913, **43**, i, 529—537).—The marls of Pontecentesimo (of which some analyses

are given) are suitable for the preparation of both rapid and slow setting cements, the properties of which have been investigated by the author. R. V. S.

Action of Nitrogen on Strontium Carbide. SAMUEL A. TUCKER and Y. T. YANG (*Eighth Inter. Cong. App. Chem.*, 1912, **21**, 121—126).—Tucker and Moody (A., 1911, ii, 883) have investigated the action of nitrogen on lithium carbide. A similar study has now been made with strontium carbide. The results of the experiments show that when strontium carbide is heated at 1000—1200° under atmospheric pressure, it absorbs nitrogen with formation of cyanide, cyanamide, and a little dicyanodiamide. E. G.

Fusion of Carbonates under Carbon Dioxide Pressure. II. HENDRIK ENNO BOEKE (*Chem. Zentr.*, 1913, i, 1909—1910; from *Mitt Naturforsch. Ges. Halle*, **3**, 1—12. Compare A., 1912, ii, 760).—*The three modifications of Barium Carbonate.*—In addition to the reversible transformation of barium carbonate at 811° (compare A., 1906, ii, 753), there is a second transformation at 982°, accompanied by a very small heat change. The same transition point is observed on heating a polished plate of witherite. β-Barium carbonate is probably hexagonal, and α-barium carbonate regular in crystalline form. The presence of isomorphous calcium carbonate lowers the transition point at 811°. Neither the β- nor the α-form could be prepared at the ordinary temperature. The m. p. of barium carbonate is about 1740°. The following series of changes are established: γ-$BaCO_3$ (witherite, rhombic-pseudo-hexagonal) $\overset{811^\circ}{\rightleftharpoons}$ β-$BaCO_3$ (hexagonal) $\overset{982^\circ}{\rightleftharpoons}$ α-$BaCO_3$ (regular) $\overset{1740^\circ}{\rightleftharpoons}$ melts.

System Barium Carbonate–Calcium Carbonate.—The experiments were made under a high pressure of carbon dioxide to prevent dissociation. The diagram corresponds with the formation of isodimorphous mixed crystals with a eutectic at 1139° containing 52·5 molecules % of calcium carbonate. There is no indication of the formation of a monoclinic compound, such as barytocalcite ($BaCO_3,CaCO_3$). The conversions $CaCO_3 \rightleftharpoons$ α-$CaCO_3$ and β-$BaCO_3$ $\rightleftharpoons$ α-$BaCO_3$ were only very vaguely indicated. The conversion of β-$BaCO_3$ into witherite in presence of calcium carbonate was clearly evident to about 70% of barium carbonate, and showed a depression of 150°.

The molecular volumes of the fusions were determined pyknometrically in toluene, and plotted in a diagram. Those for mixtures containing 0—65% of barium carbonate lay on a straight line extending from the calcspar to the witherite points. Accordingly, the unstable rhombohedric barium carbonate has a molecular volume 46·3, D=4·26. The molecular volumes of mixtures with 25—30% of calcium carbonate lay on the line joining aragonite and witherite, that is, much lower; they correspond with the rhombic alstonite, which is only stable up to about 30 molecules % of calcium carbonate, and is then replaced by trigonal barytocalcite.

Strontium carbonate shows a transition point at 929° on heating, and 920° on cooling. α-Strontium carbonate is hexagonal. Pure strontium carbonate has m. p. 1497°. E. F. A.

Corrosion of Lead by Calcium Hydroxide. WILHELM VAUBEL (*Zeitsch. angew. Chem.*, 1913, **26**, 423—424. Compare A., 1912, ii, 1172; this vol., ii, 706).—The author shows that the corrosion of lead by calcium hydroxide is due to the presence of hydrated calcium peroxide in the hydroxide. The formation of the peroxide is attributed to the presence of iron. The reaction is expressed by the following equations: (*a*) $2FeO + O_2 = Fe_2O_4$; (*b*) $Fe_2O_4 + Ca(OH)_2 = Fe_2O_3 + CaO(OH)_2$; (*c*) $CaO(OH)_2 + Pb = PbO + Ca(OH)_2$. A further reaction is also supposed to take place, indicated by the equation: $Pb + O_2 + Ca(OH)_2 = PbO + CaO(OH)_2$. J. F. S.

The Action of Water on the Carbides of the Rare Earths. A. DAMIENS (*Compt. rend.*, 1913, **157**, 214—216. Compare this vol., ii, 700).—Varied results having been obtained by previous workers, the author has made a detailed study of the action of water on the carbides of the metals of the cerium group. The results show that in no case is methane produced, but that the principal gaseous products are members of the acetylene series, including acetylene, allylene, and higher homologues, together with small proportions of ethylene and ethane and their homologues. Some hydrogen is also obtained, and the production of ethylene and ethane probably arises from direct hydrogenation of the acetylene. In every case the metal was left in the form of its hydrated sesquioxide. The cerous hydroxide so obtained was white, and remained white even after desiccation out of contact of air. It rapidly absorbed oxygen to give ceric hydroxide. W. G.

Baking of Clays. PAUL BRAESCO (*Compt. rend.*, 1913, **157**, 123—125).—Clays, when mixed in the form of a paste, air-dried, and then subjected to heat, first dilate until a certain temperature is reached, when they cease to dilate, and begin to contract. The author has determined for a number of clays the temperatures at which contraction begins. Up to 1000°, mica, similarly treated, shows no sign of contraction, and when mixed with clays it raises the temperature at which contraction commences. W. G.

Crystallisation of Steel. II. FEDERICO GIOLITTI and N. BOYER (*Atti R. Accad. Sci. Torino,* 1913, **48**, 827—835. Compare *ibid.*, 609).—From the microscopic examination of steels tempered at various temperatures, the authors find that the production of a reticulate structure in hypoeutectic steels is not due to the crystallisation of ferrite at the periphery of the primary mixed crystals, but to the fact that the first crystals of ferrite formed act as "germs of crystallisation" for those subsequently produced as crystallisation proceeds. R. V. S.

Influence of Intercrystalline Cohesion on the Mechanical Properties of Metals. JOHN C. W. HUMFREY (*Iron Steel Inst. Carnegie Mem.*, 1913, **5**, 86—99. Compare Rosenhain and Ewen, this vol., ii, 119).—Microscopical observations are adduced to show that the intercrystalline junctions in iron and steel offer a great resistance to plastic deformation. When two neighbouring crystals have similar orientation, slipping along gliding-planes is readily transmitted. The crystals of metals are to be regarded as enclosed in a hard, continuous skin, highly elastic, but incapable of plastic deformation. The skin would appear to be of more than molecular thickness. The hypothesis is applied to explain the behaviour of overstrained metals. C. H. D.

A Thermometrically Recognisable Tempering of Quenched Steel at 100°. HERMANN SCHOTTKY (*Ferrum*, 1913, **10**, 274—275). —When a sensitive thermometer is inserted into a hole drilled in a mass of hardened steel weighing about 50 grams, heated by means of a steam-bath, on approaching 100° the temperature of the steel rises suddenly, and then slowly falls. The effect is measured by making a parallel experiment with annealed steel, in which there is no such development of heat. The rise amounts to about 0·4°, and increases slightly with the temperature of quenching. It increases with the carbon content up to 1·22%, when the rise is 0·55°, and then falls. If interrupted before the development of heat is complete, and again heated, a second smaller rise of temperature is observed. A visible change of microscopic structure is not produced. C. H. D.

Specific Heat of Cold-worked Metals. C. CHAPPELL and MAX LEVIN (*Ferrum*, 1913, **10**, 271—273).—Experiments have been made with steel containing respectively 0·07, 0·11 and 0·52% C, and with two tin bronzes containing about 6% of carbon. The materials are subjected to different degrees of cold working, and are also annealed in a vacuum. The specific heat is not found to vary more than the average experimental error, although on the whole the cold-worked specimens have a slightly higher specific heat. The density of the cold-worked specimens is about 0·3% less than that of the annealed metals. C. H. D.

Specific Resistance and Hardness of Nickel-Cobalt Alloys. RUDOLF RUER and KIOSUKE KANEKO (*Ferrum*, 1913, **10**, 257—260).—Cast alloys of nickel and cobalt, twice melted in porcelain tubes, are used, and are turned to 7·45 mm. diameter and 5 cm. long. The fall of potential with a current of from 25 to 50 amperes is measured in a paraffin-bath at 18°. The specific resistance of nickel rises rapidly with addition of cobalt, reaches a maximum at 20% Co, and then falls in a linear manner.

The hardness, determined by Brinell's ball test, is almost constant from 10 to 60% Co, rises sharply at 70% Co, and afterwards passes through a maximum at 90% Co. The discontinuity at 70% Co is also observed in the micrographic structure and the magnetic

properties (A., 1912, ii, 1059). Annealing at 1150° is necessary in order to equalise the hardness of the alloys in different portions.

C. H. D.

Autoxidation of Chromous Salts. JEAN PICCARD (*Ber.*, 1913, **46**, 2477—2486).—Chromous salts on autoxidation in neutral or acid solution give rise to the formation of chromic acid as well as chromic salts. Intermediate products are formed having very marked oxidising powers, which, contrary to the usual opinion, are stable for a measurable period. These compounds can be titrated separately.

Oxide No. 1, $Cr(OH)_2 \cdot O \cdot O \cdot Cr(OH)_2$ (?), which is very easily decomposed, acts on potassium iodide in almost neutral solution. It decomposes rapidly into an extremely labile oxide, 1*b*, which, in the absence of potassium iodide, forms chromic acid, but which, in its presence, is reduced more rapidly than it can form chromic acid. The rate of decomposition into oxide 1*b*, $Cr(OH)_2O$, is unimolecular.

Oxide No. 2, $Cr(OH)_2{<}\genfrac{}{}{0pt}{}{O}{O}\!\!|$, is reduced by potassium iodide in weak acid solution within two minutes. The formulæ ascribed to these oxides are purely hypothetical.

E. F. A.

Thoromolybdates. GIUSEPPE A. BARBIERI (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 781—786).—Normal *ammonium thoromolybdate*, $(NH_4)_8Th(Mo_2O_7)_6,8H_2O$, is obtained as a white precipitate when 10 grams of anhydrous thorium sulphate, dissolved in 200 c.c. of water, are added to 250 c.c. of a 30% solution of ammonium heptamolybdate. A solution of the thoromolybdate is almost completely precipitated by silver nitrate in presence of nitric acid, and the amount of silver nitrate required corresponds with 7·7 atoms Ag per molecule. The *sodium* salt, $Na_8Th(Mo_2O_7)_6,15H_2O$, crystallises in needles and behaves similarly.

Ammonium hydrogen thoromolybdate,

$$(NH_4)_6H_2Th(Mo_2O_7)_6,11H_2O,$$

is prepared by adding a concentrated solution of an ammonium salt to a nitric acid or hydrochloric acid solution of the above-described ammonium thoromolybdate. It is precipitated by silver nitrate. The corresponding *sodium* salt, $Na_6H_2Th(Mo_2O_7)_6,17H_2O$, behaves similarly.

Silver thoromolybdate, $Ag_8Th(Mo_2O_7)_6$, is a white powder.

These salts do not give a precipitate with oxalic acid in the cold, but, on boiling, thorium oxalate is slowly deposited. The existence of these thoromolybdates is a point of similarity between thorium and the earlier members of group IV. The formulæ assigned to them (based on the views of Miolati [A., 1908, ii, 595]) are in good agreement with their properties.

R. V. S.

An Allotropic Modification of Bismuth. ERNST COHEN and A. L. TH. MOESVELD (*Chem. Weekblad*, 1913, **10**, 656—658).—Bismuth exists in two enantiotropic modifications, the transition temperature being 75°/760 mm. The transformation of the form

stable below this temperature (α) into the other modification (β) is accompanied by considerable increase in volume. The β-variety can exist in the metastable condition below the transition point.

A. J. W.

Precipitation of Gold by Manganous Salts. A. D. BROKAW (*J. Ind. Eng. Chem.*, 1913, **5**, 560—561).—When gold chloride solutions of varying concentrations are mixed with manganous chloride solutions (from $N/0{\cdot}5$ to saturation), no reaction could be detected even after prolonged boiling. When, however, a very small amount of alkali is added to the cold mixture, manganese dioxide and gold are at once precipitated. The same result is obtained when a crystal of calcium carbonate is added to the mixture; there is a slight effervescence, and after a few hours the crystal is covered with manganese dioxide containing flakes of gold.

Amorphous manganous carbonate reacts at once with gold chloride with production of the dark brown hydrated dioxide. Crystallised manganous carbonate acts slowly, but after a day becomes coated with the dark brown hydrated oxide and flakes of gold.

N. H. J. M.

A Convenient Arrangement for Reduction with Colloidal Platinum or Palladium. OTTO STARK (*Ber.*, 1913, **46**, 2335—2336).—In order to avoid the common danger of the introduction of mercury from the gas burette and the intrusion of air in experiments requiring the measurement of the absorbed volume of gas, the author uses, to contain the liquid for reduction, a glass holder provided with two taps and a tap funnel. At the commencement of an experiment, after the introduction of the solution to be reduced, hydrogen is passed through the vessel, passing on through the other tap and the attached india-rubber tubing to the empty gas burette, finally reaching the open atmosphere through the empty mercury reservoir. When all the air has been displaced, mercury is run into the reservoir and so into the graduated gas burette, whilst at the same time the tap by which the hydrogen entered is closed. The colloidal solution of platinum or palladium is subsequently introduced through the tap funnel, the mercury reservoir attached to the gas burette being lowered for the purpose.

D. F. T.

Osmium. ALEXANDER GUTBIER (*Chem. Zeit.*, 1913, **37**, 857—859).—The author, in working up a quantity of osmium residues which contained quantities of organic substances, finds that the metal is not converted into the chloride when treated with chlorine, and in consequence the purification of the metal could not be effected in the usual way by means of the insoluble ammonium osmichloride. The following method has been evolved for the recovery of the metal from such residues. The dried residues are placed in porcelain boats in a hard glass tube, heated, and a current of oxygen is passed over; this burns away all carbonaceous matter, and the osmium is converted into the tetroxide, which distils over

into a series of U-tubes containing various reducing agents. As reducing agents, the author employs alcohol in slightly alkaline solution, ammoniacal alcohol containing ammonium chloride and an alcoholic solution of hydrazine hydrate. The reduced solution is evaporated to dryness on the water-bath, and then converted into the metal by heating in hydrogen and allowing to cool in carbon dioxide. The author shows that by this process it is possible to recover 2·83 grams of osmium from an artificially prepared mixture containing 3·0 grams of osmium. J. F. S.

Mineralogical Chemistry.

Mineralogical-Chemical Investigation of Marcasite, Pyrites, and Magnetic Pyrites. Erich Arbeiter (*Chem. Zentr.*, 1913, i, 1933—1934; from *Jahresber. Schles. Ges. Vaterländ. Kultur*, 1913. Compare Beutell, A., 1911, ii, 485, 728, 1094; 1912, ii, 652).—Pyrites has the composition $(FeS_2)_2$, and the formula $S\langle{}^{Fe\cdot S}_{Fe\cdot S}\rangle S$, The constitution of the isomorphic cobalt-glance is accordingly $As\langle\substack{Co\cdot S \\ \text{———} \\ Co\cdot S}\rangle As$. That of marcasite is probably either $Fe\langle{}^{S\cdot S}_{S\cdot S}\rangle Fe$ or $S\langle{}^{Fe\cdot Fe}_{S—S}\rangle S$. Marcasite is converted into pyrites between 400° and 500°. Magnetic pyrites does not correspond with any definite chemical formula. That derived from meteorites approximately corresponds with FeS; probably the excess of sulphur has been lost during the heating of the meteorite. Magnetic pyrites is regarded as a solid solution of FeS with a higher iron sulphide, probably one of low density. Lower sulphides are not present, and the supposition that dissolved sulphur is present is highly improbable. E. F. A.

Chromite Segregations in the Platiniferous Dunites of the Urals. Louis Duparc and Santiago Piña de Rubies (*Bull. Soc. franc. Min.*, 1913, **36**, 20—25. Compare this vol., ii, 714).—Irregular patches of granular chromite intermixed with some olivine occur in the dunites (olivine-rocks) of the Urals. The following analyses are of materials from different localities:

	TiO_2.	SiO_2.	Cr_2O_3.	Al_2O_3.	FeO.	MgO.	CaO.	Total.
I.	0·24	0·82	53·60	9·68	23·20	12·26	0·34	100·14
II.	0·24	0·90	53·19	9·63	21·16	14·33	0·27	99·72
III.	0·40	0·82	52·67	10·56	23·37	12·23	0·24	100·29
IV.	—	1·83	35·88	8·57	42·61	10·04	—	98·93
V.	1·14	0·98	33·10	14·78	37·99	8·73	0·23	96·95

Deducting olivine, these analyses are re-calculated as follows:

	$MgAl_2O_4$.	$MgCr_2O_4$.	$FeCr_2O_4$.	$FeFe_2O_4$.
I.	13·82	35·95	38·95	12·12
II.	13·83	45·69	27·50	13·94
III.	15·12	32·66	41·57	11·44
IV.	12·62	21·25	31·09	37·64
V.	22·40	1·48	51·24	26·73

These analyses, taken in conjunction with those of the platinum ores from the same districts (A., 1911, ii, 733), suggest that chromite rich in the $FeFe_2O_4$ molecule is accompanied by platinum ores rich in osmium. L. J. S.

Minerals from the Federated Malay States. (ANON.) (*Bull. Imp. Inst.*, 1913, **11**, 243—248).—Several samples of tin-bearing sands and concentrates containing cassiterite, monazite, wolframite, ilmenite, etc., are briefly described, and partial analyses given. An analysis is also given of an impure manganese ore, containing MnO_2, 46·2; MnO, 11·45%. L. J. S.

Minerals from the Pegmatites of Madagascar. LOUIS DUPARC, R. SABOT, and MAX WUNDER (*Bull. Soc. franç. Min.*, 1913, **36** 5—17).—The minerals described occur in pegmatite near Ambatofotsikely, north-west of Antsirabe. Fine large crystals of monazite have D 5·2735, and on analysis gave the results under I. Columbite is found as crystals of various habits and groupings, and also as large, crystalline masses weighing several kilograms; D 5·2726; analysis II. A radioactive mineral occurring in some abundance is referred (by reason of its composition, analysis III) to Lacroix's ampangabeite (A., 1912, ii, 567). It is resinous and reddish, but brownish-yellow on the exterior; D 3·3484 to 3·9236 in different specimens. The indistinct, rounded crystals are often intimately associated with columbite, and they are possibly pseudomorphous. The radioactivity of this mineral is about half that of pitchblende. The monazite and columbite are also slightly radioactive:

	SiO_2.	TiO_2.	ZrO_2.	ThO_2.	U_3O_8.	Cb_2O_5.	Ta_2O_5.	Ce_2O_3.
I.*	2·87	nil.	0·11	11·23	—	—	0·24	26·95
II.†	0·40	1·50	—	—	2·02	63·77	11·33	—
III.	1·75	2·10	—	1·30	12·50	50·60		5·75

	$(La,Di)_2O_3$.	$(Y,Er)_2O_3$.	Al_2O_3.	Fe_2O_3.	MnO.	CaO.	Ign.	Total.
I.*	32·60	0·30	0·15	0·60	nil.	trace	0·56	101·51
II.†	—	—	trace	—	8·79	—	—	99·64
III.§	2·10	1·35	1·20	7·20	1·53	1·83	11·55	101·06

* Also P_2O_5, 25·90. † Also FeO, 11·38; SnO_2, 0·45.
§ Also SnO_2+WO_3, 0·30; Cerium oxide as CeO_2, 5·75.

L. J. S.

Potassium-salt Deposits of Wittelsheim, Upper Elsass. ROLF VON GÖRGEY (*Tsch. Min. Mitt.*, 1912, [*i.e.*, 1913], **31**, 339—468).—A detailed description is given of the extensive deposits

of potassium salts recently discovered by boring in the Oligocene beds at depths of about 650 metres near Wittelsheim, north-west of Mühlhausen. Several analyses are given of mixed salts rich in sylvite, carnallite, etc., and of the associated anhydrite and dolomite rocks. L. J. S.

Identity of the So-called Ihleite from Elba with Copiapite. ERNESTO MANASSE (*Jahrb. Min.*, 1913, i, *Ref.* 386—388; from *Proc. verb. Soc. Toscana Sci. Nat.*, 1911, **20**, 65—76).—A sulphur-yellow finely crystalline to powdery mineral, occurring together with other decomposition-products of pyrites and marcasite, has been described as ihleite by Görgey in 1907. A re-examination of this material proves its identity with the Chilean copiapite. The optical characters of the minute rhombic plates suggest orthorhombic, rather than monoclinic, symmetry. Analysis I of material from Vigneria, and II from Capo d'Arco. Deducting considerable amounts of admixed melanterite and alunogen, these analyses correspond with the copiapite formula, $Fe_4S_5O_{21},16H_2O$. The impure, powdery mineral thus resembles the "misy" from the Harz:

	SO_3.	Fe_2O_3.	Al_2O_3.	FeO.	MgO.	H_2O.	Insol.	Total.
I.	38·87	21·91	4·15	0·94	trace	33·33	0·61	99·81
II.	38·37	26·10	trace	4·06	—	30·68	0·71	99·92

L. J. S.

Cuspidine from the Inclusions in the Peperino of the Monti Albani. F. STELLA STARRABBA (*Atti R. Accad. Lincei*, 1913, [v], **22**, i, 871—875).—The cuspidine occurs in metamorphosed limestone near Ariccia, in the form of crystals having D 2·95, $a:b:c=$ 0·7243 : 1 : 1·9342, β 89°22′. R. V. S.

Epidesmine, a New Mineral. VOJTĚCH ROSICKÝ and STANISLAUS J. THUGUTT (*Centr. Min.*, 1913, 422—426).—This new mineral forms together with orthoclase a crystalline crust on large crystals of calcite from the Gelbe Birke mine at Schwarzenberg, in the Saxon Erzgebirge. The minute, water-clear crystals are orthorhombic with a prismatic habit. There are pinacoidal cleavages (100) and (010). D 2·16 and n_{Na} 1·498 are both very low. The acute negative bisectrix coincides with the vertical axis, and the optic axial plane is parallel to (100); $\gamma-\alpha_{Na}$ 0·015. The mineral is decomposed by dilute hydrochloric acid with separation of sandy-gelatinous silica. The following analysis gives, after deducting a small amount of admixed orthoclase, the formula $3(Ca,Na_2,K_2)Al_2Si_6O_{16},20H_2O$, identical with that of stilbite. The microchemical colour reactions given by epidesmine are also the same as for stilbite:

SiO_2.	Al_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Insol.	Total.	D^{17}.
56·66	16·00	7·58	0·06	0·67	0·88	18·69	0·44	100·98	2·152

The orthorhombic epidesmine and the monoclinic stilbite (Germ. desmin) are thus dimorphous. A similar case of dimorphism

amongst the zeolites is afforded by epistilbite and heulandite (Germ. stilbit). These being alteration products of the felspars, it is possible that their dimorphism bears some relation to the dimorphism of the latter (orthoclase-microcline and albite-barbierite).

L. J. S.

Montmorillonite from Bordes, Vienne, France. L. Azéma (*Bull. Soc. franç. Min.*, 1913, **36**, 111—113).—The material forms a bed one metre in thickness in gravel, and consists of the following varieties: I, clear rose montmorillonite; II, greyish-white steargillite; III, ochre-yellow common clay. These gave the following results on material dried at 100°:

	SiO_2.	Al_2O_3.	Fe_2O_3.	CoO,MnO,NiO.	MgO.	CaO.	K_2O.	Na_2O.	H_2O.	Total.
I.	59·57	22·83	1·07	traces	3·82	2·21	—	—	10·46	99·96
II.	58·82	23·62	0·99	—	3·92	2·07	—	—	10·56	99·98
III.	59·00	18·62	11·39	—	1·04	1·04	2·38	0·13	6·45	100·05

Only fractional percentages of silica are soluble in alkalis. The formula is probably $H_2Al_2Si_4O_{12},nH_2O$.

L. J. S.

Minerals [Chrysocolla] from the Belgian Congo. Henri Buttgenbach (*Ann. Soc. géol. Belg., Publications relatives au Congo Belge*, 1913, 31—70).—Descriptions are given of a number of mineral species from this region. Chrysocolla occurs in the Étoile du Congo and several other mines in Katanga. It forms bright blue mamillated masses, interlaminated with malachite. Under the microscope, it shows a finely fibrous structure, with the fibres nearly perpendicular to the surfaces of crystallisation; the material is optically uniaxial and positive, and has a mean refractive index of 1·39. D 2·400—2·417. Analyses correspond with $CuSiO_3,2H_2O$:

CuO.	SiO_2.	H_2O.	Insol. (CoO,CaO,Al_2O_3).	Total.
44·05	33·61	19·06	3·28	100·00
43·11	33·41	19·95	3·53	100·00

In a vacuum over sulphuric acid, the material loses 60·4% of its water, this being reabsorbed in a moist atmosphere; at 98°, 63·4%; at 255°, 85·4%; and it is completely dehydrated at 310°.

It has been suggested that chrysocolla is only a hydrated form of dioptase ($CuSiO_3,H_2O$, which also is optically uniaxial and positive), or that it consists of dioptase mixed with other substances. The two minerals are, however, shown to be quite distinct by their difference in density and refractive index, and by their behaviour when heated (dioptase loses no water at 100°, and only 5% of the total water at 255°).

L. J. S.

The Matted-Fibrous Asbestos of Bohemia and Moravia. Alex. E. Fersmann (*Jahrb. Min.*, 1913, i, Ref. 381—382; from *Abh. böhm. Akad.*, 1912, No. 15).—In connexion with his work on palygorskite (A., 1908, ii, 603), the author has examined minerals of a similar nature from several localities in Bohemia and Moravia. These are referred to zillerite (tremolite- or actinolite-asbestos),

zermattite (serpentine-cork), β-palygorskite (1A + 1B, where A = parasepiolite, $H_4Mg_2Si_3O_{10}$, and B = paramontmorillonite, $H_6Al_2Si_4O_{14},2H_2O$), β-pilolite (3A + 1B), and parasepiolite. Analyses are given of the following: I, β-palygorskite from Dobešovic, Mies, Bohemia. II and III, ferruginous β-pilolite from Kuttenberg, Bohemia, occurring as a coating on calcite crystals in crevices in serpentine; IV, ditto from Příbram; V, β-palygorskite from Obřan, Brünn, Moravia:

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.	CaO.	H_2O below 110°.	H_2O above 110°.	Total.
I.	51·42	13·08	2·74	0·51	—	9·30	1·16	7·65	14·36	100·22
II.	56·04	trace	10·95	0·14	0·61	17·22	—	8·43	6·60	99·99
III.	54·68	1·83	9·67	0·67	trace	14·98	—	10·24	7·92	99·99
IV.	50·66	1·87	9·62	1·45	1·03	19·65	—	8·08	7·64	100·00
V.	54·17	13·56	$\underbrace{\qquad\qquad}_{0·22}$		—	9·55	0·41	9·58	11·87	99·36

L. J. S.

Dehydration of Micas. ALBERT BRUN (*Bull. Soc. franç. Min.*, 1913, **36**, 44—45).—The dehydration of powdered mica commences in a vacuum at 98° and proceeds regularly; at 360° one-quarter of the water is lost in the case of white micas, and four-ninths with black micas. Plates of mica are completely dehydrated when heated for half an hour at 830°, or for ten to twelve days at 510—540°. The material suffers no change in its optical properties, but, owing to the liberation of gas between the lamellæ, the plates become opaque (this can, however, be avoided by heating in a vacuum under certain conditions). All the micas when heated give off carbon dioxide, hydrocarbons, hydrogen, and nitrogen. The quantity of hydrogen liberated depends on the rate of heating, less being obtained when the material is heated very slowly. The water is regarded as existing in the micas in a state of solid solution. L. J. S.

Spectrographic Study of Some French Mineral Waters. JACQUES BARDET (*Compt. rend.*, 1913, **157**, 224—226).—The author has examined spectrographically the dry residues from some fifty-four French mineral waters, with a view to furnish conclusive proof of the presence of some of the elements reported as present only in minute traces. In some cases he has proved the presence of metals not already noted, examples being gallium and germanium.

W. G.

Analytical Chemistry.

Application of Dialysis for Quantitative Estimations. A. GOLODETZ (*Zeitsch. physiol. Chem.*, 1913, **86**, 315—321).—A form of Soxhlet apparatus is described and figured, in which the liquid contained in a dialyser is placed in the Soxhlet tube surrounded

by distilled water, which passes into the receiver below, where it is boiled and condensed so as to flow back to the dialyser. In the case of easily decomposable substances the boiling can be done in a vacuum at a temperature of 40°. A concentrated solution of the material which dialyses is thus obtained in the receiver, and can be analysed. E. F. A.

A New Indicator. FERENCZ ARON (*Chem. Zentr.*, 1913, ii, 381; from *Pharm. Post*, 1913, **46**, 521—522).—Di-*o*-hydroxydistyryl ketone, $CO(CH:CH\cdot C_6H_4\cdot OH)_2$, is turned pale yellow by acids, and orange-red by alkali, the transformation being very sharp. The indicator is applicable for use with strong and weak acids and strong alkali, but not with ammonia. Three to four drops of a 1% solution suffice for 100 c.c. of liquid. E. F. A.

Sodium Thiosulphate Solutions. CHARLES H. HAMPSHIRE and W. R. PRATT (*Pharm. J.*, 1913, **91**, 142—143).—The strength of *N*/2- and *N*/10-sodium thiosulphate solutions remained unchanged when the solutions were kept for eight months under varying conditions as to exposure to light and the colour of the bottles in which they were stored. In certain cases small quantities of sulphur separated, but the decomposition was not of such a degree as to affect the titre of the solutions. W. P. S.

Mercuric Oxide as a Standard for Volumetric Analysis. LEOPOLD ROSENTHALER and A. ABELMANN (*Pharm. J.*, 1913, **91**, 144—145).—The use of pure mercuric oxide is recommended for standardising volumetric solutions of acids, alkalis, iodine, potassium permanganate, etc. W. P. S.

Estimation of Chlorine in Natural Waters. JOSEF TILLMANS and O. HEUBLEIN (*Chem. Zeit.*, 1913, **37**, 901—903).—The conclusions arrived at are as follows: The amount of potassium chromate added as indicator when titrating with silver nitrate is generally too small; 1 c.c. of a 10% solution should be added to 100 c.c. of the sample. Water containing less than 7·5 mg. of chlorine per litre should first be suitably concentrated. Waters containing a deposit of ferric hydroxide should be cleared by means of a little zinc oxide; dissolved manganese does not interfere. Acid effluents should be neutralised by means of a slight excess of magnesium oxide or sodium hydrogen carbonate; a blank titration experiment is recommended. Coloured waters may be bleached in acid solution by means of permanganate; the liquid is then neutralised as directed, and filtered. Amounts not exceeding 100 mg. per litre of peptone, phenol, soap, albumin, or urea do not interfere with the titration. L. DE K.

New Form of Apparatus for the Estimation of Dissolved Oxygen in Water. GEORGE A. SOPER (*Eighth Inter. Cong. App. Chem.*, 1912, **26**, 265—266).—The apparatus described permits of the addition of reagents to the water without exposing it to the air.

It consists of a bottle of about 500 c.c. capacity, with a long, funnel-shaped lip. A stopper, which is convex at the bottom, fits into the neck, and allows about 15 c.c. of liquid to stand in the funnel. The capacity of the bottle is determined with the stopper in its place. The estimation of dissolved oxygen is carried out in the following manner. The bottle is filled with the water up to the funnel, and the stopper is inserted. The excess of water in the funnel is poured off. The stopper is removed, and 6 c.c. of a standard solution, containing 48 grams of ferrous sulphate and 5 c.c. of concentrated sulphuric acid per litre, are delivered by a pipette to the bottom of the bottle. The stopper is replaced, and the water which rises in the funnel is poured off. Five c.c. of sodium carbonate solution (200 grams per litre) are then poured into the funnel, and the stopper is raised sufficiently to allow the solution to sink through the water to the bottom of the bottle. The stopper is re-inserted, the water in the funnel poured off, and the bottle is shaken until all the oxygen has been absorbed. Sulphuric acid (10 c.c. of a 50% solution) is now poured into the funnel, and the stopper raised sufficiently to permit it to diffuse through the liquid. The contents of the bottle are poured into a flask and titrated with a solution of potassium permanganate, each c.c. of which is equivalent to 1 c.c. of oxygen.

If the water contains much organic matter or sodium chloride, a blank experiment must be made, and the difference between the amount of permanganate required by the blank and that used in the actual analysis represents the quantity of dissolved oxygen present. E. G.

Practical Field Method for the Estimation of Dissolved Oxygen in Water. GEORGE A. SOPER and PAYN B. PARSONS (*Eighth Inter. Cong. App. Chem.*, 1912, **26**, 267—269. Compare Soper, preceding abstract).—The sample of water is collected in a separating funnel of 350 c.c. capacity after it has been filled and emptied several times by means of a special device described in the original. Solutions of ferrous sulphate and sodium carbonate are delivered by means of a pipette to the bottom of the funnel, which is then stoppered and shaken well. Sulphuric acid is now introduced through the stem of the funnel, the stopcock being opened for this purpose. The funnel is shaken and left for about five minutes, and the contents are then transferred to a flask and titrated with potassium permanganate. A blank experiment is now carried out by filling the separating funnel as before, adding sulphuric acid, shaking, and then adding the same volume of ferrous sulphate solution as in the previous experiment. The presence of the sulphuric acid prevents the dissolved oxygen from reacting with the ferrous salt. The funnel is shaken again, and the contents poured into a flask and titrated with the permanganate solution. The difference between the results of the two titrations gives the amount of ferrous salt oxidised by the dissolved oxygen.

E. G.

Estimation of Oxygen in Iron and Steel. JOSEPH A. PICKARD (*Iron Steel Inst. Carnegie Mem.*, 1913, **5**, 70—85).—An improved hydrogen reduction method is described. The steel is placed in a nickel boat (previously ignited in hydrogen) contained in a silica tube closed at one end. This tube is provided with a glass extension carrying a T-piece. Hydrogen, generated from zinc and sulphuric acid containing ferrous sulphate, and purified by passing through potassium hydroxide, calcium chloride, and phosphoric oxide, is used for filling. About 20 grams of drillings are weighed and placed in the tube, a small unweighed boat containing phosphoric oxide being placed in the cool part of the tube, which is then exhausted. After a few minutes, hydrogen is admitted up to atmospheric pressure, the cap is removed, and a weighed boat containing phosphoric oxide is substituted for the other. The tube is washed out with hydrogen, and after admitting hydrogen up to one-half or two-thirds atmospheric pressure, an electric furnace, previously heated to 1000°, is slipped over the tube, and allowed to remain for forty-five minutes. After cooling, the boat is weighed. The correction for moisture introduced during the changing of boats is made by means of a blank, or by estimating the moisture in the air directly, the latter method being quicker. Carbon oxides and ferric oxide are completely reduced. Manganous oxide is not reduced when alone, but is apparently reduced when present in a steel. Slag is not reduced. C. H. D.

The Employment of Methyl-orange as Indicator for the Titration of Free Sulphuric Acid in Solutions of Copper Sulphate. ALFRED WOGRINZ (*Chem. Zeit.*, 1913, **37**, 869).—Copper may be estimated in fresh copper-plating baths by titrating, in one sample, the total sulphuric acid after precipitation with hydrogen sulphide, and the free sulphuric acid in another portion. Methyl-orange may be employed for the latter purpose, sufficient being added to give such a reddish-violet colour that the colour of the copper ions is masked. At the neutral point the tint changes to light yellowish- or rush-green, but care must be taken to shake the liquid so that any precipitated copper hydroxide is redissolved.

J. C. W.

Detection of Small Quantities of Selenious Acid. JUL. MEYER and J. JANNEK (*Zeitsch. anal. Chem.*, 1913, **52**, 534—538).—To 1 c.c. of the solution containing selenium dioxide is added 0·1 gram of sodium hyposulphite ($Na_2S_2O_4$), and any free acid already present or formed by oxidation is neutralised with a few granules of sodium carbonate. The least traces of selenium present cause a red coloration due to colloidal selenium.

The reagent may be used for the detection of selenium in commercial sulphuric acid. In the absence of selenium, the precipitate consists of white colloidal sulphur, which is, however, yellow should selenium be present. Aqueous solutions, if too dilute for the test to show (limit 1 : 20,000), may be suitably concentrated; sulphuric acid, however, on concentration, loses its selenium content.

The Schultz petroleum test for the presence of selenium in sulphuric acid (formation of a dark brown colour) was found to be trustworthy. L. DE K.

A Study of the Lassaigné Reaction. S. P. MULLIKEN and C. L. GABRIEL (*Eighth Inter. Cong. App. Chem.*, 1912, **6**, 208—211).—The authors perform the Lassaigné test by dropping the substance, in compressed pellets, into a red-hot iron test-tube containing 0·25 gram of sodium. It is often advantageous to make the pellets with naphthalene or sugar, and positive results have even been obtained by moistening pellets of naphthalene with a dilute solution of the substance. The amount of nitrogen fixed as cyanide was determined for several substances. Diazo-compounds give no cyanide. J. C. W.

Estimation of Ammonia and Nitrogen. KNUBLAUCH (*Zeitsch. angew. Chem.*, 1913, **26**, 425—431).—Convenient forms of apparatus are described for the estimation of ammonia and total nitrogen in such substances as spent oxide and other gas-works products. In the estimation of total nitrogen, the addition of mercury in the digestion with sulphuric acid must be omitted when the substances under examination contain thiocyanates, ferrocyanides, and double cyanides. It is recommended that, in this case, the substances should be treated with sulphuric acid, allowed to remain for five minutes, then heated gently for twenty minutes, and finally boiled for ten minutes. A quantity of 0·25 gram of mercury or 0·05 gram of cupric oxide is now added, and the mixture is boiled for one hour. The addition of mercury at this point does not matter, as the preliminary treatment with sulphuric acid decomposes the substances mentioned. In the subsequent distillation of the ammonia, the mercury ammonium compounds must be decomposed by the addition of a sulphide or of zinc dust, but in the latter case a definite excess of alkali must be present. W. P. S.

Estimation of Ammonia and Trimethylamine. KOLOMAN BUDAI (*Zeitsch. physiol. Chem.*, 1913, **86**, 107—121).—The aqueous solution of the hydrochlorides is mixed with an excess of formaldehyde (neutralised with 10 c.c. of phenolphthalein), and titrated, in presence of phenolphthalein, until a slight coloration is produced. The amount of ammonia is then calculated. The solution is now considerably diluted, made strongly acid with concentrated hydrochloric acid, and boiled down to one-third. When cold, it is transferred to a Kjeldahl flask, distilled with alkali into standard acid, and titrated as usual. The result gives the nitrogen as tertiary amine. N. H. J. M.

Detection of Very Small Quantities of Nitric Acid in Waters. S. ROTHENFUSSER (*Chem. Zeit.*, 1913, **37**, 897).—One gram of diphenylamine is dissolved in 100 c.c. of pure (contact) sulphuric acid, of which 1 c.c. is then introduced into a stoppered glass cylinder. One drop of fuming hydrochloric acid is added, and

then pure sulphuric acid up to 100 c.c. After shaking, 20 c.c. of the mixture are placed in a beaker, and 10 c.c. of the sample of water to be tested for nitrates are rapidly added. On shaking, a blue colour appears, which increases in intensity. The reagent may be used for a ring test by placing 10 c.c. into a test-tube and pouring 5 c.c. of the water carefully over the surface. The coloration is very permanent. L. DE K.

Estimation of Nitrates in Sea Water. WILLIAM R. COPELAND and GEORGE A. SOPER (*Eighth Inter. Cong. App. Chem.*, 1912, **26**, 211—213).—A trustworthy method for the estimation of nitrates in sea water is of importance in connexion with the pollution of tidal harbours and the sea by sewage. It has been found that accurate results can be obtained by electrolytic reduction of the nitrates to ammonia by the copper-zinc method or the aluminium foil method, and subsequent estimation of the ammonia in the usual way. Various samples of land water, harbour water, and sea water have been tested, and nitrates were found to be present in every case. E. G.

Quantitative Volatilisation and Separation of Phosphoric Acid from Metals of the Copper Group, and from Aluminium, Tin, and the Alkali Metals. PAUL JANNASCH and ROBERT LEISTE (*J. pr. Chem.*, 1913, [ii], **88**, 129—167).—In continuation of previous work (A., 1909, ii, 759), the authors find that, when mixed with powdered quartz and heated to redness in a stream of carbon tetrachloride vapour, the phosphates of copper, silver, lead, cadmium, mercury, bismuth, potassium, and sodium may be completely decomposed and the phosphoric acid quantitatively volatilised.

The time required to effect complete decomposition is shortened, and the temperature at which the reaction proceeds lowered, if carbon dioxide and carbon tetrachloride are passed intermittently over the heated phosphates.

In the case of the phosphates of aluminium and tin, the addition of powdered quartz is insufficient to effect a quantitative separation of the phosphoric acid; complete volatilisation of the latter may, however, be accomplished if the phosphate is mixed with potassium chloride.

The paper contains a sketch and description of the apparatus employed in carrying out the decomposition by the intermittent method. F. B.

Simple Method for Preparing Neutral Ammonium Citrate Solution. ANDREW J. PATTEN and W. C. MARTI (*J. Ind. Eng. Chem.*, 1913, **5**, 567—568).—Fifty c.c. of a citrate solution are diluted to 250 c.c. Five c.c. of the diluted solution are treated with 4 c.c. of a neutral 40% formaldehyde solution, and titrated with $N/10$-sodium hydroxide, with phenolphthalein as indicator. The colour should remain when the solution is heated to boiling. The ammonia is estimated by distilling with magnesia. The difference

between the acid and ammonia titration gives the number of c.c. of $N/10$-ammonia required to neutralise 1 c.c. of the acid citrate solution, from which the amount of a stronger solution of ammonium hydroxide required to neutralise any given amount of the acid solution may be calculated.

The method is accurate and easy; and it shows that the ratio of ammonia to anhydrous citric acid in the neutral solution should be 1 : 3·765, and that one litre of D 1·09 should contain $NH_3=44·76$ and $C_6H_8O_7=168·57$ grams. N. H. J. M.

Estimation of Phosphoric Acid in Soils. RICHARD HORNBERGER (*Landw. Versuchs-Stat.*, 1913, **82**, 299—302).—When hydrochloric acid extracts of soils containing titanium are precipitated with ammonium molybdate, more or less titanic acid separates, which remains undissolved when the molybdate is dissolved in ammonia. Owing to its fine state of division and partly colloidal state, some of the titanic acid passes through the filter, and afterwards forms flakes. When filtered and washed, it again passes through the filter. The separation of titanic acid cannot be overcome completely, and as the precipitate contains small amounts of phosphoric acid, a slight minus error is introduced when the precipitate is removed, and a plus error when it is not removed, before precipitating with magnesia mixture.

The error may be avoided by fusing the precipitate with sodium carbonate, extracting with water and, after expelling the carbon dioxide, estimating the phosphoric acid by the molybdate method.

N. H. J. M.

Estimation of Hypophosphites, with Notes on Commercial Samples. T. TUSTING COCKING and JAMES D. KETTLE (*Pharm. J.*, 1913, **91**, 132—134).—The use of potassium dichromate for the titration of hypophosphites is recommended. A quantity of 2·5 grams of the salt under examination is dissolved in water, an excess of a 10% lead acetate solution is added to precipitate phosphites, the mixture is diluted with water to 50 c.c., and set aside until the supernatant liquid is clear. Ten c.c. are then transferred to a flask, mixed with 50 c.c. of $N/1$-potassium dichromate solution and 10 c.c. of sulphuric acid, and heated on a water-bath for one hour. After cooling, the excess of dichromate is titrated with thiosulphate solution after the addition of potassium iodide. The method may be applied to calcium, potassium, manganese, and iron hypophosphites, and results of analyses of these salts are recorded. In the case of hypophosphorous acid itself, it is necessary to neutralise the acid with sodium hydroxide before the addition of the lead acetate. W. P. S.

Estimation of Hardness in Very Hard Waters. SANTIAGO PIÑA DE RUBIES (*Ann. Chim. anal.*, 1913, **18**, 266—271; *Anal. Fis. Quim.*, 1913, **11**, 98).—When determining the hardness in waters, the

sample has occasionally to be largely diluted, so that the experimental error becomes greatly multiplied.

Hence, in the absence of alkali carbonates, the author recommends the acidimetric method of Hehner or that of Wartha-Pfeifer, which both give excellent results. L. DE K.

Proposed Standard Method of Analysis for Zinc. FRANK C. BREYER (*Eighth Inter. Cong. App. Chem.*, 1912, **25**, 7—37).—A study has been made of the relative merits of the various methods of zinc analysis, and as a result the following standard method has been devised, which not only gives accurate results for ores and zinc materials of a high degree of impurity, but has also proved satisfactory for the common sulphide and carbonate ores.

The material, 0·5 gram if containing more than 50% of zinc, or 1 gram if containing a smaller proportion, is placed in a 150 c.c. beaker with a little water and 10 c.c. of hydrochloric acid (D 1·20). The beaker is covered, and the mixture boiled for about half an hour. Ten c.c. of sulphuric acid (1 : 1) are added, and the product is evaporated until fumes of sulphuric acid are produced. The solution is then diluted to 40—50 c.c., and about a gram of powdered aluminium added. The beaker is again covered, and the contents are boiled until colourless. By this means the iron is reduced, and all the metals of the hydrogen sulphide group are precipitated except cadmium. After filtration, 1 c.c. of sulphuric acid (1 : 1) is added to the filtrate if the cadmium is to be removed electrolytically, the solution diluted to 125 c.c., and electrolysed with 0·8—1 ampere per 100 sq. cm. electrode for one to one and-a-half hours at about 3 volts. If the cadmium is to be removed with hydrogen sulphide, 5 c.c. of sulphuric acid (1:1) are added, and after diluting to 100 c.c. hydrogen sulphide is passed rapidly through the solution for fifteen minutes. Dilute ammonia is then added, drop by drop, until yellow cadmium sulphide begins to be precipitated. The solution is heated to 70—90°, the passage of hydrogen sulphide being continued, and then filtered. The precipitate is washed with cold, 8—10% sulphuric acid, and afterwards with hot water. After boiling the filtrate to remove hydrogen sulphide, the solution is cooled, nearly neutralised with potassium hydroxide and sodium hydrogen carbonate, and 2—4 c.c. of 5% sulphuric acid are added. A rapid stream of hydrogen sulphide is then passed through the solution for forty minutes. The zinc sulphide is collected, washed, and then returned to the beaker in which it was precipitated. Hydrochloric acid (10 c.c.) and water are added, and the solution is boiled to remove hydrogen sulphide; 13 c.c. of ammonia (D 0·90) are added, and afterwards neutralised with 3 c.c. of hydrochloric acid (D 1·20); excess of the latter is then added, and the whole diluted to 200 c.c. This solution is titrated with potassium ferrocyanide solution, 1 c.c. of which is equivalent to 10 mg. of zinc, and which has been standardised with amounts of zinc corresponding closely with those present in the sample of ore. The method is much shorter when cadmium is absent or present in quantities of less than 0·05%. E. G.

Estimation of Zinc and Cadmium. HERMANN WEIL (*Zeitsch. anal. Chem.*, 1913, **52**, 549—553).—The author estimates zinc by the well-known titration process with ferrocyanide in presence of ferric tartrate in ammoniacal solution, with dilute acetic acid as external indicator. Cadmium may be estimated similarly, but the author finds that it consumes exactly double the amount of ferrocyanide required by zinc.

When the two metals are both present, a preliminary separation with hydrogen sulphide is recommended; the precipitated cadmium sulphide is then redissolved in boiling dilute hydrochloric acid, oxidised with bromine, and titrated. The filtrate containing the zinc is treated similarly.

Should other heavy metals be present, these must be removed by the usual processes. L. DE K.

Estimation of Small Amounts of Cadmium in the Dry Way. FRANK C. BREYER (*Eighth Inter. Cong. App. Chem.*, 1912, **25**, 1—5). —Biewend (A., 1903, ii, 105) has described a method for detecting cadmium in zinc ores by heating 0·1—0·5 gram of the sample in a narrow glass tube with a reducing agent, such as ferrous carbonate, iron, or aluminium. A deposit of cadmium or its oxide is obtained, which can be converted into the characteristic sulphide by igniting it in presence of sulphur vapour.

A modification of this method is described, in which a Rose crucible is substituted for the closed tube. The material to be tested (200 mg.) is placed in the crucible; the Rose stem is introduced so that it nearly touches the substance on the bottom, and a small stream of gas is admitted sufficient to give a flame a quarter of an inch long. The crucible is gradually heated to bright redness, and maintained at this temperature until zinc oxide vapour begins to rise. After the crucible has cooled, a ring or patch of cadmium oxide appears. If the sample contains as little as 0·1% of cadmium, the oxide is plainly visible. As the proportion of cadmium increases, the patch becomes a ring of increasing breadth and thickness. From the appearance of the sublimate, it is possible to judge the amount of cadmium present to within 0·1%, when occurring in quantities of 0·1—0·6%. If 200 mg. of the sample do not yield a brown patch, there is less than 0·1% of cadmium present, and if 400 mg. give a slight coating, between 0·05 and 0·1% is present. Very small traces of cadmium can be estimated by means of Biewend's tube method if the tube is drawn out to a capillary; in this way, 0·001% in ores and light compounds, and 0·0005—0·0001% in spelter and alloys, can be estimated.

Comparison with the usual methods has shown that these new methods give trustworthy results. The methods are chiefly of value as obviating the application of processes for effecting the separation of cadmium in zinc analysis or for estimating cadmium when the metal is either absent or only present in traces. E. G.

Titration of Copper by means of Methanal-sulphurous Acid. PHILIPPE MALVEZIN (*Bull. Soc. chim.*, 1913, [iv], **13**, 721—722).—A

solution for titration is prepared by adding excess of sulphur dioxide to 40% formaldehyde solution and diluting to a suitable concentration. The copper solution is treated with ammonia and titrated with the standard solution until the colour disappears.

J. F. S.

Analysis of Brass. BERTHOLD KOCH (*Chem. Zeit.*, 1913, **37**, 873—874).—A modification of Lunge's process. One gram of turnings is dissolved in a tall, narrow 200 c.c. beaker, covered with a watch-glass, in 10 c.c. of nitric acid (D 1·2), applying a gentle heat. The solution is diluted with 100 c.c. of water, 15 c.c. of dilute sulphuric acid (1 : 1) are added, and then again water up to 150 c.c. The liquid is then raised to the desired temperature and electrolysed.

With a current of 9 amperes and at 90°, the separation of the copper is complete within twenty to thirty minutes; with 6 amperes and at 70°, in forty minutes; and with 1 ampere and at 50°, in 120 minutes. Wire gauze electrodes are used. The author, however, prefers working with a current of 3 amperes and 3·5 volts at 70—75°; it then takes sixty minutes for complete precipitation. When the electrolysis is finished the electrodes are removed and instantly rinsed with water. The current is then stopped, and after the deposit is washed with alcohol and ether it is dried in an air-bath at 90—100°.

L. DE K.

Electro-analysis of Copper, Antimony, Bismuth, and Tin with Acidified Chloride Electrolytes. EUGENE P. SCHOCH and DENTON J. BROWN (*Eighth Inter. Cong. App. Chem.*, 1912, **21**, 81—91).—It has been considered hitherto that solutions of metallic chlorides acidified with hydrochloric acid are unsuitable for electro-analytical work on account of the oxidising action of the chlorine which is liberated. The liberation of chlorine can be prevented, however, by the addition of a suitable reducing agent, and it has been found that copper, antimony, bismuth, and tin can be deposited quantitatively by employing formaldehyde, hydroxylamine hydrochloride, or oxalic acid. In these experiments, the electrolysis was effected with A. Fischer's modification of Sand's electrodes. The deposits are obtained in a satisfactory form, and are probably free from inclusions.

The deposition of tin in presence of hydroxylamine hydrochloride is complete in about ninety minutes at temperatures between 30° and 70° and with a current of 1·5 amperes. This metal can also be estimated by effecting the deposition of the greater part of it in absence of a reducing agent, and then adding ammonium oxalate and oxalic acid; an excellent deposit is thus obtained in about ninety minutes.

Copper can be completely deposited with a cathode potential as low as −0·40 volt against the normal calomel electrode, and this fact renders possible its separation from tin. Both metals can be estimated in the same sample of electrolyte, and the following simple method is recommended for the analysis of bronze. The

alloy is dissolved in aqua regia, and after the solution has been evaporated, 2 grams of hydroxylamine hydrochloride and 5—15 c.c. of hydrochloric acid (D 1·20) are added together with sufficient water to make the total volume 200 c.c. Electrolysis is now effected, the cathode potential being limited to −0·40 volt. The copper is completely deposited in twenty to forty minutes, and the end-point is recognised by the fact that the current must be reduced to zero to prevent the rise of the cathode potential above −0·40 volt. The beaker is lowered from the electrodes, and the latter are washed with a few c.c. of water and the washings added to the electrolyte. The cathode is now detached, rinsed with alcohol and ether, dried quickly, and weighed. This electrode can now be used for the deposition of the tin. A further quantity of hydroxylamine hydrochloride (3 grams) is added to the solution, and the latter treated with a constant current of 1·5 amperes. The deposition of the tin is complete in twenty to forty minutes.

Antimony can be estimated in solutions acidified with hydrochloric acid if hydroxylamine hydrochloride is added, the solution heated to 50—75°, and the cathode potential limited to −0·40 volt. Bismuth can be estimated in a similar manner, but in order to obtain a good deposit, the cathode potential should be limited to −0·25 volt until most of the metal has separated, and then gradually raised until it reaches −0·60 volt. Both antimony and bismuth are deposited completely in a few minutes. E. G.

New Method for the Analytical and Quantitative Separation of Mercury from Bismuth. Adolfo P. Castañares (*Eighth Inter. Cong. App. Chem.*, 1912, **25**, 39—40).—Mercury and bismuth can be separated with great precision by taking advantage of the fact that mercury is not precipitated by ammonium carbonate from hot solutions of mercuric compounds strongly acidified with nitric acid, whilst under similar conditions bismuth is totally precipitated.

The concentration of the mercury in the solution should not much exceed 0·1%. To the solution containing both metals, nitric acid (D 1·42) is added in a quantity of 5 c.c. per 100 c.c. of solution, and the mixture is heated to 60°. Solution of ammonium carbonate (10%), containing 1% of ammonia, is slowly added until the liquid is decidedly alkaline. The mixture is now heated at 80° until carbon dioxide ceases to be evolved. The precipitate is collected in a Gooch crucible, washed with 1% solution of ammonia, dried at 100°, and heated to redness until of constant weight.

If the solution contains chlorides, the precipitate obtained on adding ammonium carbonate must be collected, dissolved in dilute nitric acid, and the solution evaporated. The residue must be treated three or four times with concentrated nitric acid, and evaporated each time on the water-bath in order to convert the bismuth into the form of nitrate, which can then be precipitated by ammonium carbonate or phosphate.

In either case, the filtrate containing the mercury is warmed, treated with a slight excess of freshly prepared ammonium sulphide, and boiled for a few minutes. The precipitate is collected in a

Gooch crucible, washed first with water containing ammonium sulphide, and afterwards with alcohol, and dried at 100—110°. The mercuric sulphide is thus obtained free from sulphur, and therefore does not require to be treated with carbon disulphide.

The method is simple, rapid, and accurate. E. G.

Gravimetric Estimation of Tungsten, Chromium, Silicon, Nickel, Molybdenum, and Vanadium in Steels. S. Zinberg (*Zeitsch. anal. Chem.*, 1913, **52**, 529—534).—One gram of the sample is dissolved in dilute hydrochloric acid (1 : 4), and then heated to boiling with addition of a few c.c. of nitric acid; residue, tungstic acid. The silica is recovered from the solution by evaporation with 6 c.c. of sulphuric acid. The filtrate from the silica is treated under pressure with hydrogen sulphide; this precipitates molybdenum sulphide, convertible into oxide by ignition. The filtrate is concentrated by evaporation, oxidised with nitric acid, and poured into a boiling solution of sodium hydroxide (10 grams to 200 c.c. of water). Iron, chromium, and nickel are precipitated completely; the filtrate contains the vanadium and traces of chromate. After acidifying with nitric acid, a hot solution of barium nitrate is added in slight excess. The filtrate is then evaporated to dryness with addition of a few drops of alcohol. Water is added, and the chromium precipitated with a little ammonia; the precipitate is then added to the iron precipitate, the whole is dissolved in nitric acid, evaporated with potassium chlorate, and the chromium precipitated as usual with mercurous nitrate.

The ammoniacal filtrate contains the vanadium, which, after expelling the free ammonia, may be precipitated by a faintly acid solution of mercurous nitrate. The precipitate settles better if a drop of ammonia is next added, and may then be ignited to oxide.

Nickel is best tested for separately. After eliminating the tungsten as directed, the filtrate is mixed with 2 grams of tartaric acid, ammonia is added in slight excess, and the nickel precipitated at 70—80° by addition of 15—25 c.c. of a 1% solution of dimethylglyoxime; the precipitate is then converted by ignition into nickelous oxide.

In the absence of molybdenum and tungsten, the chromium and vanadium may be isolated by converting the iron into nitrate and fusing the dry mass with 2—3 grams of sodium potassium carbonate. Any nickel remains insoluble on lixiviating the fused mass. L. de K.

Estimation of Tungstic Acid and Silicic Acid. Hugo Hermann (*Zeitsch. anal. Chem.*, 1913, **52**, 557—568).—The separation of tungstic acid by Scheele's method by precipitation with nitric acid succeeds best with the ortho-compound. Para- and meta-compounds should therefore be rendered alkaline at first.

In presence of silicic acid, considerable amounts of silico-tungstic acids may form even in the cold, so that a portion of the tungstic acid is not separated. Even carbon dioxide will cause this. Silico-

tungstic acid, once formed, can only be resolved by prolonged warming in strongly alkaline solutions.

The formation of these complex acids may be prevented by adding an excess of nitric acid suddenly.

The conversion of silicic acid into silico-tungstic acid renders possible its quantitative estimation with great accuracy. The characteristic precipitate yielded by that acid with luteocobalt solution serves as a microscopical test for silica. L. DE K.

Separation of Tungsten from Thorium, Lanthanum, Cerium, Erbium, Didymium or Silica. MAX WUNDER and A. SCHAPIRA (*Ann. Chim. anal.*, 1913, **18**, 257—260).—*Separation of the Oxides of Tungsten and Thorium.*—The oxides (about 0·35 gram) are fused over the blowpipe with 5 grams of sodium carbonate for one hour. The mass is boiled with water for twenty minutes, and the residue washed with hot water containing a little sodium carbonate. After washing the thorium oxide with 5% hydrochloric acid, it is ignited and weighed. From the filtrate, the tungsten is recovered by acidifying with nitric acid and precipitating as mercurous tungstate, which is then ignited to oxide.

Oxides of Tungsten and Lanthanum.—The process is exactly the same as for thorium.

Oxides of Tungsten and Cerium.—The mixture cannot be ignited without loss; after fusion with sodium carbonate, the cerium remains insoluble, and is treated as directed for thorium. The same applies to *tungsten* and *erbium*, with this difference, that the latter oxide dissolves in 5% hydrochloric acid, and must be reprecipitated with ammonia.

Tungsten and Didymium.—On ignition, volatilisation takes place, but on fusion with sodium carbonate and filtering the solution (as in the case of erbium) when cold, the oxide of didymium remains insoluble, and is purified by dissolving in 5% hydrochloric acid and reprecipitation with ammonia.

Oxide of Tungsten and Silica.—This is a more troublesome process. The fusion (including alumina) is dissolved in boiling water, and then boiled with an excess of ammonium nitrate, which precipitates the alumina and part of the silica; after igniting and weighing, the silica is removed by means of hydrofluoric and a few drops of sulphuric acid, and found from the loss. The filtrate is then precipitated with mercurous nitrate; the precipitate, after ignition, consists of tungstic acid and some silica, which is then removed by means of hydrofluoric acid as directed. The filtrate from the mercurous tungstate still contains silica, which is recovered by evaporation, drying of the residue at 110°, and treating this with dilute nitric acid. L. DE K.

Estimation of Paraffin in Native Asphalt and Petroleum Asphalt. J. MAREK (*Zeitsch. anal. Chem.*, 1913, **52**, 553—556).—One gram of the sample is dissolved in 2 c.c. of chloroform, 50 c.c. of light petroleum (b. p. 70°) are added, and after an hour the solution is filtered through cotton wool moistened with light

petroleum, and covered with 40—60 grams of powdered animal charcoal. The mass is then washed thrice with 30 c.c. of light petroleum. The liquid is distilled off, and the residue dissolved in 10 c.c. of ether. After adding 10 c.c. of absolute alcohol and cooling to $-20°$, the paraffin is collected; a special apparatus for cooling and filtering is described and figured.

Of asphaltic stones, a larger quantity is taken, and the powder heated to boiling with 50 c.c. of light petroleum. When cold, the solution is decolorised as described for asphalt. L. DE K.

Identification of Hydrocarbons of the Benzene Series. H. ROSSET (*Ann. Chim. anal.*, 1913, **18**, 260—262).—The members of the benzene series may be distinguished from those of the methane series by the miscibility test with alcohol. Whereas a satisfactory reading will be obtained on heating 5 c.c. of light petroleum with 5 c.c. of alcohol, it is necessary to take 10 c.c. of xylene, toluene, or commercial benzene, and 15 c.c. of pure benzene, in order to ensure a good reading. Mixtures may thus be recognised (compare also this vol., ii, 353). L. DE K.

The Oxidation Assay of Essential Oils. FRANCIS D. DODGE (*Eighth Inter. Cong. App. Chem.*, 1912, **6**, 86—92).—The stability of the constituents of essential oils towards cold permanganate is described. Camphor, fenchone, bornyl acetate, eucalyptol, paraffins and aliphatic ketones are the only common substances which remain unaffected. In some cases, as with borneol and fenchyl alcohol for example, the oxidation is limited to the formation of a stable ketone, but, generally speaking, the destruction is complete. Phenolic ethers exhibit peculiarities. Anethole and methylchavicole yield anisic acid, methyleugenol and *iso*methyleugenol give veratric acid, but the methylene ethers as, for example, safrole and *iso*-safrole, are completely oxidised.

For practical purposes a measured volume (10 c.c.) of the oil is run into a narrow-necked litre-flask, and shaken with small portions of concentrated potassium permanganate in the cold until the colour is permanent during a few hours. Sulphurous acid is then carefully added to dissolve the precipitate, and the oil is allowed to rise and is finally measured. The process may be applied to the detection of petroleum products in turpentine or Ceylon citronella oil, and to the differentiation between bornyl acetate and its isomerides. Hesse and Müller used the same method for separating benzyl and linalyl acetates (A., 1899, i, 441). J. C. W.

Direct Estimation of Caoutchouc Applicable to Specifications on Vulcanised Rubber Goods. CHARLES R. BOGGS (*Eighth Inter. Cong. App. Chem.*, 1912, **9**, 45—58).—The method proposed is a modification of the bromination process described originally by Budde (*Gummi Zeit.*, 1907, **21**, 1205). The sample is ground to pass a 20-mesh sieve, extracted with acetone, and dried in an atmosphere free from oxygen. A quantity of about 0·1 gram of the powder is then boiled for three hours with 20 c.c. of toluene,

the greater part of the latter is then removed by evaporation on the water-bath, and, after the addition of 50 c.c. of carbon tetrachloride, the cold mixture is treated with 50 c.c. of a solution containing 16 grams of bromine and 1 gram of iodine in 1 litre of carbon tetrachloride. After twenty-four hours, 50 c.c. of absolute alcohol are added, and, after the lapse of a further sixteen hours, the precipitate is collected on a filter, washed with a mixture consisting of 2 vols. of carbon tetrachloride and 1 vol. of alcohol, then with alcohol, boiling water, and again with alcohol. The air-dried precipitate is ignited with a large excess of sodium carbonate and potassium nitrate, and the bromide is estimated in the usual way. The amount of bromine found is multiplied by the factor 0·425 to give the quantity of caoutchouc. No correction is applied for the sulphur in the bromide. W. P. S.

New Method for the Identification of Methyl Alcohol. PAUL N. RAIKOW (*Eighth Inter. Cong. App. Chem.*, 1912, **25**, 417—419).—When a solution of nitromethane is treated with ammonia, and solution of sodium nitroprusside is added drop by drop, an intense indigo-blue coloration is produced even if only traces of nitromethane are present. The blue colour gradually changes through green to yellow or yellowish-red. On further addition of the sodium nitroprusside solution, the blue colour is restored and again fades; this reappearance and disappearance of the blue colour can be repeatedly effected. If the higher nitroparaffins and acetone are treated in this way, only cherry-red colorations are produced.

This reaction has been applied to the detection of methyl alcohol in ethyl alcohol. About 200 c.c. of the ethyl alcohol are acidified with phosphoric acid and submitted to distillation with the aid of a fractionating column. The first 10 c.c. of distillate are placed in a 60 c.c. flask with 4 grams of red phosphorus. A reflux condenser is attached, and 25 grams of iodine are gradually added. After twenty minutes the mixture is fractionated, and the first 5 c.c. of distillate are treated with 2—3 grams of silver nitrite and slowly distilled to dryness. The distillate is collected in quantities of 3—4 drops, and these are tested for nitromethane by the method already described. E. G.

Detection and Estimation of Methyl Alcohol. ROLAND SCHMIEDEL (*Pharm. Zentr.-h.*, 1913, **54**, 709—716).—The method proposed for the detection of methyl alcohol in the presence of ethyl alcohol consists in rendering the mixture of alcohols alkaline, and adding dilute hydrogen peroxide in small quantities at a time; the oxidation must be carried out at a temperature of about 5°, and under these conditions methyl alcohol is converted into formic acid, ethyl alcohol yielding acetic acid. The presence of the former acid is then detected by its reducing properties. The method may be rendered quantitative by distilling the acids with steam, collecting the acid distillate in calcium carbonate, and eventually estimating the formic acid by the mercuric chloride

process. Each gram of mercurous chloride obtained corresponds with 0·0678 gram of methyl alcohol. W. P. S.

Estimation and Detection of Methyl Alcohol. THEODORE VON FELLENBERG (*Chem. Zentr.*, 1913, ii, 309—310; from *Mitt. Lebensmittelunters. Hyg.*, 1913, **4**, 122—146).—When 40% methyl alcohol is shaken with an equal volume of ether, the aqueous-alcoholic layer increases in volume, whilst the ethereal layer diminishes. With ethyl alcohol of similar strength, the reverse is the case, the aqueous-alcoholic layer decreasing. When 50 c.c. of each liquid are used at 15°, the increase is +4·15 in the case of methyl alcohol, and the decrease is −6·48 for ethyl alcohol. Mixtures of the two alcohols give intermediate values, from which their proportions can be calculated. In analysing spirits the aldehydes, esters, terpenes, etc., have first to be removed. Mixtures of pure alcohols can be analysed with an error of only 0·2—0·4%. For the detection of methyl alcohol, Denigès' (A., 1910, ii, 461) method is considered the best. Ethyl alcohol and the higher homologues may be salted out from admixture with methyl alcohol by means of potassium carbonate, so enriching the solution with methyl alcohol that it becomes possible to detect 1 part in 100,000. E. F. A.

Estimation and Detection of Small Quantities of Methyl Alcohol in the Blood and Tissues. MAURICE NICLOUX (*Eighth Inter. Cong. App. Chem.*, 1912, **19**, 259—260).—The tissues are minced into 6—8 times the weight of saturated picric acid solution, and a fifth of the bulk of the liquid is then distilled off. The addition of picric acid prevents frothing. The methyl alcohol is estimated by means of potassium dichromate solution by the same process as that employed by the author for the estimation of ethyl alcohol. The methyl alcohol is further characterised by determining the amount of carbon dioxide formed in the reaction and the CO_2/O_2 ratio, which for this alcohol is 0·915. S. B. S.

Gabriel Bertrand's Method of Sugar Estimation. G. SONNTAG (*Biochem. Zeitsch.*, 1913, **53**, 501—503).—The author calls attention to the fact that the principles involved in what is now generally known as Bertrand's process were already suggested by Schwarz in 1852, and actually employed by Mohr for dextrose estimation in 1873, and by the author himself in a form only slightly differing from that used by Bertrand in 1903. His experimental method is recapitulated; and it is claimed that it is as feasible as that of Bertrand. S. B. S.

Electrolytic Apparatus for Use in Invert Sugar Estimations. B. B. ROSS (*Eighth Inter. Cong. App. Chem.*, 1912, **8**, 75—77).—The cuprous oxide obtained in the usual way by boiling the invert sugar solution with an excess of Fehling's solution is collected on a small asbestos filter contained in a tapped funnel. The cuprous

oxide is washed with hot water and then dissolved by filling the funnel (after closing the tap) about three-fourths full with nitric acid (4 c.c. of nitric acid, D 1·42 per 100 c.c. of water). A platinum cylinder is then immersed in the solution, and serves as the cathode, whilst a platinum spiral fused through the funnel just above the tap acts as the anode, and the copper is deposited on the cathode by the application of a current of suitable density. The deposited copper is, finally, dried and weighed on the cathode. W. P. S.

Estimation of Cellulose by means of Nitric Acid. VENKATA RAO and BERNHARD TOLLENS (*J. Landw.*, 1913, **61**, 237—244).—Comparative estimations of cellulose in various substances by the nitric acid method proposed by Dmochowski and Tollens (A., 1910, ii, 554) and by the chlorine process described by Cross and Bevan (T., 1889, **55**, 199) showed that the factor 1·1 given by Dmochowski and Tollens is not applicable in every case. A slightly different factor has to be used for various classes of substances in order that the results obtained by the nitric acid method may agree with those found by the chlorine process. For instance, in the case of jute, the factor is 1·16, for buckwheat flour, 1·30, cocoa husk, 1·19, and cotton-wool, 0·98. W. P. S.

Impossibility of Separating Tartrate and Free Tartaric Acid in Wine. W. I. BARAGIOLA (*Chem. Zentr.*, 1913, ii, 179; from *Schweiz. Woch. Chem. Pharm.*, 1913, **51**, 289—291. Compare Baragiola and Godet, A., 1912, ii, 981).—Since wine represents a solution in which there is equilibrium between the free and fixed tartaric acid, it is obvious that the slightest disturbance of the conditions with the object of analytical determination of the acid will change the equilibrium. It is possible only to determine the total tartaric acid, and calculate its state of combination on physico-chemical data when all the acids and all the bases have been determined. Calculations based on the total, the soluble and insoluble alkalinity of the ash lead to incorrect results. E. F. A.

Estimation of Tartaric Acid. PAUL B. DUNBAR (*Eighth Inter. Cong. App. Chem.*, 1912, **26**, 361—373).—It has been shown by Dunbar and Bacon (A., 1912, ii, 699) that malic acid can be estimated by measuring the increase in rotation produced by treating the solution with uranyl acetate. It was pointed out that the specific rotation of *d*-tartaric acid is also increased by uranium salts, and that the presence of this acid therefore interferes with the estimation of malic acid. The present work was undertaken with the object of devising a method for estimating tartaric acid, and which could be applied to the estimation of both malic and tartaric acids in the same solution. In this paper an account is given of a method for estimating tartaric acid.

If a solution of tartaric acid or tartrates containing from 0·2 to 3·0 grams of the acid per 100 c.c. is treated with uranyl acetate, each gram of acid in 100 c.c. produces a rotation of $+19·6°$ *V*, the ratio of tartaric acid concentration to rotation being 0·051. Hence,

in the absence of malic acid, tartaric acid can be estimated by treating the solution with uranyl acetate, polarising, and multiplying the reading by 0·051. In presence of other optically active substances, a portion of the solution must be freed from tartaric acid by precipitation with lead acetate and polarised separately. The difference between this reading and that obtained with the solution treated with uranyl acetate gives the polarisation due to the uranyl tartaric complex. E. G.

Estimation of Malic and Tartaric Acids in the Same Solutions. PAUL B. DUNBAR (*Eighth Inter. Cong. App. Chem.*, 1912, **26**, 375—385).—Dunbar and Bacon (A., 1912, ii, 699) and Dunbar (preceding abstract) have shown that malic and tartaric acids, when occurring separately, can be estimated by observing the increase in rotation produced on treating the solutions with uranyl acetate.

A method has now been devised for estimating both acids in the same solution, which is based on the facts: (1) that the rotations of both acids are increased independently by treatment with uranyl acetate under definite conditions, and (2) that both acids can be oxidised quantitatively to oxalic acid by heating with potassium permanganate in alkaline solution. When determinations have been made of the total rotation produced on addition of uranyl acetate, and the amount of oxalic acid formed on oxidation or the quantity of permanganate reduced, the amounts of malic and tartaric acids present can be calculated. The method is interfered with by the presence of substances which form oxalic acid on oxidation, and which cannot be removed before treatment with the permanganate. E. G.

The Significance of the Marchi Reaction. W. CRAMER, HENRY O. FEISS, and W. E. BULLOCK (*Proc. physiol. Soc.*, 1913, li—lii; *J. Physiol.*, **46**).—In the degeneration of nerve-fibres, ordinary fats, but no cholesterol esters are formed; it is the ordinary unsaturated fat that is responsible for the Marchi reaction, for which it is a specific stain. The method can be applied to ascertain microchemically the composition of fat droplets in cells. W. D. H.

Detection of Acetaldehyde in Paracetaldehyde. II. GEORG HEYL (*Chem. Zentr.*, 1913, ii, 85; from *Apoth. Zeit.*, 1913, **28**, 306—307. Compare this vol., ii, 636).—When 6 c.c. of paracetaldehyde are shaken with a mixture of 2 c.c. of potassium hydroxide and 4 c.c. of water, the aqueous layer should not become yellow or brown within an hour; 0·2% of acetaldehyde is enough to give a positive reaction, and some pure commercial preparations of paracetaldehyde also give the reaction. Ten c.c. of a 2·5% aqueous solution of paracetaldehyde, when shaken with 20 drops of a freshly prepared 1% solution of sodium nitroprusside and 3 drops of piperidine, should not give a blue coloration. E. F. A.

Estimation of Benzaldehyde and Oil of Bitter Almond. FRANCIS D. DODGE (*Eighth Inter. Cong. App. Chem.*, 1912, **17**, 15—20).—Of the various methods which have been proposed for

the estimation of aldehydes, Denner's hydrazone method, Bennett's oxime method (A., 1909, ii, 192), and the sodium hydrogen sulphite method yield trustworthy results in the case of benzaldehyde. It is essential, however, in the latter method, to maintain the temperature of the reacting substances at 0°; the time of contact of the benzaldehyde with the sodium hydrogen sulphite solution should be two hours. Approximately correct results may also be obtained by a method which is based on the reaction between benzaldehyde and potassium hydroxide according to the equation: $2C_6H_5{\cdot}CHO + KOH = C_6H_5{\cdot}CO_2K + C_6H_5{\cdot}CH_2{\cdot}OH$. The benzaldehyde is treated with an excess of 2·5*N*-potassium hydroxide solution, and, after remaining for twenty-four hours, the excess is titrated with *N*/2-hydrochloric acid. The presence of hydrocyanic acid interferes to some extent when any of these methods is applied to the estimation of benzaldehyde in oil of bitter almonds. The author has isolated about 0·2% of a heavy yellow oil from natural benzaldehyde; the nature of this oil has not been ascertained, but it is probable that it has some influence on the aroma of the natural oil. W. P. S.

Detection of Ionone. MAURICE HANRIOT (*Eighth Inter. Cong. App. Chem.*, 1912, **25**, 373—374).—If ionone is dissolved in concentrated hydrochloric acid, an intense golden-yellow coloration is produced; on adding chloral hydrate and heating the mixture, the liquid becomes dull violet. If the solution, when cold, is shaken with ether, it is decolorised, and on evaporating the ethereal solution, a violet substance is obtained which is soluble in water and is immediately decolorised by ether. *iso*Ionone gives the same reaction, and it is probable that it takes place with ionone only after the latter has been transformed into *iso*ionone by the hydrochloric acid. ψ-Ionone and natural essence of violets do not respond to the test. The test is of value for the detection of ionone in commercial perfumes, and does not seem to be interfered with by the presence of natural essences. E. G.

Estimation of Urea in Blood by means of Sodium Hypobromite (Mercury and Water Ureometers). ANDRÉ GUILLAUMIN (*J. Pharm. Chim.*, 1913, [vii], **8**, 64—70).—Small quantities of urea present in blood may be estimated equally accurately by the sodium hypobromite method, using either a mercury or water ureometer to measure the gas liberated. E. F. A.

Estimation of Urea. JOHN ALEXANDER MILROY (*Biochem. J.*, 1913, **7**, 399—409).—The procedure is as follows. The phosphates present in the sample of urine are removed by precipitation with baryta mixture. Twenty-five c.c. of the filtered urine are titrated with *N*/10-hydrochloric acid until neutral to methyl-red, 5 c.c. of neutral formaldehyde are added, and the titration with decinormal alkali is completed. This gives the approximate amount of nitrogen in the form of pre-formed ammonia and amino-acids.

Ten c.c. portions of the filtrate are heated with 8 c.c. of *N*-sulphuric acid at 155° for 1·5 hours in an autoclave. After filtering, the formaldehyde titration is effected in the usual manner; it gives the pre-formed ammonia and amino-acids above, for which deduction can be made, together with amino-acids set free by hydrolysis and the ammonia derived from the urea. The distillation methods give the pre-formed ammonia and that formed by hydrolysis of urea. Comparative experiments show the formaldehyde titration method to give a positive error of 1·7% of urea, but it has the advantage of being quicker and giving at the same time an approximate estimate of the pre-formed ammonia and amino-acids.

E. F. A.

Cadmium Nitrate in Qualitative Analysis. ANTON VORISEK (*Eighth Inter. Cong. App. Chem.*, 1912, **17**, 91—102).—Cadmium nitrate may be employed in the analysis of the second group of anions to remove S, $Fe''(CN)_6$, and $Fe'''(CN)_6$. The minimum amounts of cadmium nitrate and potassium hydroxide required for a complete precipitation were ascertained; for instance, at least 6·7 c.c. of *N*/5-cadmium nitrate solution and 2 c.c. of *N*/5-potassium hydroxide solution must be used for 10 c.c. of *N*/10-potassium ferrocyanide solution. The amount of potassium hydroxide consumed is out of proportion to the acidity of the cadmium solution, and the alkali evidently takes part in the formation of the precipitates. Of the cyanogen ions more than 80% remain unprecipitated, so that cyanogen ions may be detected in the filtrate from the cadmium precipitate and apart from $Fe''(CN)_6$ and $Fe'''(CN)_6$. A procedure for the subdivision of the anions of the second group is outlined.

Ammonium acetate and thiocyanate are the most effective ammonium salts for preventing the precipitation of calcium tartrate. Tartaric and citric acids may be precipitated completely from neutral solutions by cadmium nitrate and potassium hydroxide. In the case of tartaric acid, 10 c.c. of the *N*/5-solution require at least 22 c.c. of *N*/5-cadmium nitrate solution and 11 c.c. of *N*/8-potassium hydroxide solution, whilst an equivalent quantity of citric acid requires 11·2 c.c. of cadmium nitrate and 2·2 c.c. of potassium hydroxide. The precipitate formed with tartaric acid appears to have the formula $Cd_2(OH)_2C_4H_4O_6$, but with citric acid the results failed to indicate an agreement with any one of the formulæ extant. A process for the detection of these two acids and the removal of certain ions of the second group in one treatment is given.

W. P. S.

Micro-sublimation of Alkaloids under Reduced Pressure. R. EDER (*Chem. Zentr.*, 1913, ii, 91—92; from *Schweiz. Woch. Chem. Pharm.*, 1913, **51**, 228—231, 241—245, 253—256).—A simple apparatus is described which allows the determination of the temperature of sublimation under 10 mm. pressure. The sublimation points of the pure alkaloids are as follows: Cocaine, 75—90°;

atropine, 93—110°; codeine, 100—130°; quinine, 133—148°; narcotine, 146—156°; brucine, 158—175°; solanine, 168—174°. The sublimates were studied with the lens during formation, and their crystallographic appearance and microchemical reactions noted. The alkaloids are classified as follows:

A. Those which sublime without melting. 1. Caffeine, theobromine, cinchonine, solanine, cantharidine give direct crystalline sublimates. 2. A number of alkaloids give at first a homogeneous sublimate, consisting of minute, amorphous droplets, which subsequently becomes crystalline as the layer thickens. 3. Others give a deposit in which sometimes irregular crystals appear subsequently, or it remains amorphous.

B. 4. Those which give a sublimate above their melting point, consisting either of minute, amorphous droplets or crystals, for example, narceine, pilocarpine, veratrine, emetine, colchicine.

C. 5. Sparteine sulphate and nicotine hydrochloride give no sublimate on account of dissociation or decomposition.

The stability of the amorphous droplets is smaller, and the crystallisation takes place more easily and quickly the lower the compound sublimes below its melting point, that is to say, the higher the vapour pressure of the alkaloid. Compounds in group 1 above have a high vapour pressure, and therefore are crystalline from the start. In group 2 the vapour pressure is lower, and crystallisation takes place with difficulty. In groups 3 and 4 the vapour pressure is still lower, and crystallisation is only occasional.

E. F. A.

Estimation of Uric Acid in Urine. FRANZ HERLES (*Eighth Inter. Cong. App. Chem.*, 1912, **19**, 141—144).—The principle of this quick process consists in precipitating the urate by ammonium chloride as ammonium salt, according to the method of Hopkins and others, treating this precipitate with excess of $N/10$-sulphuric acid, and estimating the excess of acid added by titration with alkalis, using methyl-orange as an indicator, as this is not affected by the uric acid. One c.c. of $N/10$-acid is equivalent to 0·01682 gram of uric acid. If the urine is not clear, the uric acid precipitate is dissolved in water with addition of alkali, sufficient of which must be added to produce a red colour with phenolphthalein, the mixture is heated, made up to a definite bulk, and an aliquot part is filtered off from the phosphates precipitated. In this portion the uric acid is estimated by the method described above.

S. B. S.

The Chemical Nature of Substances from Alcoholic Extracts of Various Foodstuffs which Give a Colour Reaction with Phosphotungstic and Phosphomolybdic Acids. CASIMIR FUNK and A. BRUCE MACALLUM (*Biochem. J.*, 1913, **7**, 356—358).—Folin and Macallum (A., 1912, ii, 495; this vol., ii, 80) introduced a phosphotungstic acid solution as a colour reagent for uric acid, and Folin and Denis (A., 1912, ii, 1011) a mixture of phosphotungstic and phosphomolybdic acids for polyphenols.

The action on a large number of related substances of the two reagents was investigated. The uric acid reagent gives a reaction with certain purine and tyrosine derivatives and the polyphenol reagent appears to be specific for purine derivatives and polyphenols. Amino-acids, polypeptides, and diketopiperazines are negative to both reagents. The replacement of one hydrogen atom in the purine ring lessens or abolishes the uric acid reaction. In the case of the phenol reagent this occurs when two hydrogen atoms are replaced.

The alcoholic extracts of different foodstuffs rich in vitamines give both reactions markedly; as the vitamine fractions are purified the reactions gradually disappear, and their curative power for polyneuritis lessens. The reactions are sensitive, and so may be used to ascertain the purity of phosphatides, caseinogen, and other food products. W. D. H.

Estimation of Aspirin. A. ASTRUC (*J. Pharm. Chim.*, 1913, [vii], **8**, 5—8).—To verify the purity of aspirin, it is proposed first to titrate 1·8 grams with *N*-potassium hydroxide solution in presence of phenolphthalein, and secondly to saponify with alcoholic potassium hydroxide and show that double the former quantity of alkali is required. E. F. A.

Detection of Bile Pigments in Urine. C. J. REICHARDT (*Pharm. Zeit.*, 1913, **58**, 591—592).—Attention is drawn to the fact that very dark-coloured urines fail to give a positive reaction with Gmelin's test. Only when the urine has been exposed to air and light, and probably to bacterial decomposition, the bilirubin oxidised to biliverdin, and the chromogens and indigo compounds reduced, is it possible to detect the presence of bile pigments. W. P. S.

The Separation of Cystine and Tyrosine. R. H. ADERS PLIMMER (*Biochem. J.*, 1913, **7**, 311—317).—Cystine and tyrosine can be separated by means of phosphotungstic acid; the precipitation of cystine is almost complete, but loss occurs in its recovery from the precipitate; almost the whole of the tyrosine can be recovered from the filtrate and washings. The two substances can be imperfectly separated by mercuric sulphate in 5% sulphuric acid; the cystine is not completely precipitated, and the tyrosine which is recovered is impure. A complete and quantitative separation can be brought about by absolute alcohol saturated with hydrogen chloride. The tyrosine is rapidly converted into tyrosine ester, and goes into solution. It can be recovered by boiling the solution when diluted with water, and then neutralising with ammonia. Almost the whole of the cystine is insoluble; the portion which goes into solution is precipitated by adding an equal volume of absolute alcohol. The cystine is not converted into its ethyl ester, since after dissolving the insoluble portion in dilute hydrochloric acid, it is precipitated in typical crystals on the addition of ammonia. W. D. H.

The Estimation of Tyrosine in Proteins by Bromination. R. H. ADERS PLIMMER and (Miss) ELIZABETH C. EAVES (*Biochem. J.*, 1913, **7**, 297—310).—The estimation of small quantities of tyrosine can be effected by Millar's method of bromination, but it is preferable to add excess, and titrate the non-absorbed halogen with thiosulphate solution. Tyrosine cannot be directly estimated in the presence of protein, because tryptophan and histidine both absorb bromine; the latter can be removed by precipitation with phosphotungstic acid. The absorption of bromine by tryptophan is not wholly eliminated after boiling with acid, so that tyrosine cannot be estimated by this method in solutions containing the products of acid hydrolysis which contain tryptophan. Values for the tyrosine content of proteins, agreeing with those obtained by isolation and weighing, are obtained when the bromine absorption of a tryptic digest is measured after an interval of about six hours.

W. D. H.

Estimation of Tryptophan in Protein. JESSE A. SANDERS and CLARENCE E. MAY (*Biochem. Bull.*, 1913, **2**, 373—378).—The method recommended is, in outline, to subject the proteins to pancreatic digestion, innoculate the digest with fæcal bacteria, and estimate the indole liberated colorimetrically. W. D. H.

Hopkins and Cole's Modification of the Adamkiewicz Test for Protein. VERNON H. MOTTRAM (*Biochem. J.*, 1913, **7**, 249—259).—This test fails in the presence of small amounts of oxidising agents, but traces of these improve the reaction when pure sulphuric acid is used. With commercial sulphuric acid the result is probably due to oxidising agents contained in it. The reaction rate is increased by temperature. W. D. H.

The Estimation of Albumin-Nitrogen, Ovomucoid-Nitrogen, Free and Combined Carbohydrates in the White of Incubated Eggs. HUBERT W. BYWATERS (*Proc. physiol. Soc.*, 1913, xxxv—xxxvi; *J. Physiol.*, **46**).—Total nitrogen is estimated by Kjeldahl's method. The egg-white is then diluted, and heat coagulated after appropriate acidification; the ovomucoid nitrogen is estimated in the filtrate and washings, so also is the sugar; when ovomucoid is boiled with 5% hydrochloric acid, the sugar in combination is set free, and this is estimated by Pavy's method.

W. D. H.

The Behaviour of Blood with Hydrazine Hydrate. GEORGE A. BUCKMASTER (*Proc. physiol. Soc.*, 1913, xlviii—xlix; *J. Physiol.*, **46**).—Hydrazine hydrate reduces oxyhæmoglobin, and nitrogen is evolved in exactly equivalent volume to that of the oxygen removed. No other constituent of the blood does this. If the quantity of oxygen evolved by the ferricyanide method is measured, it is equal to that of nitrogen evolved by hydrazine hydrate, but the latter reagent does not liberate carbon monoxide from carboxy-

hæmoglobin as ferricyanide does, nor is there any liberation of gas from reduced hæmoglobin. It is therefore possible in a given sample of blood to determine the relative quantities of oxyhæmoglobin, carboxyhæmoglobin, and reduced hæmoglobin.

W. D. H.

Evaluation of Medicinal Papain Preparations. R. DELAUNAY and O. BAILLY (*Chem. Zentr.*, 1913, i, 1895—1896; from *Bull. Soc. Pharmacol.*, **20**, 141—147).—When allowed to act for six hours, papain behaves as a peptonising enzyme, and only as a very weak peptolysing enzyme. It dissolves and hydrolyses coagulated proteins, such as fibrin, forming filtrates which are no longer precipitated on the addition of nitric acid, and have a low amino-index. Papain thus resembles pepsin, but differs in that the optimum temperature is about 80°, and the medium must have a neutral or faintly alkaline reaction. Papain differs from pancreatin in its low peptolysing powers. To evaluate papain, the amount of fibrin which passes into solution in a given time under the conditions of maximum activity is determined. The disappearance of the power of nitric acid to cause a precipitate or the alteration in the amino-index are not trustworthy indications of the activity of papain.

E. F. A.

General and Physical Chemistry.

Rotatory Dispersion of Free *l*-Bornylxanthic Acid. LEO TSCHUGAEV (*Bull. Soc. chim.*, 1913, [iv], **13**, 793—796).—The necessary ethereal solutions of *l*-bornylxanthic acid are obtained by dissolving a known quantity of sodium *l*-bornylxanthate in water, washing the solution with ether, cooling with ice, acidifying with a slight excess of sulphuric acid, and extracting with ether. A series of experiments has been made at definite intervals of time for the rays $\lambda = 656$, 589, 527, and 499 $\mu\mu$.

The free acid is lævorotatory for all wave-lengths, and also exhibits abnormal rotatory dispersion. The values corresponding with the red end of the spectrum diminish progressively with the time, whilst those corresponding with the green and blue end increase. Consequently, the maximum of rotation becomes displaced towards the violet portion of the spectrum, and the abnormal dispersion is gradually replaced by that characteristic of borneol, and, more generally, of substances possessing normal dispersion. This is attributed to the decomposition of *l*-bornylxanthic acid into *l*-borneol and carbon disulphide. H. W.

Rotatory Dispersion of Certain Derivatives of β-Pinene (Nopinene). LEO TSCHUGAEV and A. KIRPETCHEV (*Bull. Soc. chim.*, 1913, [iv], **13**, 796—803).—The present work has been undertaken to test the previous conclusion (Tschugaev, A., 1912, ii, 822) that, whilst optically active alcohols generally have normal dispersion-coefficients, the ratio a_F/a_C for hydroaromatic ketones rises to 3·5, and, further, that this exaltation is connected with the selective absorption in the ultra-violet portion of the spectra of the latter.

Nopic acid (compare Wallach and Blumann, A., 1907, i, 936), when dissolved in alcohol ($c = 26·55$), has $[\alpha]_C - 11·41°$, $[\alpha]_D - 14·46°$, $[\alpha]_E - 18·53°$, $[\alpha]_F - 22·60°$, $[\alpha]_F/[\alpha]_C$ 1·98°.

Nopinol, m. p. 101—102° (Wallach and Blumann's α-nopinol), has $[\alpha]_C^{20} - 7·01°$, $[\alpha]_D^{20} - 9·17°$, $[\alpha]_E^{20} - 12·19°$, $[\alpha]_F^{20} - 15·15°$ in ethyl alcoholic solution ($c = 14·059$), and therefore exhibits practically normal rotatory dispersion.

The specific rotation of nopinone has been determined in a variety of solvents (methyl alcohol, chloroform, ethyl iodide, in the pure state, in ether, benzene, *iso*pentane, and carbon disulphide). Abnormal rotatory dispersion is observed in each case, the value of the coefficient $[\alpha]_F/[\alpha]_C$ varying from 2·98 for the first-named solvent to 7·95 for the last-named. Further, the specific rotation for any particular ray is greatly dependent on the nature of the solvent, but is very little influenced by change of temperature.

The absorption spectra of nopinol and nopinone have also been investigated. The former only absorbs in the extreme ultra-violet, and gives no characteristic band; the latter absorbs strongly, its

spectrum presenting a diffuse band, the maximum of which is situated towards 3550 rec. A.U. In this case, therefore, the strong and selective absorption corresponds with an abnormal exaltation of the dispersive power. H. W.

Influence of Pressure on the Absorption of Rays of Very Long Wave-length in Gases. EVA VON BAHR (*Ber. Deut. physikal. Ges.*, 1913, **15**, 673—677).—Measurements are recorded of the variation in the absorption of long waves (100—350 μ) in the gases hydrogen chloride, sulphur dioxide, and hydrogen bromide at a series of pressures (20 mm.—760 mm.). The absorption curves are similar to those previously obtained for short wave-lengths (A., 1909, ii, 630; 1910, ii, 914). J. F. S.

Ultra-red Absorption of Gases. EVA VON BAHR (*Ber. Deut. physikal. Ges.*, 1913, **15**, 710—730).—The ultra-red absorption bands of carbon dioxide, carbon monoxide, nitrous oxide, ether vapour, and carbon disulphide have been examined at a series of pressures and temperatures by means of a radiomicrometer using a slit of 0·1 mm. It is shown that the absorption bands at low pressure are not continuous. The discontinuity is less marked as the pressure is increased, so that when the maximum absorption is reached the bands are practically continuous. An increase in the temperature of carbon monoxide brings about a separation of the two maxima of its absorption bands, and also a lateral broadening of the bands. The consequences of the experimental results of the present and previous work is compared with the requirements of the Bjerrum theory of the ultra-red absorption spectra, and generally the agreement between theory and experiment is found to be satisfactory. J. F. S.

Critical Study of Spectral Series. III. Atomic Weight and its Import in the Constitution of Spectra. WILLIAM MITCHINSON HICKS (*Proc. Roy. Soc.*, 1913, *A*, **89**, 125—127. Compare A., 1912, ii, 512).—It is shown that there is a definite quantity in connexion with each element which is of fundamental importance in the building up of its spectrum. This quantity is proportional to the atomic weight, and if w represents the atomic weight divided by 100, its value is $(90·4725 \pm 0·013)w^2$. This quantity is termed the oun ($\omega\nu$). The evidence for its existence is based on the arc spectra for helium, the elements of the groups I and II, the aluminium sub-group and scandium, also of oxygen, sulphur, and selenium. It is found that the Δ values which give the doublet and triplet separations are all multiples of their respective ouns, and that the corresponding quantities, which give the satellite separations in the D series, are also multiples of the oun. The F series also shows satellites depending in a similar way on the oun. In a large number of cases, lines are related in such a way that the differences of their denominators are multiples of the oun, and that frequently in place of an expected line, which is not observed, another occurs related to it in this manner. It is said

to be collaterally displaced. The paper then deals with the constitution of the D and F series. J. F. S.

Ultra-red Absorption Spectra of Some Gases. WILHELM BURMEISTER (*Ber. Deut. physikal. Ges.*, 1913, **15**, 589—612).—The absorption spectra of chlorine, bromine, hydrogen, oxygen, hydrogen chloride, hydrogen bromide, cyanogen, hydrogen cyanide, acetylene, carbon monoxide, and carbon dioxide have been determined in the ultra-red region 1μ—22μ. It is shown that for the elements there are no absorption bands; for the other substances the heads of the absorption bands lie at the following points: hydrogen chloride [3·40, 3·55], hydrogen bromide [3·84, 4·01], cyanogen [3·79, 3·93], 4·65, 13·50, 16·07; hydrogen cyanide, 3·04 [6·95, 7·22], [13·60, 14·33]; acetylene, 2·52, 3·07, 3·77 [7·39, 7·66], [13·50, 13·95]; carbon monoxide, 2·35 [4·60, 4·72]; and carbon dioxide [14·70, 15·05]; the bracketed values represent double bands. The similarity between the spectra of the gases cyanogen and acetylene and the dissimilarity between the spectra of cyanogen and hydrogen cyanide are remarkable. J. F. S.

Band Spectrum Attributed to Carbon Monosulphide. L. C. MARTIN (*Proc. Roy. Soc.*, 1913, *A*, **89**, 127—132).—A continuation of the work of Strutt and Fowler (A., 1912, ii, 214). It is shown that the arc spectrum of sulphur contains a series of ultra-violet bands extending over the range λ 2436—2837. This band series is also obtained when a spark discharge is passed through carbon disulphide vapour, but not when spark discharges are passed through sulphur vapour, or sulphur chloride vapour. It was observed occasionally in the latter case, but the carbon band λ 2478 was also visible, due to a rubber connexion. The new series of bands, therefore, depends on the presence of both sulphur and carbon, but is unlike the spectra of either element alone. The spectrum of the light produced, when carbon monosulphide is removed from a liquid air cooling mixture, contains the same bands in the ultra-violet. J. F. S.

New Band Spectrum Associated with Helium. W. E. CURTIS (*Proc. Roy. Soc.*, 1913, *A*, **89**, 146—149. Compare this vol., ii, 539).—A number of bands were observed in the helium spectrum, the chief bands having their heads at λ 6400, 5732, 4649, and 4626. The band 5732 is degraded toward the violet end of the spectrum, and the others in the opposite direction. The author's description of the spectrum is generally the same as that of Goldstein (*loc. cit.*). The spectrum is attributed to helium, although it may possibly be due to hydrogen, because hydrogen has always been present in the tubes. J. F. S.

Principal and Other Series of Lines in the Hydrogen Spectrum. ALFRED FOWLER (*Zeitsch. wiss. Photochem.*, 1913, **12**, 357—371).—The principal and sharp series of hydrogen lines are observed when a strongly condensed discharge is passed through

a mixture of hydrogen and helium. Four members of the principal series and three of the ζ Puppis series were identified. The lines of the principal series have a somewhat smaller wave-length than that calculated by von Rydberg. The wave-length of the first line is $\lambda\lambda$ 4685·98 on the Rowland system, which agrees sufficiently well with that observed for the same line in the solar chromosphere and the stars. A second principal series of hydrogen lines was discovered, of which the first line has a wave-length $\lambda\lambda = 3203 \cdot 30$. The lines in this series converge to the same value as the first principal series. The production of the new lines gives a further proof of the probability that there is no different kind of matter in the stars than that on the earth, and that most of the spectra observed in stars can be reproduced in the laboratory.

J. F. S.

The Red Lithium Line and the Spectroscopic Determination of Atomic Weights. P. ZEEMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 155—157).—The lithium red line 6708, previously shown by Zeeman to be a close doublet, has been further examined, and the components shown to be 0·144 Ångström unit apart. It is shown that the regularities found between the differences of the frequencies of the pair lines and the squares of the atomic weights for the elements sodium, potassium, rubidium, and cæsium do not hold for lithium. J. F. S.

New Series in the Spark Spectrum of Magnesium. ALFRED FOWLER (*Proc. Roy. Soc.*, 1913, *A*, **89**, 133—136).—The spark lines were produced when an arc was passed between magnesium electrodes in a vacuum. Five new lines were photographed which are related to the lines λ 4481, 3106·5, and 2659·5. The eight lines make up two series, E_1 and E_2, and are expressed by the Hicks formulæ:

$$E_1(m) = 49775 \cdot 81 - \{109675/(m + 0 \cdot 996679 + 0 \cdot 001552/m)^2\}$$

and $$E_2(m) = 49776 \cdot 30 - \{109675/(m + 0 \cdot 496395 + 0 \cdot 002884/m)^2\}.$$

The two magnesium spark series are similar to the two principal series of hydrogen and run nearly parallel with them. J. F. S.

Additional Triplets and Other Series Lines in the Spectrum of Magnesium. ALFRED FOWLER and W. H. REYNOLDS (*Proc. Roy. Soc.*, 1913, *A*, **89**, 137—145. Compare preceding abstract).—An examination of the arc spectrum of magnesium in a vacuum has shown eight additional triplets, six of which belong to the diffuse and two to the sharp series. Four additional lines belonging to the Rydberg series have been photographed, and it is shown that even a four constant formula does not accurately represent this series. Four strong solar lines of hitherto unknown origin have been identified with lines of the Rydberg series, namely, $\lambda = 4167 \cdot 44$, 4057·67, 3986·90, and 3938·55. A previously unknown line, $\lambda = 4354 \cdot 53$, may be united in a series with the known lines λ 5711·31 and 4730·21 having the same limit as the Rydberg series.

This series is probably of the sharp type. Several previously known lines have been remeasured, and improved values obtained.

J. F. S.

Series in the Lines of Mercury Spectrum. JOHANNES STARK (*Ann. Physik*, 1913, [iv], **42**, 238—240).—Polemical. Reply to Paschen (this vol., ii, 361) with respect to the placing of the lines λ 2536·72 and λ 4078·05 in the same series.

J. F. S.

Reflection Spectra of Compounds of Neodymium. PAUL JOYE (*Arch. Sci. phys. nat.*, 1913, [iv], **36**, 41—58, 113—138).—The reflexion spectra of a number of neodymium compounds have been photographed and measured. The substances measured include three hydrates: $Nd_2O_3,3H_2O$, $2Nd_2O_3,3H_2O$, Nd_2O_3,H_2O, the oxide, sulphide, sulphate, chloride, bromide, carbonate, oxalate, and nitrate. The absorption spectra of solutions of the nitrate and chloride are also described. A full list of the absorption bands measured is given, and the relationships between the various bands are discussed.

J. F. S.

The Radiations from Nitrogen. MAURICE HAMY (*Compt. rend.*, 1913, **157**, 253—257).—An extension of the work of Fabry and Buisson (compare *J. Physique*, 1912, June) to the spectra of bands, and in particular to those which do not appear to be sensitive to a magnetic field, the example chosen being those obtained from nitrogen and lying between λ 440 and λ 410. The method of measurement has already been described (*ibid.*, 1906, 189). The results show that the optical width of the radiations composing the refrangible bands of the positive spectrum of nitrogen obey the same law as that of the rays of the line spectra, a law which is independent of the theories relying on the generation of the luminous vibrations.

W. G.

Spectroscopic Investigations in Connexion with the Active Modification of Nitrogen. III. Spectra Developed by the Tetrachlorides of Silicon and Titanium. WILFRED JEVONS (*Proc. Roy. Soc.*, 1913, *A*, **89**, 187—193. Compare Fowler and Strutt, A., 1911, ii, 482, 678; 1912, ii, 214).—The author has introduced the vapours of silicon tetrachloride and titanium tetrachloride into the after-glow of active nitrogen, and examined the spectra. In the former case a number of bands between λ 3800 and 4950 have been observed; these are attributed to a nitride of silicon, whilst in the latter case there is no evidence of a nitride of titanium. The new silicon nitride bands degrade towards the red, and show intense minima near the heads, corresponding with the modifications of the cyanogen after-glow bands.

J. F. S.

Arc and Spark Lines of Oxygen in Canal Rays. JOHANNES STARK, G. WENDT, and H. KIRSCHBAUM (*Physikal. Zeitsch.*, 1913, **14**, 770—779).—The spectra of oxygen in helium and oxygen canal rays have been measured. It is shown that increasing the cathode

potential fall from 3200 volts to 15,000 volts causes an increase in the intensity of all lines of oxygen in oxygen canal rays. It is also shown that there are two series of oxygen spark lines characterised as sharp and unsharp lines. Two arc spectra are also observed, and it is shown that the carriers of the lines of the first spectrum are positive univalent oxygen molecules. J. F. S.

Series Lines of Oxygen in Canal Rays. JOHANNES STARK (*Physikal. Zeitsch.*, 1913, **14**, 779—780).—Polemical. A further criticism of Wilsar's work (this vol., ii, 172, 359; see also Stark, this vol., ii, 172). J. F. S.

Band Spectrum of Silicon Tetrafluoride. C. PORLEZZA (*Gazzetta*, 1913, **43**, ii, 124—128).—The author has re-investigated this spectrum, already measured by Dufour, and the new measurements are recorded in the present paper. Three new lines (wave-lengths 4616·57, 4609·61, 4605·25) have been observed. The measurements refer to the spectrum of undecomposed silicon tetrafluoride which is obtained when no condenser is employed. If the intensity of the discharge is increased by the use of condensers, however, a line spectrum is obtained due to silicon and fluorine; this has already been described (A., 1912, ii, 876). R. V. S.

The Origin of Some Groups of Bands in the Spark Spectrum of Salts of Strontium. S. PIENKOWSKI (*Bull. Acad. Roy. Belg.*, 1913, 607—613).—The spark spectrum of strontium chloride is measured, both in air and in hydrogen. The spark is produced by a coil fed with a current of 20—25 amperes at 110 volts, using a Wehnelt interrupter making 350—400 breaks per second. The spark in this way is 0·7 cm. long. It is shown that the bands at λ 4583, 4565, 4545, 4524, 4421, 4401, 4340, 4305, and 4281 are due to the oxide. J. F. S.

Arc Spectrum of Tellurium. HORACE SCUDDER UHLER and R. A. PATTERSON (*Amer. J. Sci.*, 1913, [iv], **36**, 135—140).—The arc spectrum of pure tellurium has been determined, using gratings of 1 metre radius of curvature and 18159 lines in 4·6 cm. and 6·55 metres radius of curvature and 5905 lines per cm. Fifteen lines have been measured lying between 3175·130 *A* and 2081·8 *Å*, measured on the international scale. The line 3175·130 is shown to be distinct from the tin line 3175·044, and the line 2769·653 distinct from the antimony line 2769·939 by mixing tellurium with tin and antimony respectively, and photographing the spectrum of the mixtures when the two lines in each case are obtained. The arc was produced in an atmosphere of carbon dioxide between tellurium electrodes for the earlier measurements, and later by placing pieces of tellurium on the lower carbon pole of a carbon arc. J. F. S.

Absorption Spectrum of Aqueous Vapour. EVA VON BAHR (*Ber. Deut. Physikal. Ges.*, 1913, **15**, 731—737).—The bands at

$5 \cdot 9 \mu$ and $6 \cdot 5 \mu$ have been re-measured, and from the measurements it is shown that both parts of the bands are made up of a number of separate lines. The rotation wave-lengths calculated from these lines coincide with those found by Rubens in the region of the residual rays. It is shown that the bands $5 \cdot 9 \mu$ and $6 \cdot 5 \mu$ are probably to be regarded as Bjerrum double bands. J. F. S.

Inflexion Point in the Absorption Boundary Curve; Long Wave-length Absorption Bands of Acetone. JOHANNES STARK (*Physikal. Zeitsch.*, 1913, **14**, 845—847).—The conditions under which a point of inflexion can occur in an absorption spectrum curve are considered, and it is shown that a point of inflexion in one branch of a band of an absorption boundary curve or an absorption index-wave-length curve is an indication of the presence of a less intense band in the same wave-length region as the first band. The absorption curve of acetone is then considered, and since this shows a point of inflexion (Bielecki and Henri, *Physikal. Zeitsch.*, 1913, **14**, 516; see this vol., ii, 363), it is concluded that acetone, in addition to the known short wave-length bands, has a still less intensive long wave-length ultra-violet band above λ 330 $\mu\mu$. J. F. S.

The Presence of Absorption Bands in the Ultra-violet Spectrum of Some Abnormal Alcohols of the Fatty Series. GUSTAVE MASSOL and A. FAUCON (*Compt. rend.*, 1913, **157**, 386—388). —A study of the ultra-violet absorption spectra of some normal, primary, secondary, and tertiary alcohols, and also of three abnormal primary alcohols. All the alcohols exhibit a progressive absorption for radiations of short wave-length. The secondary alcohols are slightly more transparent than the normal primary alcohols with the same carbon content, whilst the tertiary alcohols are markedly more transparent. The three abnormal primary alcohols studied showed two absorption bands, the one from $\lambda = 2500$ to 2700, and the other from λ 3060 to 3150. These bands are special to the alcohols, and cannot be found either with the fundamental hydrocarbon, with the other alcohols, or with the corresponding alkyl haloids. The corresponding aldehydes present one single broad band coming between the two bands of the alcohols. W. G.

Quantitative Study of the Absorption of the Ultra-violet Rays by Some Acids of the Ethylene Series. JEAN BIELECKI and VICTOR HENRI (*Compt. rend.*, 1913, **157**, 372—375).—The authors have determined the absolute values of the absorption of the ultra-violet rays for a number of acids containing an ethylene linking, and from a comparison with the corresponding saturated acids have determined the influence of such a linking, and also of its position with respect to the carboxyl group.

The ethylene linking in acids produces a rise in the absorption, the increase being greater the nearer the linking is to the carboxyl group. In the case of geometrical stereoisomerides, the *cis*-isomeride

absorbs less than the *trans*. The influence of the ethylene linking cannot be expressed in the form of an additive constant, but as a factor according to the following law: For a substance of formula ABC . . ., the molecular constant of absorption ϵ is equal to a product, $\epsilon=(abc\ \ldots)\ (\alpha\beta\ \ldots)$, where $a, b, c, \ldots$ are factors corresponding with the different molecular groups A, B, C . . ., and $\alpha, \beta, \ldots$ are factors which indicate the effect of the linking, configuration, and reciprocal positions of the groups. These results are borne out by a similar study of the alcohols. W. G.

Absorption Spectra of the Red Dyes Sanctioned for Use in Confectionary. GUSTAVE MASSOL and A. FAUCON (*Bull. Soc. chim.*, 1913, [iv], **13**, 803—807. Compare this vol., ii, 264, 542, 742).—The method of investigation used is that previously described. The spectra of eight dyes have been studied. Those derived from naphthaleneazonaphthol (Bordeaux B., crystal-ponceau, Bordeaux S, new coccine, fast red) and those from xyleneazonaphthol (ponceau RR, scarlet R) show similar spectra, both in the visible and invisible portions, yielding a broad band which extends from the yellow to the violet for small thicknesses, and covers the whole of the latter in the case of layers of 30 to 50 mm. They are very absorbent for the ultra-violet.

Acid magenta, on the other hand, is very transparent to the violet rays, and gives a band covering the green and blue which, for short layers (8 to 18 mm.), separates into two distinct bands. Unlike the other reds, acid magenta is very transparent to the invisible rays of wave-length greater than 320—330; for layers of 10 mm. the spectra show a sharp alteration in the absorption between $\lambda=270$ and $\lambda=300$.

A short summary of the results of this series of investigations is also given. H. W.

Emission of Series Lines by Canal Rays. JOHANNES STARK (*Ann. Physik*, 1913, [iv], **42**, 163—180).—The intensity of the series lines is brought about by the collision of canal ray particles with the non-luminous atoms, the canal ray particle passing through their periphery and bringing about an ionisation. The relationship of the intensity of the higher valence lines to that of the univalent lines increases with increasing velocity of the light of the canal rays. Helium-canal rays tend to produce low valence lines of other elements. It is shown to be probable that the collision of heavy canal-ray particles on aluminium atoms occasions changes of both light energy and kinetic energy. The canal rays of heavy elements allow helium atoms, which lay in their path, to pass through their outside layer without any marked change in their kinetic energy.

J. F. S.

Fluorescence of the Elements of the Sixth Group of the Periodic System. Sulphur, Selenium, and Tellurium Vapours. WALTER STEUBING (*Physikal. Zeitsch.*, 1913, **14**, 887—893).—The four elements of the sixth group of the periodic system show a

marked fluorescence in the gaseous condition. The fluorescence moves from regions of short wave-length to regions of longer wave-length with increase of atomic weight. For oxygen, fluorescence is exhibited below λ 2000 Å.; for sulphur, between λ 2500 Å. and λ 3200 Å.; for selenium, from λ 3000 Å into the visible region, and for tellurium in the most refrangible part of the visible region. A definite density and temperature is necessary for production of fluorescence; for example, in the case of sulphur vapour a temperature of 400—500° is necessary. The fluorescence spectra are discontinuous, and show more or less feeble groups of lines which have the appearance of bands. The fluorescence is greatly weakened by mixing the vapours with other gases or vapours. J. F. S.

Phosphorescence of Mercury Vapour after Removal of the Exciting Light. F. S. PHILLIPS (*Proc. Roy. Soc.*, 1913, *A*, **89**, 39—44).—The phosphorescence of mercury vapour has been observed by directing a beam of light $\lambda = 2536$ from a water-cooled quartz mercury lamp on to an exhausted quartz tube, in which a stream of mercury vapour is produced by distilling mercury from one limb into the other. The mercury fluoresces at low pressures, and persists after the vapour has passed the exciting beam of light. The fluorescence of the vapours of iodine, anthracence, and retene was examined by the same method, but with negative results.

J. F. S.

Rotatory Power of Some Organic Complexes of Molybdic Acid. ARRIGO MAZZUCCHELLI, C. RANUCCI and A. SABATINI (*Gazzetta*, 1913, **43**, ii, 26—59. Compare Mazzucchelli, A., 1911, i, 10; Mazzucchelli and Borghi, A., 1911, i, 11).—From the authors' measurements with solutions of mixtures of tartaric and molybdic acids, as well as from those of Rosenheim and Itzig (A., 1900, i, 135, 272), it appears that the rotatory power of the organic acid in presence of any given quantity of molybdic acid is not absolutely fixed, but varies within limits which exceed those of experimental error. It is suggested that the solutions may present a case of false equilibrium.

The rotatory power of solutions containing molybdic acid, tartaric acid, and a third indifferent, inactive acid (acetic acid, hydrochloric acid), is not seriously affected by the presence of the last-named, so that polarimetric measurements may be used to determine the partition of molybdic acid in a solution between tartaric acid and any other acid capable of forming molybdic complexes but inactive.

The difference between the white and yellow molybdic acids in regard to tartaric acid, confirmed in the previous paper (*loc. cit.*), has since been found not to exist; where the differences are not accidental they may be referred to the methyl alcohol present. The same similarity of behaviour towards tartaric acid was also observed in the case of molybdic acid from other sources (by acidification of ammonium paramolybdate "Merck," acid ammonium

molybdate, $3(NH_4)_2O,8MoO_3,4H_2O$, and potassium trimolybdate, respectively).

Further measurements of the rotatory power of solutions containing tartaric acid and various molybdates of sodium and potassium show that the rotatory power depends only on the relative proportions of the constituents, and not on the order of addition or on the nature of the molybdate added (compare *loc. cit.*). Hence if a solution of an alkaline tartrate does not dissolve more than an equimolecular quantity of molybdic acid, this is due only to the slowness of the heterogeneous reaction.

Towards malic acid the white and yellow molybdic acids behave alike; in both cases indications of the existence of two compounds, $C_4H_6O_5,MoO_3$ and $C_4H_6O_5,2MoO_3$, are found.

The white and yellow molybdic acids behave similarly towards quinic acid. The rotatory power of the solutions is altered by addition of ethyl alcohol, as well as by that of methyl alcohol, and the rotatory power is also considerably affected by changes of concentration.

Measurements of the rotatory power of mixtures of molybdic and tartaric acids to which hydrogen peroxide had been added showed the existence of two peracids, $C_4H_6O_6,MoO_3,H_2O_2$ and $C_4H_6O_6,2MoO_3,H_2O_2$. There may be also compounds in the proportions 1:2:2, 1:3:2, and 1:3:3, or the values observed at these concentrations may be due to dissociation of the compound 1:2:1. In any case, compounds other than these do not exist (compare Mazzucchelli and Borghi, *loc. cit.*). When the ratio $MoO_3:H_2O_2$ exceeds 1:2, the rotatory power diminishes considerably.

The rotatory power of mixtures of malic acid, molybdic acid, and hydrogen peroxide does not change appreciably on keeping; the values obtained are not much influenced by temperature, but vary considerably with the total concentration of the solution. The addition of the peroxide diminishes the rotatory power, which becomes negative when the concentration reaches $MoO_3,2H_2O_2$.

The addition of peroxide to solutions of quinic acid and molybdic acid also causes a diminution of rotatory power. R. V. S.

The Photochemical Equivalent. EDWARD C. C. BALY (*Physikal. Zeitsch.*, 1913, **14**, 893—896).—The theory of electric fields surrounding molecules is developed by the author, and experimental evidence is advanced to show the addition of a molecule of an acid to a base to form an additive compound before the formation of a salt takes place. These actions are studied spectroscopically in the case of *p*-aminobenzaldehyde and hydrochloric acid, and in the sulphonation of quinol dimethyl ether (compare Baly and Rice, T., 1912, **101**, 1475). It is shown that experiments of Henri and Wurmser (this vol., ii, 369) give values for the quantity of light absorbed by the photochemical reactions they have observed, which are too small, and it is suggested in opposition to the above authors that a portion of the necessary energy is derived from the solvent.

J. F. S.

Theory of Photochemical Reaction Velocity. MAX BODENSTEIN (*Ber. Deut. physikal. Ges*, 1913, **15**, 690—704).—A theoretical paper in which an hypothesis of the mechanism of photochemical reactions is put forward and examined in connexion with a large number of published photochemical changes. It is assumed at the outset that every photochemical reaction is a photoelectrical change in which a molecule is divided, with absorption of light energy, into an electron and a positive residue with a free valency. Both parts are then capable of reaction; the positive residues react either with one another or with other molecules, the electrons by combining with other molecules and rendering them capable of reaction. This leads to reactions of two kinds, primary light reactions occurring between the positive residue and other molecules, and secondary light reactions between molecules which have been rendered active by combining with an electron. Both types of reactions are developed in the paper. J. F. S.

Influence of Oxygen on the Selective Photo-effect of Potassium. ROBERT POHL and P. PRINGSHEIM (*Ber. Deut. physikal. Ges.*, 1913, **15**, 625—636).—When potassium is brought into contact with oxygen at low pressure a dark-coloured surface layer is formed, which consists of a solution of colloidal potassium in a compound of potassium and oxygen. This mixture is strongly photoelectrically active, so much so that in the violet end of the spectrum a yield of 240×10^{-4} coulomb per light calorie is observed. The maximum of this selective activity is displaced 7% from that of pure potassium in the direction of smaller wave-length, from $\lambda = 436 \mu\mu$ to $\lambda = 405 \mu\mu$. At the same time, there is a large increase in the electron emission below $\lambda = 280 \mu\mu$, which is to be regarded as the normal photo-effect of potassium oxide. J. F. S.

The Rôle of Uranium Salts as Photochemical Catalysts. DANIEL BERTHELOT and HENRY GAUDECHON (*Compt. rend.*, 1913, **157**, 333—335).—A continuation of experiments on the behaviour of uranium salts as photochemical catalysts (compare A., 1911, ii, 170). Apart from salts of uranium, neither the fluorescent nor radioactive substances, experimented with, accelerated photochemical reactions. The accelerating influence of the uranium salts is limited to a special class of reactions, namely, the decomposition of open-chain acids, especially dibasic or complex acids. These are reactions which occur spontaneously in ultra-violet light, and, under the influence of the catalyst, they take place in visible light. The catalyst thus lowers the vibration frequency of the photochemical reaction, in the same way as an ordinary catalyst lowers the temperature of a chemical reaction. W. G.

Negative Photocatalysis of Hydrogen Peroxide. VICTOR HENRI and RENÉ WURMSER (*Compt. rend.*, 1913, **157**, 284—287).—The addition of traces of numerous different substances to hydrogen peroxide renders it stable towards ultra-violet rays, alkalis being more active than acids in this respect. The authors suggest that,

in many of the cases of catalysis by ferments and colloidal metals, the action of poisons is on the substances undergoing transformation, and not on the catalyst itself. Further, that the action of certain ferments is quite comparable to that of the ultra-violet rays. W. G.

Absorption of Ultra-violet Rays by Some Mineral Colouring Matters in Aqueous Solution. GUSTAVE MASSOL and A. FAUCON (*Compt. rend.*, 1913, **157**, 332—333. Compare this vol., ii, 742).—A study of the absorption of the ultra-violet rays by aqueous solutions of such substances as potassium ferrocyanide, gold chloride, copper sulphate, &c. These colouring matters exhibit various powers of absorbing ultra-violet rays, and are far less powerful than synthetic organic dyes, although qualitatively the absorption is of the same order, and in the case of band spectra, broad absorption bands occur in the same regions of the spectrum, these depending on the colour, and not on the chemical constitution of the substance. W. G.

Rays of Positive Electricity. SIR JOSEPH J. THOMSON (*Proc. Roy. Soc.*, 1913, *A*, **89**, 1—20).—The Bakerian Lecture. The properties of positive rays are considered, together with the author's method of examination by subjecting them to electric and magnetic fields. The use of this method of investigation is considered, and its application to the analysis of the gases in excited tubes. The author shows that the heavier constituents of the atmosphere probably contain a gas of atomic weight about 22, and that neon is probably a mixture of two gases of atomic weights respectively about 20 and 22. The production of a gas of atomic weight 3. (X_3) is considered; this gas is produced along with helium when metals and salts are bombarded by cathode rays, and the production of the gas is not diminished when the salts are dissolved in water or alcohol, evaporated to dryness, and then bombarded. The possible nature of the gas X_3 is considered. It is shown that it may be stored over mercury for weeks; it may be heated in a quartz tube to a red heat without change; sparking with oxygen and heating with phosphorus have no action on the gas, and it does not combine when heated with sodium vapour. On the other hand, it combines with mercury vapour when an electric discharge is sent through the mixture, and it combines to some extent with red hot copper. In a note added to the paper the author shows that there is a genuine production of helium and X_3 apart from liberation of absorbed gas when salts of the alkali and alkaline-earth metals are bombarded. This is regarded as remarkable, since potassium has been already shown to be radioactive. In the case of potassium iodide evidence was obtained of the existence of a gas of atomic weight 35, which represents the difference between the atomic weights of potassium and helium. J. F. S.

Collisions Between Gas Molecules and Slow Moving Electrons. II. J. FRANCK and GUSTAVE HERTZ (*Ber. Deut. physikal. Ges.*, 1913, **15**, 613—620. Compare this vol., ii, 548).—The conclusion

arrived at in Part I., namely, that the collisions between electrons and gas molecules are more elastic the smaller the electron affinity of the gas molecule, is confirmed. It is shown for the gases helium, hydrogen, and oxygen that the energy necessary for ionisation is not obtained by the electrons on a single free path. In the case of helium the ionisation energy can be obtained during any number of collisions; in the case of hydrogen the number is limited by the energy loss at the collision, and in oxygen it is still smaller, since the strong electronegative character of oxygen conditions markedly inelastic collisions between electrons and molecules. J. F. S.

Radium Content of Certain Varieties of Mud. ERNST HENDRIK BÜCHNER (*Chem Weekblad*, 1913, **10**, 748—751).—The presence of radium as sulphate has been detected in samples of blue and brown mud from Rockanje. A. J. W.

Determination of the Strength of Radium Preparations. WILLEM P. JORISSEN (*Chem. Weekblad*, 1913, **10**, 710—711)—A description of an application of Rutherford's method to the valuation of a radium preparation accidentally contaminated with foreign material. A. J. W.

Complex Nature of Radio-actinium and the Position of Actinium in the Periodic System. OTTO HAHN and LISE MEITNER (*Physikal. Zeitsch.*, 1913, **14**, 752—758).—By means of determinations on the change of the α- and β-ray activity of actinium which had been freed from radio-actinium-I the authors are unable to find any evidence of the existence of an intermediate product between radioactinium and actinium-X. Such a substance, radio-actinium-2, is stated to exist by Chadwick and Russell (this vol., ii, 274), and to have a half-life of thirteen hours. The position of actinium in the periodic system and in uranium series is discussed. It is held that actinium is tervalent, and is derived from a quinquevalent parent substance which emits α-rays. The following scheme is put forward to indicate the position of actinium in the uranium family:

$$\underset{\alpha}{\overset{6}{\mathrm{Ur.I}}}\text{—}\overset{4}{\mathrm{Ur.}X_1}\begin{cases}\underset{\beta}{\overset{5}{\mathrm{Ur.}\ X_2}}\text{—}\underset{\alpha}{\overset{6}{\mathrm{Ur.\ II}}}\text{—}\underset{\alpha}{\overset{4}{\mathrm{Io.}}}\text{—}\underset{\alpha}{\overset{2}{\mathrm{Ra}}}\\ \underset{\alpha}{\mathrm{Act.\ I}}\longrightarrow\underset{(\beta)}{\overset{3}{\mathrm{Act.\ II}}}\text{—}\underset{\alpha,\,\beta}{\overset{4}{\mathrm{Radio\text{-}act.}}}\text{—}\underset{\alpha}{\overset{2}{\mathrm{Act.}\ X.}}\end{cases}$$

J. F. S.

Uranium-X_2. OTTO HAHN and LISE MEITNER (*Physikal. Zeitsch.*, 1913, **14**, 758—759).—A method of isolation of uranium-X_2 is given. Uranium-X is separated from uranium by means of ammonium carbonate. The uranium-X is dissolved in fairly strong acid, and filtered through a filter paper on which tantalum pentoxide had previously been filtered. In this way the uranium-X_2 is held back and freed from all but about 1% of uranium-X_1. From measurements of the activity of the tantalum pentoxide the half-

life of uranium-X_2 is determined as 1·17 minutes. Uranium-X_2 is shown to have properties homologous to those of tantalum, and its penetrating β-rays are identical with those of the undivided uranium-X. There is no evidence to show whether uranium-X_2 is the origin of the slow β-rays found in the original uranium-X. It is held that uranium-X_2 is a direct product of uranium-X_1.

J. F. S.

Liquid Helium. II. The Electrical Resistance of Pure Metals, etc. VII. The Potential Difference Necessary for the Electric Current Through Mercury Below 4·19°*K*. H. KAMMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 113—124. Compare this vol., ii, 748).—A theoretical paper, in which the local heating and consequent resistance changes of a thread of mercury at temperatures below 4·19° *K*. are discussed. It is shown that a different crystalline form of the solid mercury is not sufficient to account for the increased resistance at 3·65° *K*. These superconducting points cannot be accounted for on the Wiedemann and Franz or the Lorenz relationships. An electronic theory is put forward and discussed. J. F. S.

Electrical Conductivity of Concentrated Aqueous Solutions. ALEXANDER N. SACHANOV (*Zeitsch. Elektrochem.*, 1913, **19**, 588—589). —The conductivities of concentrated solutions of silver nitrate, lithium chloride, and lithium chlorate have been measured. The viscosities of the same solutions have also been determined, and the conductivity values corrected for the change in viscosity by means of the formula $L=\lambda(\eta/\eta_0)^m$, in which L is the corrected conductivity, λ the measured conductivity, η_0 the viscosity of the solvent, and η that of the solution; m is a constant with a value approximating to unity. It is shown in this way that the conductivity of concentrated solutions is abnormal, inasmuch as the molecular conductivity increases with increasing concentration. The values of Kohlrausch for ammonium nitrate, potassium bromide, and potassium iodide have been treated in the same way, and these salts are also shown to be abnormal. J. F. S.

Electrical Conductivity of Alloys of Copper and Tin. NIKOLAI A. PUSCHIN and A. V. BASKOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 746—752).—The curves showing the variation of (1) the specific resistance, and (2) its temperature-coefficient with the composition of copper–tin alloys consist each of six branches, corresponding with the following ranges of composition (atom. % of tin): 0—7, 7—20, 20—25, 25—40, 40—50, 50—100. The resistance curve shows a minimum and the temperature-coefficient curve a maximum at 25 atom. % of tin, the magnitude of the coefficient being similar to the values obtained for pure metals; these results indicate the existence of a definite chemical compound, Cu_3Sn, and are in agreement with those of thermal analysis, etc.

The low value of the temperature-coefficient corresponding with

the composition Cu_4Sn indicates the formation, not of a definite compound, but of a solid solution.

Whilst the addition of tin to copper causes a very rapid increase in the resistance, copper produces but little change in the resistance of tin. T. H. P.

Experimental Determination of a Dropping Electrode Potential in Water Alcohol Mixtures. H. KRUMREICH (*Zeitsch. Elektrochem.*, 1913, **19**, 622—636).—The author has determined the potential of a dropping electrode in aqueous and aqueous-alcoholic solutions of potassium nitrate. The values obtained are compared with those deduced from the electro-capillarity curve for the same solutions, and it is shown that they are generally in good agreement. Measurements were also made to show the dependence of the potential on the mercurous ion concentration in the same solutions. It is shown in this connexion that the agreement is much better in the aqueous-alcoholic solutions than in the aqueous solutions. Very full details are given of the apparatus employed and of the precautions which must be observed to obtain reproducible and correct measurements. J. F. S.

Influence of Pressure on the *E.M.F.* of the Lead Accumulator. ERNST COHEN and G. DE BRUIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 161—164).—The paper deals with the experimental determination of the relationship between the influence of pressure on the *E.M.F.* of a galvanic cell and the volume changes which occur when the quantity of electricity $d\epsilon$ passes through it. This is represented by the equation:

$$-(dE/dp)_{Tv} = (dv/d\epsilon)_{Tv},$$

where E is the *E.M.F.* of the cell, p the pressure, and dv the change of volume. This change can be calculated if the specific volume of the system before and after the passage of the current $d\epsilon$ is known, or it can be determined experimentally. The authors fitted two perforated lead electrodes in a dilatometer filled with dilute sulphuric acid, and after forming the electrodes the apparatus was placed in series with two silver voltameters, a milliammeter, and a resistance. The temperature was kept at 15·00°±0·005, and a current passed for twenty hours. The silver deposited was weighed, and the volume change determined from a graduated capillary tube, into which the liquid of the dilatometer was forced. In this way from three experiments it is found that the volume increase is 3·67 c.c. per gram-equivalent. Calculating from the change in the specific volume the value 3·54 c.c. was obtained. J. F. S.

Tantalum as a Cathode Material. G. OSTERHELD (*Zeitsch. Elektrochem.*, 1913, **19**, 585—587).—Experiments have been made with tantalum with the object of testing its suitability as a cathode. It is shown that in a $2N$-sulphuric acid solution the overvoltage is 1·14 volts. It is also shown that as a reducing electrode in the case of benzophenone, caffeine, and nitrobenzene, it gives exceedingly poor yields. It is also shown to absorb hydrogen

and at the same time to lose its elastic properties and become crystalline and brittle. A series of discharge potential measurements made in $2N$-sulphuric acid are recorded. It is thus shown that tantalum can have but a very restricted use as a cathode material. J. F. S.

Electrolytic Valve Action of Metals. W. WINTER (*Physikal. Zeitsch.*, 1913, **14**, 823—828).—It has been shown by Schultze (A., 1907, ii, 842; 1908, ii, 350, 560, 658; 1909, ii, 371; 1911, ii, 365; 1912, ii, 126, 529) that many metals in addition to aluminium exhibit a valve action on the alternating current. It has been suggested that the valve action is brought about by an active layer on the electrode, which of itself is non-conducting. The current is conveyed by a series of pores filled with electrolyte, except in the immediate neighbourhood of the electrode, where a thin gas layer exists, and consequently the current can only be conveyed in the direction of the metal. The author has tested this explanation by binding sheets of several metals on the outside of a porous pot filled with an electrolyte in which a carbon electrode was placed. It is shown that in potassium hydroxide solution under these conditions the metals magnesium, aluminium, zinc, cadmium, iron, cobalt, nickel, lead, tin, antimony, bismuth, copper, silver, platinum, gold, and chromium show a strong anodic valve action, whilst in dilute sulphuric acid all except the last three show the same action. Hydrochloric acid and nitric acid show a very slight valve action in some cases, but generally there is no valve action under the experimental conditions. An amalgamated gold electrode in dilute sulphuric acid showed the valve action. The cause of the action is considered, and it is shown that electrolytic and Wehnelt effects do not explain the phenomenon. It is considered likely that the metals under investigation form layers which in ordinary circumstances would be dissolved and removed from the surface of the electrode. J. F. S.

Partition of Electrolytes between Water and a Second Solvent. NILRATAN DHAR and ASWINI KUMAR DATTA (*Zeitsch. Elektrochem.*, 1913, **19**, 583—585).—The authors have determined the partition of lithium chloride and cadmium iodide between water and amyl alcohol, and the latter salt between ether and water. The object of the investigation was to determine from the results the degree of dissociation of the dissolved salts. The results, however, show that the method is unsuitable for such determinations; the values obtained in this way differ as much as 58% from those obtained from conductivity determinations. J. F. S.

The Dissociation of Good Electrolytes and the Law of Mass Action. PAUL TH. MULLER and R. ROMANN (*Compt. rend.*, 1913, **157**, 400—403. Compare this vol., ii, 679).—A theoretical discussion of results obtained and previously given (compare *loc. cit.*) in support of their view that the results must be due to the fact that the base and acid generators of a good electrolyte themselves

follow the law of mass action and possess ions the hydration of which is constant at dilutions above 1 gram-molecule in 100 litres of water. W. G.

Formation of Sodium Hypochlorite with Cooled Anodes. PAUL H. PRAUSNITZ (*Zeitsch. Elektrochem.*, 1913, **19**, 676—680).—A cooled platinum anode has been used in the preparation of hypochlorite solutions; it is shown that in a $5N$-sodium chloride solution at 20° electrolyte temperature, an improved hypochlorite concentration can be obtained if a somewhat higher anode current density (C_A) is employed. Without cooling, the highest value obtainable is 41·6 grams of bleaching chlorine per litre, whilst if the anode temperature is maintained at 15° the value rises to 90 grams per litre and at 3—4° to 100 grams per litre, C_A in the above cases being 1·25 amperes per sq. cm. The current efficiency at the beginning of the process is high, but afterwards falls off somewhat. Gradual raising of the temperature of the water flowing through the anode showed that with the electrolyte at 20—25° and $C_A = 1·25$ amperes per sq. cm., the temperature of the anode must have been about 40°. Cooling the anode to 20° and raising the temperature of the electrolyte ($5N$-NaCl) to 48° gave a maximum yield of 70 grams of bleaching chlorine per litre with a terminal potential reduced 20%, and a current efficiency of over 50%. In a N-sodium chloride solution, cooling the anode is without influence. At smaller values of C_A, for example, 0·47 ampere per sq. cm. in $5N$-sodium chloride solution and with the anode at 12°, an increase in concentration from 39·7 to 49·1 grams of bleaching chlorine per litre is obtained. Platinising of the anode and cooling gives at $C_A = 0·47$ ampere per sq. cm. an increase of from 47 to 60 grams of bleaching chlorine per litre. The current efficiency is in this case as high as in the case where Turkey-red oil and chromate are used with platinised electrodes (Prausnitz, this vol., ii, 49). J. F. S.

Departures From the Curie Law in Connexion with the Zero Energy Point. E. OOSTERHUIS (*Physikal. Zeitsch.*, 1913, **14**, 862—866).—Instances are quoted to show that a large number of substances do not obey the Curie law, χT = constant, for at low temperatures the value decreases. This divergence is discussed, and it is shown that the three types of divergence from the Curie law can be united under the theory of a zero rotational energy point. The zero energy point is shown to be a reality by the course of the specific heat of hydrogen at low temperatures (Einstein and Stern). The theory of free electrons in metals is explained by the theory of quanta, using the conception of a zero energy point. J. F. S.

Present State of the Temperature Scale. GEORGE KIMBALL BURGESS (*J. Chim. phys.*, 1913, **11**, 529—542).—Some uncertainty attaches to the corrections to be applied to the readings of the gas thermometer to convert them to absolute thermodynamic tempera-

tures, but helium and hydrogen between $-50°$ and $+75°$ depart so little from perfect gases that the correction in constant volume thermometers is less than 0·001°.

The usual secondary standards are mercury in glass or quartz up to 755° and toluene or pentane in glass for low temperatures. The readings depend on the kind of glass and its previous history. The platinum resistance thermometer from 200° to 1000° is very exact, and the constant in Callendar's formula for the particular piece of platinum may be determined by measurements at 0°, 100°, and 32·383° (transition point of sodium sulphate), or $444·6° \pm 0·1°$ (boiling point of sulphur). The error at 1100° is less than 2°. With the platinum resistance thermometer 0·0001° is appreciable at $+25°$.

The platinum–rhodioplatinum thermo-junction is of inferior accuracy, necessitating rather large corrections, and being subject to unknown errors due to lack of homogeneity in the wires.

The author gives a list of twenty-four boiling, fusing, and transformation points ranging from $-252·7°$ to $+3000°$, which are available as fixed points in thermometry, noting the degree of approximation of each.

The International Bureau of Weights and Measures has now a scale of temperatures from 0° to $+100°$ with a maximum error of 0·002°. Outside of these limits there is no general agreement as to the basis of temperature measurements. Between $+450°$ and $+1550°$ the nitrogen thermometer is commonly used, and above 1550° radiation pyrometers, the constants of which have been determined at lower temperatures. It should be possible to establish an international scale up to 1000°. R. J. C.

An Easy Method of Obtaining Temperatures as Low as $-211°$ by the Use of Liquid Nitrogen. GEORGES CLAUDE (*Compt. rend.*, 1913, **157**, 277—279, 397).—By rapidly bubbling hydrogen, previously passed through a copper spiral immersed in liquid nitrogen, through liquid nitrogen in a silvered vacuum vessel, the temperature rapidly falls. In one experiment it reached $-200°$ after two minutes, $-206°$ after six minutes, and $-210°$ after twelve minutes. The hydrogen should pass at the rate of 20—25 litres per minute.

In the second paper the author points out that Dewar has already described this process in 1904. W. G.

New Designs for Specific Heat Apparatus. ARDEN R. JOHNSON and BERNARD W. HAMMER (*J. Amer. Chem. Soc.*, 1913, **35**, 945—948).—The principle of the one apparatus is that a definite amount of heat is supplied to the liquid in the calorimeter by immersing an electric lamp in it and passing the current for a definite time. Using water in the one case, and the liquid under investigation in the other, and making appropriate corrections for radiation, the specific heat of the liquid under investigation is readily determined. The determination may also be made by comparing the amounts of electrical energy necessary to raise

given weights of water and the other liquid through a definite range of temperature. For this apparatus a very constant voltage is required.

In another apparatus a variable voltage may be used. An electric light bulb is fastened into a copper vessel containing 100 grams of water. The whole is raised to a definite temperature by means of the lamp, and is then used as the hot body for immersion in the liquid in the calorimeter. T. S. P.

Calculation of Specific Heats from Elasticity Constants. ARNOLD EUCKEN (*Ber. Deut. physikal. Ges.*, 1913, **15**, 571—577).—A theoretical paper in which the calculation of specific heats by means of the formulæ of Born and Kármán and Debye is discussed. It is shown that probably the theoretically deduced relationship exists between elasticity and heat content for crystals at low temperatures. J. F. S.

Experimental Examination of the T^3 Law for the Course of the Specific Heat of Solid Substances at Low Temperatures. ARNOLD EUCKEN and FRÉDÉRIC SCHWERS (*Ber. Deut. physikal. Ges.*, 1913, **15**, 578—588).—The specific heats of lead, fluorspar, and pyrites have been determined at a series of low temperatures with the object of confirming Debye's law (A., 1912, ii, 1134). The determinations were carried out by an electrical method and with the least possible weight of apparatus, in order to reduce the quantity of heat required to raise the temperature of the calorimeter and its contents. The measurements were made for lead between 15·95° and 92·0° abs., fluorspar 17·5° and 86·0° abs., and pyrites 21·7° and 84·0° abs. At these temperatures the molecular heat of fluorspar and pyrites varies proportionally to the cube of the absolute temperature, the values varying between 0·07 cal. and 1·0 cal. Consequently, within this region the theory of Debye, which was supposed to hold for monatomic substances only, is applicable to regular polyatomic crystals. The molecular heat of fluorspar follows the Debye theory over the whole temperature range, whilst that of pyrites ceases to agree at higher temperatures. J. F. S.

Theory of Space Grating Oscillations and the Specific Heat of Solid Substances. HANS THIRRING (*Physikal. Zeitsch.*, 1913, **14**, 867—873. Compare Born and Kármán, *Physikal. Zeitsch.*, 1912, **13**, 297, and this vol., ii, 101).—The author shows that the equation deduced by Born and Kármán on the specific heat of regular crystalline substances can be strictly developed mathematically. The specific heat of copper, rock salt, and sylvine is calculated for low temperatures, and values obtained which in cases differ from the observed values of 6—16%. These divergencies can in every case be explained theoretically. J. F. S.

Atomic Specific Heats between the Boiling Points of Liquid Nitrogen and Liquid Hydrogen. I. Mean Atomic Specific Heats at 50° Absolute of the Elements a Periodic Function of the Atomic Weights. SIR JAMES DEWAR (*Proc. Roy. Soc.*, 1913, *A*, **89**, 158—169).—The specific heat of 53 elements

has been determined between the temperatures of boiling nitrogen and boiling hydrogen. The substances were cut into pieces of uniform shape, and cooled in a jacket containing liquid nitrogen; they were then allowed to drop into a calorimeter containing liquid hydrogen, and the volume of hydrogen gas given off was measured. After a number of corrections were applied the specific heat was calculated, and it is shown that the specific heat is a periodic function of the atomic weight, and that the atomic specific heat curve has a similar form to the Lothar Meyer atomic volume curve.

J. F. S.

Specific Heat of Hydrated Salts. LUIGI ROLLA and LUIGI ACCAME (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 109—116).—An expression for the difference of the specific heats of the last molecules of water of crystallisation of two hydrated salts may be deduced from thermodynamical considerations. By experiment the molecular heat of $ZnSO_4,7H_2O$ at 9° is found to be 93·66, that of $ZnSO_4,6H_2O$ 80·75, so that the last molecule of water has a molecular heat of 12·91 cal. (calculated 12·91). The molecular heat of $MgSO_4,6H_2O$ is found to be 79·657 cal., and, Kopp's value for $MgSO_4,7H_2O$ being 88·97, the molecular heat of the last molecule of water is 9·31 (calculated 10·09). The author's experiments, however, give a value for the molecular heat of $MgSO_4,7H_2O$ which would reduce the value for the difference from that of the hexahydrate to 6·86 cal. Measurements of the molecular heat of $FeSO_4,7H_2O$ and $FeSO_4,4H_2O$ give 92·147 and 63·587 cal. respectively, the difference being 28·56 (calculated 27·16). R. V. S.

Determination of the Freezing Point. A. VAN RAALTE (*Chem. Weekblad*, 1913, **10**, 709).—A description of a perforated, metallic cylinder recommended as a protection for the glass tube employed in cryoscopic work. A. J. W.

Apparatus for the Determination of Boiling Points. A. A. BESSON (*Chem. Zeit.*, 1913, **37**, 1035).—The apparatus is so arranged that the thermometer does not come into contact with the condensed liquid falling back into the flask from a return condenser. This is attained by placing the thermometer in a wide tube opening through the stopper of the flask. At the upper end of this tube is a side-tube, through which the vapours pass, connecting with another wider tube; the end of the condenser opens into the top of this wider tube, the bottom of which connects with a narrow tube leading through the stopper to the bottom of the flask, thus allowing the condensed liquid to return to the flask without coming in contact with the thermometer. T. S. P.

Determination of the Vapour Pressure and Density Curves of Oxygen; Construction of an Apparatus for Determining Critical Data. F. E. E. GERMANN (*Physikal. Zeitsch.*, 1913, **14**, 857—860).—An apparatus designed by Nernst and Eucken is employed. The temperature measurements are made by means of

a lead resistance thermometer, which is shown to change its resistance more regularly than platinum in the region 20—60° absolute, and can be read to 1/100 of a degree. It is shown that a vacuum vessel can be kept at a constant temperature by the use of liquid air and an electrical heater simultaneously. Using this apparatus the vapour-pressure curve of oxygen has been determined for pressures from 1 to 25 atmospheres. The density of liquid oxygen over the same pressures has also been obtained, and the values found to lie between 1·0605 at 2·72 atms. and 100·25° absolute and 0·8474 at 23·59 atms. and 136·10°. J. F. S.

Vapour-pressure Curve of Oxygen and the Determination of the Critical Data of Hydrogen. FRITZ BULLE (*Physikal. Zeitsch.*, 1913, **14**, 860—862).—Using a slightly modified Nernst-Eucken apparatus, the author has determined the vapour-pressure curve of oxygen, and obtained values which do not differ more than 1/10° from those of Germann (see preceding abstract). By means of the same apparatus the critical constants of hydrogen have been determined, and the values critical temperature 31·95°±0·10 and critical pressure 11·0 atm. have been obtained. J. F. S.

Fixed Points in Thermometry between 100° and 400°. Vapour Tensions of Naphthalene, Water, and Benzophenone. I. Vapour Tensions of Naphthalene. J. M. CRAFTS (*J. Chim. phys.*, 1913, **11**, 429—477).—The boiling point of water is suitable as a thermometric standard for temperatures between +70° and +170°. Only two substances, namely, naphthalene and benzophenone, have been found sufficiently stable for use above +170°. Naphthalene, purified by fractional crystallisation, retained its boiling point unaltered after boiling continuously for twelve months. The boiling point was 218·25°, 219·09°, and 218·46° on different mercurial thermometers.

A complete series of pressure-boiling point values for naphthalene was obtained by direct comparison with a constant volume nitrogen thermometer between 231·16 mm. (+171·23°) and 2149·31 mm. (+269·51°), and an interpolation formula worked out which satisfactorily covers the whole of this range.

The specially designed ebullioscope charged with one kilo. of naphthalene was mounted as nearly horizontally as possible to avoid the error due to the weight of the vapour column. The naphthalene vapour was liquefied in a condenser maintained at +80° by circulating water. The variation in temperature from one part of the vapour space to another was less than 0·01°.

The thermometer filled with atmospheric nitrogen was used in conjunction with a special form of open-type manometer, and a syphon barometer in which the levels were determined electrically with great precision by platinum contact points attached to the verniers. For pressures less than atmospheric the syphon barometer was used alone as a manometer. The average temperature of the mercury column was indicated by a thermometer the bulb of which was of the same dimensions as the whole barometer

After every measurement the fixed points 0° and 100° of the gas thermometer were redetermined so as to avoid errors due to the hysteresis of the glass.

The boiling point of naphthalene at 760·00 mm. is 218·06° at 28 metres above sea level at the latitude of Boston, U.S. (42°21′).

R. J. C.

Heat of Formation of Silicon Nitride. CAMILLE MATIGNON (*Bull. Soc. chim.*, 1913, [iv], **13**, 791—793).—Silicon nitride is formed by heating a mixture of silica and carbon in a stream of nitrogen at 1400—1500° according to the equation:

$$3SiO_2 + 6C + 2N_2 = Si_3N_4 + 6CO.$$

When using a mixture of nitrogen with 30% of carbon monoxide the author finds that union with nitrogen proceeds at 1500°, but not at 1400°, and that it appears to commence at 1450°. He thus deduces that the system is in equilibrium between 1400° and 1450° for this pressure of carbon monoxide. By substituting the values so obtained in Nernst's formula, he calculates the heat of formation of silicon nitride to be 159·3 Cal. H. W.

Stability of Cyclic Compounds from a Thermochemical Point of View. P. V. ZUBOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 753—766. Compare A., 1902, i, 144).—By dividing the molecular heats of combustion of ethylene, *cyclo*propane, etc., by 2, 3, etc., the author obtains the heat effect corresponding with CH_2. Some of the values thus derived are as follows:

Ethylene	166·65 Cals.	Propylene	164·23 Cals.
*cyclo*Propane	166·47 ,,	Methyl*cyclo*butane	159·98 ,,
*cyclo*Pentane	159·86 ,,	Methyl*cyclo*pentane	159·49 ,,
*cyclo*Hexane	159·20 ,,	Methyl*cyclo*hexane	159·28 ,,
*cyclo*Heptane	158·80 ,,	Methyl*cyclo*heptane	159·10 ,,

Other series of homologous derivatives give similar results.

It is seen that the interatomic linkings in the different rings are not identical, and that the heats of formation increase from the lower to the higher rings.

Comparison of these heat effects for the cyclic carboxylic acids with those for the corresponding hydrocarbons shows that replacement of one or more carboxyl groups by one or more hydrogen atoms is accompanied by no appreciable change in the heat of combustion.

Stohmann and Kleber (A., 1892, 1040) are of the opinion that the stability of atomic rings may be measured by the heat effects observed when cyclic compounds are converted into open-chain compounds by combination with a molecule of hydrogen. Such a conclusion is, however, controverted by Stohmann's own results, which showed that the amount of heat developed on rupture of a four-carbon atom ring varies with the position of rupture. A similar refutation is furnished by the author's results. T. H. P.

Sublimation of Metals at Low Pressures. GEORGE W. C. KAYE and DONALD EWEN (*Proc. Roy. Soc.*, 1913, *A*, **89**, 58—67. Compare Harker and Kaye, this vol., ii, 661).—The disintegration

of a number of metals by heat is examined. It is shown that when heated to 950°, copper, iron, and tungsten are disintegrated, and emit particles at right angles to their surface, leaving an etched surface. This emission of particles is distinct from the natural volatilisation, and is more marked when the heating is effected by passing a direct current through the metal than when the heating is external to the metal. A number of theories are considered to account for the disintegration, and it is suggested that particles are charged and a repulsion causes the disintegration. The results are regarded as of a preliminary nature. J. F. S.

Some of the Conditions Affecting Explosions of Coal Gas and Air. I. E. L. SELLARS and C. CAMPBELL. **II.** E. L. SELLARS (*J. Soc. Chem. Ind.*, 1913, **32**, 730—736).—The gas mixture used in the experiments contained 12·3% of coal gas. The propagation of the explosions was effected in glass tubes varying from 4 to 18 metres in length; for measuring the rate of propagation each tube was marked at every metre, and the time noted, by means of a special registering apparatus, at which the flame passed each mark.

Part I. deals with the initial velocity of explosion, by the initial velocity being meant the velocity with which the flame travels through that portion of the initial uniform period, where oscillations have not begun. Increase in diameter of tube means an increase in the initial velocity of a flame started by sparking near an open end of a tube, whether the further end be open or closed. The effect of increasing the length of the tube, keeping the diameter constant, on the initial velocity of a flame produced by sparking near an open end is, in the case of the further end being closed, to cause a slight decrease; when the further end is open the length has no effect. If the flame is started by sparking near an open end, the fact of the further end being closed causes the initial velocity to be slightly greater than it would be if the further end were open. The initial velocity is fairly constant.

Part II. deals with the rate of explosion, as affected by the length and diameter of the tube, by the position of the spark, and by the material of the tube, etc. The conclusions arrived at are summarised as follows: The conditions of the tube in which the explosion takes place greatly affect the distance the flame travels. The state in which the ends of the tube are put, that is, whether open or closed, may change the whole character of an explosion; for example, a flame started near an open end of a tube may be quite feeble, and the velocity slow, whereas if the flame were started near the same end, closed before ignition, the explosion might travel with considerable violence and velocity. This shows the possible effect of a closed passage on an explosion in a mine. Increase in length of the tube increases the rate of explosion up to a certain limit; in tubes less than a certain minimum diameter (10 mm., with the gas mixture used) the flame will not propagate itself. Sparking near an open end, the further end being closed, the flame travels

with a somewhat greater velocity in a lead tube than in a glass tube, although the general character of the flame is unaltered.

T. S P.

The Freezing of Nitroglycerol [Glyceryl Trinitrate]. The Heat of Transformation of the Nitroglycerol Isomerides. HAROLD HIBBERT and G. PRESCOTT FULLER (*J. Amer. Chem. Soc.*, 1913, **35**, 978—989).—The recently published experimental results on the existence of two crystalline forms of glyceryl trinitrate (Hibbert, this vol., i, 817) indicated that of the changes liquid phase ⟶ labile solid phase and labile solid phase ⟶ stable solid phase the latter was accompanied by far the greater thermal change. As the only work in this direction is that of Nauckhoff (*Zeitsch. angew. Chem.*, 1905, **18**, 17), who estimated the heat development for the transformation liquid phase ⟶ stable solid phase, the authors have applied the Bunsen ice-calorimeter to the measurement of the heat development in the above two changes.

The heat of transformation of 1 gram of liquid glyceryl trinitrate into the labile solid isomeride was found to be 5·2 calories, whilst that of the labile into the stable solid isomeride was 28·0 calories; from these figures 33·2 calories must be developed during the crystallisation of liquid glyceryl trinitrate into the stable solid form, this result diverging considerably from that of Nauckhoff, who found 23·1 calories for the change at 1·5°.

Although the labile isomeride at 0° is rapidly converted into the stable one if a little of the latter is well incorporated in it, mere contact with a crystal of the stable form requires twenty-five to thirty-five minutes to effect a complete transformation. D. F. T.

A Combination Specific Gravity Bottle and Dilatometer. CHARLES ALBERT BROWNE (*J. Amer. Chem. Soc.*, 1913, **35**, 955—958). —The specific gravity bottle is a U-shaped pyknometer, the one limb of which is made of wide tubing, into which is ground a thermometer, which at the same time acts as a stopper; the graduated part of the thermometer is completely inside the tube. The other limb is made of capillary tubing, and is graduated; it is fitted with a ground-on stopper. When the wide limb is completely filled with liquid, any change in volume caused by a reaction occurring in the liquid can be measured by readings made on the narrow limb. In this way, for example, the contraction which sugar solutions undergo during hydrolysis or inversion can be measured.

T. S. P.

Density at Absolute Zero and Critical Density of Several Gases. MAURICE PRUD'HOMME (*J. Chim. phys.*, 1913, **11**, 520—528. Compare this vol., ii, 298).—The sum of the three densities corresponding with the three volumes in van der Waal's equation is constant and equal to the density at absolute zero, which must be either three or four times the critical density; thus $d_1+d_2+d_3=D_0=3D_c$ or $4D_c$. In the former case, at the critical point $d_3=D_c$, and in the latter $d_3=2D_c$. Now d_3 has been interpreted as mean-

ing the density of the surface film between liquid and gas, and it is probable that although $d_3 = 2D_c$ in the series of esters, etc., studied by Young, it would be found with simpler substances which approximate to perfect gases that $d_3 = D_c$.

Sulphur dioxide falls into this class, since on passing from 420° abs. to 280° abs. the value of n in the equation:

$$d_1 + d_2 = 4D_c - 2D_c(T/T_c)^n$$

approaches unity. With sulphur dioxide, therefore, the density at absolute zero $D_0 = 4D_c$.

In the cases of nitrous oxide and carbon dioxide the densities are in better accord with an expression of the form

$$d_1 + d_2 = 3D_c - D_c(T/T_c)^n,$$

whence $D_0 = 3D_c$ for these gases. R. J. C.

The Weight of a Falling Drop and the Laws of Tate. XI. The Drop Weight and Surface Tension of Blood Serum. J. LIVINGSTON R. MORGAN and HAROLD E. WOODWARD (*J. Amer. Chem. Soc.*, 1913, **35**, 1249—1262).—The authors have applied the drop-weight method to the determination of the surface tension of blood serum, and obtained the following results: The surface tension of blood serum in an individual may change during the day, depending on the food which is being absorbed by the blood. It is approximately the same (about 45·4 dynes per cm. at 37°) in different individuals and different species, if account be taken of the possibility of a daily change in any one individual. In certain diseases, especially those in which the kidneys are affected, the surface tension is abnormally high.

Ascoli and Tzar's meiostagmin reaction was found to be positive in more than 80% of the cases of clinically positive syphilis investigated; in those cases where it was not positive, the Wassermann test was either weak or doubtful. T. S. P.

The Meyer Molecular Weight Calculation. PERCY N. EVANS (*J. Amer. Chem. Soc.*, 1913, **35**, 958—959).—In carrying out a determination of vapour density by V. Meyer's method, it is usual to correct for the vapour tension of water when correcting the volume of expelled air to N.T.P. This is only correct when the original air in the apparatus is quite dry. If it is moist, the corrected barometric pressure is $B - (100 - H)w/100$, where B is the barometric reading, H is the percentage of saturation at room temperature, as determined with a hygrometer, and w is the pressure of aqueous vapour. If the air used is saturated, there is no correction to be applied to the barometric pressure. In damp, warm weather, the application of the correction usually made may lead to an error of 1 in 45. T. S. P.

A Viscometer for Volatile Liquids. J. P. KUENEN and S. W. VISSER (*Proc. K. Akad. Wetensch., Amsterdam*, 1913, **16**, 75—84).—The authors have constructed a viscometer, based on the Ostwald instrument, for use with volatile liquids. The vertical capillary

has the usual bulb with two marks at the top, and projects into a larger bulb at the bottom. The wide tube is sealed on near the top of the lower bulb, and bent round and sealed to the top of the higher bulb, thus forming a closed apparatus. A side-tube, for admitting the experimental liquid, is attached to the wider tube. The apparatus has been tested for water at various temperatures, and the influence of varying the volume of the liquid has been worked out. The correction for capillarity, due to the capillary dipping into the lower liquid, is also determined. A German silver bath for use with the apparatus at low temperatures is described. Preliminary measurements were made with *n*-butane, and the following figures for η obtained: 34·5°, 0·00163; 18·5°, 0·00176; 0·0°, 0·00207; −23·6°, 0·00265. From these values it is shown that the viscosity at the boiling point corresponds well with the values found by Thorpe and Rodger for other hydrocarbons (T., 1894, **65**, 782). J. F. S.

Internal Friction of Binary Systems. B. P. WEINBERG (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 701—706).—The author has calculated for the three binary systems (1) allylthiocarbimide and piperidine, (2) phenylthiocarbimide and diethylamine, and (3) allylthiocarbimide and methylaniline, and for various ranges of temperature the values of $\alpha=(\eta_1-\eta_2)/\eta_2(t_2-t_1)$ (compare Kurnakov and Shemtschushni, this vol., ii, 190), and those of a in the formula $\eta_2=\eta_1 : a^{t_1-t_2}$, which has been employed by various authors to express the dependency on the temperature of the coefficient of internal friction of solids and supercooled liquids.

For the mixtures containing the two components in equimolecular proportions the magnitude of α varies widely for different intervals of temperature, and on this account preference is to be accorded to the second of the above expressions, the values of a showing considerably greater constancy. Further, the variations of the values of a from 1 are similar to those obtained with liquids supercooled by some tens of degrees, and the superiority of these values over those for the separate constituents explains the appearance of the maxima in the curves of the temperature-coefficients constructed by Kurnakov and Shemtschushni.

These considerations lead the author to the opinion that when equimolecular proportions of the constituents of systems (1), (2), and perhaps also (3) are brought into contact, the corresponding compounds are obtained directly in the form of supercooled liquids. Mixtures in proportions other than equimolecular may be regarded as solutions of these supercooled liquids in one of the two solvents which, being of considerably lower viscosity, causes a marked decrease in the coefficient of internal friction.

The change produced in the value of η for such an equimolecular compound by dilution with one of the two solvents may be represented by $p=(\log\eta_m-\log\eta_1)/(\log\eta_0-\log\eta_1)$, where η_m is the coefficient of viscosity with a content of m gram-mols. of solvent per $(1-m)$ gram-mols. of dissolved substance. Calculation of p

for the systems mentioned above shows that, as a first approximation, $p=m$.

These considerations necessitate certain modifications in the explanations advanced by Kurnakov and Shemtschushni for some of their results. T. H. P.

The Chemical Interpretation of Special Points on Curves. L. GAY and F. DUCELLIEZ (*Bull. Soc. chim.*, 1913, [iv], **13**, 783—784) Compare this vol., ii, 387).—A reply to Kolossovski (compare this vol., ii, 674). H. W.

Viscosity of Chlorinated Aliphatic Hydrocarbons and Their Mixtures. WALTER HERZ and W. RATHMANN (*Zeitsch. Elektrochem.*, 1913, **19**, 589—590).—The viscosities of a number of chlorinated hydrocarbons have been measured at different temperatures. The following values are recorded: *cis*-Dichloroethylene η at 25° = 0·437; *trans*-dichloroethylene η at 25° = 0·510, at 50° = 0·671; trichloroethylene η at 25° = 0·615, at 50° = 0·812, at 75° = 0·976; tetrachloroethylene η at 25° = 0·940, at 50° = 1·194, at 75° = 1·404; tetrachloroethane η at 25° = 1·808, at 50° = 2·033, at 75° = 2·154; and pentachloroethane η at 25° = 2·432, at 50° = 2·695, at 75° = 2·789. Several mixtures were examined at 25°; the mixture trichloroethylene and pentachloroethane gives a viscosity-composition curve which is a straight line lying between the values of the constituents; tetrachloroethylene and carbon tetrachloride gives a curve in which a maximum occurs, and tetrachloroethane and carbon tetrachloride gives a curve slightly convex to the composition axis. The densities of the various mixtures have also been determined. J. F. S.

Viscosity of Emulsoid Sols and its Dependence on the Velocity of Shearing. EMIL HATSCHEK (*Kolloid. Zeitsch.*, 1913, **13**, 88—96. Compare this vol., ii, 559).—The viscosity of gelatin and starch sols has been determined at different shearing velocities by means of a modified Couette apparatus previously described (*loc. cit.*). With ½% of gelatin sol it is shown that in a given case the viscosity value 2657 with a shear velocity of 3·52° fell to the value 1316 on increasing the shear velocity to the maximum value for tranquil shearing, but on reversing the process, by decreasing the velocity, the viscosity rose again to 3822, thus indicating a marked hysteresis. In the case of a potato starch sol the viscosity of 730 was obtained at the maximum velocity of 101·1°, and this with decreasing velocity increased until at 24·5° it reached the value 1233; at this point with further decreasing velocity a rapid decrease in viscosity occurred until at the minimum velocity the value 779 was reached. The velocity was then slowly increased, and the viscosity fell further, until at 52·9° it had reached 364, and at this point with increasing velocity it rose to 730. The results show that the viscosity is not a constant quantity, and calculations applied to the capillary viscometer show that such measurements made by a capillary viscometer under the same external conditions cannot be regarded as being carried out under

comparable conditions, for if a definite shear velocity is exceeded, disturbances in the sol under examination will take place.

J. F. S.

Theory of Dyeing. The Partition of Colour Substances Between Two Solvents. WILLEM REINDERS (*Kolloid. Zeitsch.*, 1913, **13**, 98—105).—The author discusses the three theories of dyeing, and a series of partition experiments with a series of organic colouring matters are carried out between water and *iso*butyl alcohol. In many cases the aqueous layer is either acidified or made alkaline. The experiments were carried out with methylene-blue G. (conc.), methylene-blue D., magenta, crystal-violet, new magenta, crystal-ponceau, patent blue, erythrosin, roccellin, quinoline yellow, alkali blue, and Congo red. It is shown that the simple partition relationship does not exist in any case, but that in some cases the factor $1/n$ of the adsorption relationship $x/m = ac^{1/n}$ is constant, and generally less than unity. The relationships observed in the case of a colouring matter and fibre are compared with the experimental results, and the conclusion is drawn that the taking up of a dye by a fabric consists mainly in the formation of a solid solution, and the assumption of the formation of an adsorbed layer is unnecessary. J. F. S.

The Form of the Ideal Electro-capillarity Curve. F. KRÜGER and H. KRUMREICH (*Zeitsch. Elektrochem.*, 1913, **19**, 617—622).—The form of the electrocapillarity curve is determined for potassium nitrate and potassium nitrate containing mercurous nitrate, and is shown to be an exact parabola. This result is in agreement with the electrical theory of electrocapillarity of Lippmann, Helmholtz, and Nernst. The capacity of the double layer is calculated from this parabola, and found to be 27 microfarads. J. F. S.

The Theory of Cohesion Pressure and the Lipoid Theory. ISIDOR TRAUBE (*Biochem. Zeitsch.*, 1913, **54**, 305—315).—The author recapitulates his theory of osmosis of substances into cells, which forms the basis of his previous investigations, and calls attention to the fact that so many of the more recent biological investigations on narcosis, plasmolysis, effect of substances on the oxydones, etc., are in better accord with this theory than with the lipoid theory of Overton and Meyer. He calls attention also to the fact that on account of their capacity to lower the surface tension of an aqueous solution, many substances may be readily taken up by lipoids from water. The solubility in lipoids is not, however, the main factor in the various phenomena. S. B. S.

Relation Between Viscosity and Heat of Fusion. J. DE GUZMÁN (*Anal. Fis. Quim.*, 1913, **11**, 353—362).—The relation is expressible by the equation $d\ln\phi/dT = W/RT^2$, where ϕ is the coefficient of viscosity, and W the molecular heat of fusion.

G. D. L.

Law of Capillary Ascent. VLADIMIR A. KISTIAKOVSKI (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 782—801).—The author advances a theoretical explanation of his capillarity rule (A., 1906, ii, 655). Experimental data are given for 141 compounds, including almost all the non-associated liquids yet investigated, satisfactory agreement with the rule being shown in all cases.

It is shown theoretically that, with non-associated liquids, the molecular weights calculated by means of this rule hold for the compound in both the liquid and gaseous phases.

With associated liquids it is impossible to make direct application of the value of the constant for the calculation of their degrees of association.

The results obtained show that the capillarity method is to be recommended for determining the molecular weights in the liquid or gaseous phase of aliphatic and aromatic hydrocarbons and their halogenated derivatives, aliphatic and aromatic amines, ethers and esters, aromatic aldehydes and ketones. T. H. P.

Theory of Narcosis. ISIDOR TRAUBE (*Pflüger's Archiv*, 1913, **153**, 276—308. Compare A., 1905, ii, 13; 1908, ii, 565; 1912, ii, 740; Overton, A., 1897, ii, 337).—A theoretical paper in which previously published work of the author and others is considered in connexion with the theory of narcosis. It is shown that narcotics are substances of small cohesion pressure in water, which consequently lower the surface tension and internal pressure of water and aqueous cell fluids, and raise the vapour pressure of the same liquids. If the cohesion pressure of a volatile narcotic in water is very small or almost zero, the lowering of the surface tension of the aqueous solution does not furnish an accurate measure of the cohesion pressure. In such cases a great decrease of the internal pressure takes place on account of the fine emulsion produced by such narcotics. Narcotics of this type possess a marked vapour pressure, both alone and in contact with water. The more a narcotic reduces the surface tension, the smaller is its cohesion pressure, and the more easily it is dissolved in lipoidic substances, absorbed by other surfaces, and "diosmosed" into the inside of cells even when the walls of such cells do not contain lipoids. There is no regularity between the lowering of the surface tension on the one hand, and lipoid solubility and absorption by non-lipoid substances on the other. The increase in lipoid content of the cells has an influence on the velocity of absorption of narcotics, and consequently on the intensity of their narcotic action, but the lipoid content is not the cause of the increased absorption and action, for lipoid-free cells can be brought under the influence of narcotics. The more a narcotic of small cohesion pressure in water lowers the surface tension and internal pressure of cell fluids, the more it changes the physical condition of the dissolved substances, for example, colloidal particles aggregate, and their solubility is decreased. Such change of condition of proteins, nucleoproteins and lipoids, and also the smaller pressure inside the liquid, have

the effect of retarding or stopping certain chemical reactions, such as oxidation. The space in which these reactions occur, and the dead space of Liebreich will be increased by the presence of narcotics. These conditions become of more importance in the polyphase lipoid regions (nerve cells), since the size and surface of the phases is increased by the semi-coagulation. Since the narcotics concentrate on the surface of separation of the cell wall from the cell liquid, they reduce the electric contact potential, and consequently directly retard the transmission of movement and sense impulses to the nerve centres. The retardation which substances of small cohesion pressure in water exercise on oxidation and other chemical reactions, and also on the electrical surface processes, is the cause of the conditions which are generally known as narcosis.

J. F. S.

Narcosis. ISIDOR TRAUBE (*Biochem. Zeitsch.*, 1913, **54**, 316—322).—The author criticises chiefly recent papers by Vernon (this vol., i, 802) and Winterstein (*ibid.*, i, 785). According to Czapek's statement, the main factor influencing exosmosis from certain plant-cells is the surface tension (measured against air) of the surrounding solutions. In the case of *Echeveria*, tannin exosmosis takes place when this surface tension is about 0·67 (water = 1). Vernon has objected to this conception of osmosis, which is in accordance with Traube's theory, in that there are several exceptions. The author attempts to explain these exceptions in some detail. He is in agreement with Winterstein in the view that narcosis cannot be explained simply as a phenomenon of asphyxia.

S. B. S.

A New Principle for the Direct Determination of Osmotic Pressure. ERNST COHEN and G. DE BRUIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 160—161).—A porous pot holding a semi-permeable medium is filled with the solution to be examined, and closed by a stopper through which passes a capillary tube and a copper wire supporting a copper electrode. A second copper electrode is placed in the surrounding water vessel. The porous pot is then immersed in the water, and the liquid immediately begins to rise in the capillary. An *E.M.F.* just sufficient to prevent the liquid rising any further is then applied to the electrodes, and the height of the liquid in the capillary measured. If h_1 represents the height of the liquid in the capillary and E_1 the counter-balancing *E.M.F.*, and P the osmotic pressure, then $P - h_1 = kE_1$, where k is a constant. On breaking the current circuit the liquid rises again to, say, k_2; an *E.M.F.* is then again applied to counter-balance this, say, E_2. From this, $P - h_2 = kE_2$; hence

$$P = h_1 + (h_1 - h_2)E_1/(E_2 - E_1).$$

The advantages of this method are: (1) The short time required for the determination; (2) the durability of the membrane, since it has a pressure on both sides; and (3) the absence of volume change of the solution by the entrance of the solvent. J. F. S.

Use of Toepler's Differential Manometer in Studying the Diffusion of a Gas. R. Foch (*Ann. Chim. Phys.*, 1913, [viii], **29**, 597—613).—The author has attempted to measure the rate of diffusion of carbon dioxide into air, using a differential manometer consisting of a U-tube of very obtuse angle, charged with xylene. One end of the manometer is connected with the air, the other with the tube from which diffusion is taking place. The movements of the xylene meniscus are recorded photographically, a full description of the necessary apparatus being given. Errors are found to arise from unsuitable atmospheric conditions, variations in temperature of the meniscus due to the illumination necessary for photographic purposes, solubility of carbon dioxide in xylene, irregularities in the manometric tube, and the inertia and viscosity of the liquid. Of these, the first is the most important, and can only be overcome by waiting for calm days. The second is largely avoided by reducing the period of illumination by placing the pendulum between the source of light and the manometer. The third source of error is eliminated by thoroughly cleansing the apparatus before each experiment; under these conditions the carbon dioxide does not come into contact with the xylene. The fourth is avoided since the errors involved occur in either direction, and can be eliminated by taking a sufficiently large number of readings, whilst the effect of the fifth can be evaluated for any particular state of the manometer, especially if the liquid is not renewed.

Experiments with carbon dioxide have shown that its coefficient of diffusion is constant from the start of the experiment. Its exact value can only be determined with an apparatus which can be more precisely calibrated. H. W.

Thermal Effects Produced by Heating and Cooling Palladium in Hydrogen. J. H. Andrew and A. Holt (*Proc. Roy. Soc.*, 1913, *A*, **89**, 170—186).—The authors have plotted the cooling and heating curves of palladium of various kinds in a vacuum and in hydrogen. It is shown that palladium is dimorphic, the stability of the two forms depending on the temperature. The rate of change of the one form into the other is extremely slow. The initial rapid occlusion of hydrogen is probably due to the presence of the amorphous form of palladium, and in the absence of such an amorphous film, palladium may be quite passive with regard to rapid occlusion of the gas in the cold. It is probable, however, that the passivity is apparent rather than real, and that if sufficient time were allowed for occlusion to take place a volume of gas equal to that occluded by active palladium would pass into solution. At temperatures above 100° a rapid occlusion of a small quantity of hydrogen occurs with both forms of palladium with the development of a constant quantity of heat. Both varieties of palladium cease to absorb hydrogen above a certain temperature, and above 150° they both have an equal affinity for the gas. J. F. S.

Physico-chemical Study of Neutralisation. EUGENE CORNEC (*Ann. Chim. Phys.*, 1913, [viii], **29**, 490—540, **30**, 63—163. Compare A., 1909, ii, 972).—The author has studied the variation of the freezing point of solutions of various acids during neutralisation by a solution of a base of the same molecular concentration. The results are graphically represented by taking depressions of the freezing point as ordinates and composition of the mixtures as abscissæ.

In the case of the neutralisation of monobasic acids (hydrochloric, chloric, perchloric, acetic, phenol) by a strong base (potassium or sodium hydroxides) the diagrams obtained are composed of two almost straight lines, the intersection of which corresponds with the normal salt. The cryoscopic method thus indicates the completion of neutralisation.

In the case of polybasic acids (sulphuric, oxalic, carbonic, resorcinol, arsenic citric), neutralised by potassium or sodium hydroxide, complete neutralisation is indicated by a minimum depression of the freezing point, and the position of this minimum indicates the basicity of the acid. Phosphoric, phosphorous, and hypophosphorous acids thus appear to be tribasic, dibasic, and monobasic respectively.

The cryoscopic method allows the detection, not merely of acidity which is too weak to be detected by methyl-orange, but even of such acidity as is not indicated by phenolphthalein (for example, the second acidity of carbonic acid). It is, however, not infallible. Certain very weak acidities, such as the second of hydrogen sulphide or the third phenolic group in pyrogallol, escape detection.

When potassium or sodium hydroxide is replaced by ammonia, analogous results are generally obtained. Certain acidities, indicated by the use of a strong base (the third of phosphoric or arsenic acids), are not shown when ammonia is employed.

In addition to the normal salts which are indicated with great clearness, the cryoscopic diagrams frequently show the formation of acid salts by breaks in the curve, which, however, are not generally well marked. In certain cases the existence of these breaks is doubtful, whilst in other instances they do not appear at all. The so-called abnormal acids salts, such as $KH_5(PO_4)_2$, $K_7H_5(PO_4)_4$, $K_5H_4(PO_4)_3$, are never indicated.

An exhaustive comparison is made between the results obtained by the above method and those derived from determinations of the electrical conductivity of similar solutions. The two methods do not yield the same results, but are complementary the one to the other. In the determination of basicity, the cryoscopic method is to be preferred.

In a number of cases the variation of the index of refraction during the course of neutralisation has been studied. When citric acid is neutralised by sodium hydroxide, the existence of the normal citrate is shown, and similar results are obtained when ammonia is used. With phosphoric acid and potassium hydroxide, evidence of the formation of monopotassium and tripotassium phosphate is

obtained (compare Féry, A., 1893, ii, 201). When ammonia is used, on the other hand, the mono- and di-ammonium salts are indicated, no certain evidence of the tri-ammonium salt being obtained. When phosphorous acid is neutralised by potassium hydroxide, the formation of the mono- but not of the di-potassium salt is shown, whilst, with ammonia, the diammonium salt is sharply indicated. With carbonic acid, evidence of the formation of the normal salt is obtained, but less definitely than when the cryoscopic method is utilised.

In the case of phosphoric acid, the variation of density during neutralisation has been similarly employed. When potassium hydroxide is used as base, evidence of the existence of mono- and tri-potassium phosphates is obtained. Indications of the formation of abnormal acid salts in solution are not obtained by this method.

Iodic acid, when neutralised with potassium hydroxide, gives a minimum depression at a point corresponding with the formation of the normal salt. A similar result is obtained by observations of the refractive index of a solution of the acid when treated with sodium hydroxide. Evidence of the existence of an acid salt is not obtained in either case. Experiments on the freezing points of aqueous solutions of iodic acid and of sodium iodate, in conjunction with the results obtained by comparative determinations of the electrical conductivity of chloric, bromic, and iodic acids, lead the author to the conclusion that the latter is probably polymerised in concentrated aqueous solution.

From observations of the depression of the freezing point during neutralisation with potassium hydroxide and of the index of refraction when neutralised with sodium hydroxide, dithionic acid appears to be dibasic. This is confirmed from determinations of the freezing point of solutions of potassium dithionate and of the freezing point and electrical conductivity of solutions of the free acid.

A cryoscopic study of the neutralisation of pyrophosphoric acid by potassium hydroxide or ammonia only indicates the existence of the normal salt, $M_4P_2O_7$. The curves for the index of refraction show definite breaks corresponding with the di- and tetra-salts, whilst, if potassium hydroxide is used as base, indications of the existence of the salt, $K_3HP_2O_7$, are also obtained.

Hypophosphoric acid corresponds with the formula $H_4P_2O_6$, a result which is confirmed by cryoscopic determinations of the solution of the acid (compare Rosenheim, Stadler, and Jacobsohn, A., 1906, ii, 744; Parravano and Marini, *ibid.*, 744; Rosenheim and Pritze, A., 1908, ii, 942; Cornec, A., 1910, ii. 122).

Solutions obtained from ordinary or crystalline phosphoric oxide, from vitreous metaphosphoric acid, or from lead metaphosphate invariably contain a certain amount of pyrophosphoric in addition to metaphosphoric acid. The latter substance in these solutions is polymerised, having at least the complexity indicated by the formula $(HPO_3)_3$, but the exact degree of polymerisation could not be ascertained (compare Holt and Myers, T., 1911, **99**, 384).

Selenious acid behaves as a mixed dibasic acid; the solutions

obtained by half-neutralisation contain the acid selenites, $MHSeO_3$, and not the pyroselenites, $M_2S_2O_5$.

Boric and arsenious acids are monobasic in solution, but no decision can be arrived at between the formulæ HBO_2 or H_3BO_3 and $HAsO_2$ or H_3AsO_3. The cryoscopic curve of boric acid gives evidence of the formation of condensed salts in solution.

Sucrose appears to combine with sodium hydroxide in aqueous solution to form a salt which can only exist in equilibrium with the products of its decomposition by water.

In the cases of chromic and periodic acids, cryoscopic curves of a peculiar kind are obtained, showing that, for these acids, the phenomenon of neutralisation is complicated by a reaction between the normal salt and an excess of base leading to the formation in solution of salts corresponding with different acids. An aqueous solution of chromium trioxide contains the acid $H_2Cr_2O_7$, the normal salt of which, $Na_2Cr_2O_7$, reacts with sodium hydroxide to yield Na_2CrO_4, the normal salt of the unknown acid, H_2CrO_4.

Periodic acid has the formula HIO_4, and yields with one molecular proportion of potassium hydroxide the normal salt, KIO_4; a second molecular proportion of base converts this into the salt, $K_4I_2O_9$; a third proportion again reacts, yielding a salt which does not contain more than one atom of iodine in its molecule. H. W.

Limits of Visibility of Precipitates. LUIGI ROLLA (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 104—108).—In the case of silver haloids, the author has verified the fact that the limits of their visibility in solution measured with the ultramicroscope coincide with their solubilities as determined electrochemically. By the same optical method he has measured the limits of visibility of some mercurous salts, in regard to some of which the electrochemical results have been discordant. He obtains for the limit of visibility (or solubility) at 17—18° the following values: $HgCl$ $4{\cdot}5 \times 10^{-6}$, $HgNO_3$ 5×10^{-6}, $HgBr$ 3×10^{-7}. The value found for mercurous chloride accords with certain theoretical considerations with which none of the values of this constant previously obtained has been in agreement. R. V. S.

Retardation in the Solution of Gold and Silver in Aqueous Cyanide Solution. IVAN IV. ANDRÉEV (*Zeitsch. Elektrochem.*, 1913, **19**, 667—672).—The influence of the addition of oxidising agents on the rate of the solution of gold and silver in dilute cyanide solution has been determined. The experiments were carried out in a constantly stirred solution. It is shown that on leading oxygen through the solution at a constant rate and increasing the concentration of the potassium cyanide, the velocity of solution in the case of gold increases up to a concentration of 0·3%, and then decreases on further concentration. Ozone and hydrogen peroxide were then used as oxidising agents. It is shown that air containing very little ozone increases the velocity of solution, but if the concentration of the ozone rises to 3—4% the velocity decreases, and at the same time the gold plate becomes coated with a red

layer of oxide. The addition of hydrogen peroxide operates in the same way as ozone. Starting with gold already coated with the oxide layer, and leading air through the solution, the oxide layer slowly disappears, and at the same time the velocity of solution slowly increases. The influence of a number of peroxides is next determined; manganese dioxide and lead peroxide alone have little influence, but when mixed with hydrogen peroxide or ozone the velocity is increased in the same way; the simultaneous action of ozone and hydrogen peroxide increases the velocity of solution in a very notable way. In the case of silver the presence of ozone or hydrogen peroxide causes a rapid increase in the velocity of solution with the rapid evolution of oxygen. In no case is the formation of an oxide layer on the metal noted. J. F. S.

Connexion Between Electrolytic and Chemical Processes. DAVID REICHINSTEIN (*Zeitsch. Elektrochem.*, 1913, **19**, 672—676. Compare Andréev, preceding abstract).—The author draws a connexion between the solution of metals as instanced by the solution of gold and silver in potassium cyanide, with the electrolytic solution of passive and active metals by electrolytic processes. This depends on the formation of an oxygen metal alloy as the first stage of the process; thus he formulates the solution of gold in potassium cyanide:

$$Au + 2OH + 2F = H_2O + Au/O;$$
$$2Au/O + H_2O + 4CN' \longrightarrow 2Au(CN)'_2 + 2OH'.$$

Should the oxygen concentration of the alloy be increased by an increase of the oxidising agent in the solution, a critical oxygen concentration will be reached, and the velocity of the process will decrease the more the concentration of the oxidising agent increases. The appearance of the oxide layer on the gold is therefore not to be regarded as the cause of the retardation of the solution, but a result of the increased oxygen concentration in the metal oxygen alloy. J. F. S.

Solubility Isotherm at 25° of Lithium Chloride in Mixtures of Alcohol and Water. SANTIAGO PIÑA DE RUBIES (*Anal. Fis. Quim.*, 1913, **11**, 422—435).—The solubility of lithium chloride in water falls regularly to about 60 water to 40 alcohol. The curve shows a minimum at 30 water to 70 alcohol. After 20 water to 80 alcohol the solubility falls, but slowly. The composition of the dissolved salt up to 10 water to 90 alcohol is $LiCl,H_2O$, whilst between 90 and 100% alcohol the salt is deposited anhydrous. The saturated pure water and pure alcohol solutions cooled to 0° deposit $LiCl,H_2O$ and $LiCl,4C_2H_6O$ respectively. G. D. L.

Mutual Solubility of the System Benzene-Acetamide. ENRIQUE MOLES and E. JIMENO (*Anal. Fis. Quim.*, 1913, **11**, 393—398).—The solubility curve is typical, showing a critical temperature 142·5°. G. D. L.

Acineta tuberosa. A Study of the Action of Surface Tension in Determining the Distribution of Salts in Living Matter. ARCHIBALD B. MACALLUM (*Proc. Roy. Soc.*, 1913, *B*, **86**, 527—550).—In *Acineta tuberosa*, a protozoan, the potassium can be shown microchemically to be localised in certain situations, and the potassium salt or salts migrate with changes in the tentacles; in retraction, for instance, they pass from the tentacles into the main cell substance. This is due to the action of surface tension. It is suggested that amino-acids are the substances which lower surface tension. The quantity of potassium salt condensed in the surface film of each tentacle appears to be of greater condensation than obtains in sea-water. W. D. H.

The Mechanical Stimulus to Crystallisation. STEWART W. YOUNG and W. J. VAN SICKLEN (*J. Amer. Chem. Soc.*, 1913, **35**, 1067—1078).—Further improvements in the apparatus previously used in these investigations (A., 1911, ii, 261, 865) are described, together with the results of new experiments on the supercooling of water. Using a hammer of carbon steel and an anvil of chrome-nickel steel, and starting with freshly polished impact parts, it was found that the impact values showed a rapid decrease as time went on, that is, the sensitiveness of the impact parts gradually increased; after a time the sensitiveness attained a value at which it remained constant for a considerable period, then becoming fluctuating and wholly untrustworthy. It was found that this was due to the impact parts becoming harder, the increase in hardness attaining a maximum after a time. The final fluctuations were possibly due to small fractures being formed, or else to some type of crystallisation being set up. The increased sensitiveness could be destroyed by repolishing.

All the experiments on supercooling were consequently carried out when the maximum sensitiveness had been obtained.

Using a stellite hammer and anvil it was possible to freeze water repeatedly at a temperature slightly under 0·02° below its normal freezing point; thus, if water possesses a metastable limit, it lies at less than 0·02° below the melting point of ice.

The relation between the energy of impact and the supercooling was found to be given by the formula: $(\sqrt{MS}-\Delta)\theta=\text{const.}$, where M is the mass of the hammer in grams, S is the fall distance in centimetres, θ is the supercooling, and Δ is a constant. T. S. P.

The Curie-Wulff Theory of Crystalline Habit. Application to Anisotropic Liquids. GEORGES FRIEDEL (*J. Chim. phys.*, 1913, **11**, 478—519. Compare Berthoud, this vol., ii, 305).—Curie's minimum potential theory of crystalline form is not in harmony with the fact that no change is observable in irregular, crystalline fragments immersed in a saturated solution. Moreover, it leads to an impossible definition of melting point, as crystals departing from the equilibrium shape would be more readily melted. The modified theory put forward by Wulff, according to which the rates of growth of crystalline faces are proportional to their capillary

constants, leads to a final condition incompatible with Curie's theory if the original crystal is not in the equilibrium habit.

The Curie-Wulff hypothesis is wholly applicable to liquid crystals if such can exist. Liquid crystals should arrange themselves as perfect polyhedra under the influence of discontinuities in the distribution of surface tension. Lehmann is mistaken in attributing the rounding up of his so-called liquid crystals to the action of surface tension. In the author's view, Lehmann's anisotropic drops are not crystals in the sense that their particles are reticulated or exhibit discontinuities in directional properties. They are merely polarised in the same sense as liquids in a magnetic field, glass under strain, etc., are polarised.

Berthoud's conclusion that specific rates of growth rather than capillary constants determine the form of solid crystals is in accordance with the author's views. It is deduced from the theory of thermodynamic potential that any shape of crystal can be in equilibrium with a limited quantity of saturated solution, but the equilibrium concentration for a given size of crystal depends to some extent on its shape. It is possible that Berthoud's growth constants are related in some way to the capillary constants of the faces. R. J. C.

Relations of Isomorphism in Organo-metallic Compounds. IV. Complementary Investigations. Paul Pascal (*Bull. Soc. chim.*, 1913, [iv], **13**, 744—752. Compare A., 1912, i, 524, 739; this vol., ii, 107).—The author has made thermal analyses of binary mixtures made from chlorobenzene, bromobenzene, iodobenzene, and fluorobenzene, the m. p.'s of which are $-44{\cdot}0°$, $-28{\cdot}1°$, $-29{\cdot}1°$, and $-40{\cdot}5°$ respectively.

Mixtures of chlorobenzene and bromobenzene give a continuous series of mixed crystals, whilst those of chlorobenzene and iodobenzene and of bromobenzene and iodobenzene probably also give a similar series, the freezing-point curves showing, however, minima in these cases. Binary mixtures containing fluorobenzene, on the other hand, yield two series of mixed crystals. According to these results, the elements of the halogen family are divisible into two groups, the first consisting of fluorine only, the second containing chlorine, bromine, and iodine.

The analogy between the cyanogen radicle and the halogens has led the author to examine the freezing-point curve of mixtures of chlorobenzene and cyanobenzene (m. p. $-12{\cdot}1°$). In this case, two series of mixed crystals are formed, from which the conclusion is drawn that the radicle is not closely related to the chlorine group. H. W.

Colloids and the Phase Rule. Ernst Hendrik Büchner (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 60—64).—A theoretical paper, in which the question of the number of phases existent in a colloidal solution is considered. The author advances reasons for regarding the colloidal solution as consisting of one phase only, like the true solutions. This is in opposition to the

view adopted by Pavlov (A., 1910, ii, 1033) and Jonker (A., 1911, ii, 103), who both regard a colloidal solution as made up of two phases. J. F. S.

Theory of the Formation of a Turbidity in Very Highly Disperse Systems. WOLFGANG OSTWALD (*Kolloid. Zeitsch.*, 1913, **13**, 121—128).—A theoretical paper, in which the author considers methods of following the change from true solutions through highly disperse solutions to colloidal solutions. The latter solutions exhibit a visible Tyndall cone, but it is shown that probably a great deal of dispersed ultraviolet light accompanies the dispersed visible light. The author considers, therefore, that true solutions which are optically homogeneous when examined in the usual way may show an ultra-violet Tyndall cone if examined photographically. It is also considered possible that associated liquids might be studied in this way. The experiments of Laue (*Bayr. Akad. Wiss.*, 1912, 303) are considered, and the formation of a Röntgen ray Tyndall cone is regarded as likely to lead to valuable information with very highly disperse or even true solutions. J. F. S.

Dependence of the Breaking Strain of Solid Disperse Systems on Temperature. FR. HAUSER (*Kolloid. Zeitsch.*, 1913, **13**, 148—150).—The breaking strain of ebonite, wax, colophony, shellac, and mixtures of these substances has been determined at a series of temperatures. The curves obtained fall into two groups: (1) those in which the strain decreases with temperature, and (2) those in which the strain increases to a maximum and then decreases rapidly with increasing temperature. Ebonite, wax, and shellac belong to the first type, and colophony to the second type. The maximum in the case of colophony lies at 30°, which is the temperature at which the coefficient of linear expansion suddenly decreases. The addition of turpentine up to 33% to shellac had a slight lowering influence on the breaking strain, but the influence of a solid substance, such as talc, had no influence on the curve for shellac or any of the turpentine shellac mixtures. On the other hand, colophony was very sensitive to the addition of other substances; thus the addition of 6% of wax changed the curve almost into that for pure wax. The addition of 10% of turpentine lowered the maximum of the curve to below zero. The addition of talc flattened the colophony curve. A mixture of shellac and colophony gave a curve which has the same form as the corresponding curve for cast iron. J. F. S.

Osmotic Pressure of Colloids and its Importance to Biology. BENJAMIN MOORE and HERBERT ELDON ROAF (*Kolloid. Zeitsch.*, 1913, **13**, 133—137).—A theoretical paper, in which the osmotic pressure experiments on colloidal substances of Moore, Roaf, and co-workers are summarised. It is shown that many colloidal solutions give rise to an osmotic pressure under conditions which eliminate the action of inorganic impurities. J. F. S.

Separation of Colloidal Solutions. RICHARD ZSIGMONDY (*Kolloid. Zeitsch.*, 1913, **13**, 105—112).—The author gives details of methods by which sols of arsenic sulphide, gold, ferric hydroxide, and silicic acid may be separated into two liquid layers. The method consists in mixing the sol with measured quantities of alcohol and ether, and then adding an excess of ether. The remainder of the paper deals with a systematic method of subdividing the subject-matter of colloidal chemistry. J. F. S.

Separation of Colloidal Solutions. WOLFGANG OSTWALD (*Kolloid. Zeitsch.*, 1913, **13**, 170—172).—Polemical (compare Ostwald, this vol., ii, 32; Zsigmondy, preceding abstract). It is shown that the cases of separation of colloidal solutions into two layers as studied by Zsigmondy have nothing to do with the typical separation of colloid solutions into two layers, since the cases studied by him are qualitatively identical with the separation of true solutions or even solvents themselves, and show nothing characteristic of colloids. J. F. S.

Mutual Precipitation of Colloidally Dissolved Substances. ANTONI VON GALECKI and M. S. KASTORSKI (*Kolloid. Zeitsch*, 1913, **13**, 143—146).—Biltz (A., 1904, ii, 324) has shown that only oppositely charged sols mutually precipitate one another without the addition of an electrolyte. The present authors have investigated this action, using ferric hydroxide sol, and gold sols prepared respectively by the action of formaldehyde and phosphorus. Measured quantities of the gold sols were added to measured quantities of the ferric hydroxide sol, and the limits determined over which mutual precipitation occurred. Using a 0·1% ferric hydroxide sol, it is shown that 1 mg. of gold, used as a sol prepared from formaldehyde, precipitates 4·98 mg. of ferric oxide, whereas 1 mg. of gold prepared by phosphorus precipitates 18·36 mg. of ferric oxide. In the case of a 0·01% ferric hydroxide sol, the quantities of ferric oxide precipitated are 4·65 mg. and 20·65 mg. respectively for 1 mg. of the two gold sols. The authors consequently draw the conclusion that a colloid phase of finely-divided particles precipitates another colloid phase of opposite charge more energetically than the same colloid consisting of larger particles. J. F. S.

The Influence of the Hydrogen-ion Concentration on Mixtures of Colloids. LEONOR MICHAELIS and HEINRICH DAVIDSOHN (*Biochem. Zeitsch.*, 1913, **54**, 323—329).—A reply to the paper of Landsteiner (this vol., i, 668). The authors do not deny that two oppositely charged amphoteric substances can act on one another over a large range of hydrogen-ion concentrations. They insist on the fact, however, that there is a maximal action at a certain concentration lying between the isoelectric point of the two substances. In order to demonstrate this point experimentally, low dilutions must be chosen, and they illustrate their statement by experiments on the precipitation of gelatin by tannin and on the combination of certain dyes with gelatin. They contend that this

"unspecific" combination of two oppositely charged electrolytes is to be distinguished from a "specific" combination (for example, formation of precipitins), when no sharp optimal point can be ascertained, even in dilute solutions. S. B. S.

A Criticism of the Lipoid and Ultra-filter Theories of the Plasma Membrane; the Influence of the Electric Charge of Colloids on Their intra vitam Deposition in the Cell. WILLY RUHLAND (*Biochem. Zeitsch.*, 1913, **54**, 59—77).—The author replies to the criticism of Höber and Nast (this vol., ii, 486), who have objected to his ultra-filter theory of the passage of dyes into a cell. It is contended, in the first instance, that the Overton-Meyer lipoid theory is insufficient, and numerous examples are quoted of both acid and basic dyes, which are soluble in lipoids (cholesterol in concentrated solution of an organic solvent which does not dissolve the dye), and which are yet incapable of permeating the cell-wall, and of permeating dyes, which are insoluble. It is contended, furthermore, in favour of the ultra-filter theory, that only those dyes in state of high dispersion can penetrate this cell-wall. As criterion for this state of dispersion, the diffusibility through gelatin is employed, and it is shown that those dyes which readily permeate the plasma membrane readily diffuse through the jelly. Attention is called to the fact, however, that a distinction must be made between the permeating capacity and the capacity to be stored in the cell. Basic dyes are readily stored, in that, in coming into contact with acid substances such as tannin, they are precipitated, and thus remain within the cells, and soon become visible. Acid dyes can penetrate without being stored, and a method is described for demonstrating their presence within the cell. The electrical charge on the colloid affects, therefore, their storage capacity, rather than their permeating qualities. S. B. S.

Starch Jellies. ARTHUR MEYER (*Koll. Chem. Beihefte*, 1913, **5**, 1—48).—A very complete investigation of solutions of arrowroot starch and the jellies produced by them has been made. It is shown that solutions produced at 138—140° are not molecular disperse systems, although in many respects they resemble such solutions. These solutions do not exhibit uniform dispersity, and in the swelling of the starch, lumps are produced which even on long heating at 138° do not dissolve. Complete solution only occurs when the starch paste particles are so small and scattered that they can readily pass into solution. The preparation of a colloidal solution of starch at 138—140° consists of two processes: (1) a swelling of the starch granules, and (2) a disintegration of the globules thus formed into tiny drops and crystals. Starch granules are made up of layered spheres of amylose, consisting chiefly of α- and β-amylose. The β-amylose changes on solution of the starch at 100° into drops of a viscous solution of water in amylose, whilst the α-amylose remains undissolved. Thereby each starch granule becomes a globule of porous drops of jelly, which adhere strongly, and the interstices of which are filled by a trichite of α-amylose which can be detected ultramicroscopically. At temperatures of

about 138° the trichite is converted into drops. The drops of the amylose solution of water are very viscous, but on increasing the temperature the viscosity decreases because more water is absorbed, and since this renders them less refractive they are more difficult to detect. The viscosity is so far diminished that at 60—100° the drops flow together to form homogeneous porous drops of irregular form. A colloidal solution of starch which has been prepared by heating at 138° is made up of two phases: (1) a very viscous phase (*Z*), and (2) a phase of low viscosity (*F*). The disperse phase, *Z*, contains particles of varying size, which are due to the varying size of the amylose crystals and the extent to which the drops have united in the preparation. Such an heterogeneous disperse system of amylose never has a greater degree of dispersity than it possesses as soon as prepared at 138°. On cooling such a solution the dispersity decreases, the slower the cooling the greater the decrease. If a dilute solution of amylose is rapidly cooled, the drops of phase *Z* maintain their original size, and only slowly unite with one another to produce conglomerates and an emulsion. If a concentrated solution, in which the drops easily come into contact, is cooled, a thin or a thick jelly is produced, depending on the concentration. With more rapid cooling only small conglomerates of irregular form are produced, whilst with slow cooling larger globules of half-melted drops are produced, from which a jelly globule of amicroscopic drops is formed. All these elements, together with those which have maintained their original form set together in various ways, compose the jelly. The various elements even at 0° possess a definite viscosity, and are not solid. The jellies are consequently porous, and contain the dispersion medium in the pores. The water in the pores is easily movable, whilst that dissolved in the amylose is bound in the sense of a dilute solution, and can consequently exhibit only a small vapour pressure. The concentration of the water in the amylose is smaller the lower the temperature of the jelly. When a jelly is dried at the ordinary temperature the water from the pores evaporates, and the jelly falls together, but maintains its structure. On placing such a dried jelly in water, the form *Z* absorbs a quantity of water corresponding with the temperature, and water enters the pores and again produces the jelly. When a freshly prepared jelly is warmed with water and the temperature constantly increased, the form *Z* takes up more and more water, and its viscosity and refractivity decrease, thereby producing a softer and more transparent jelly. At about 100° the half-melted drops begin to separate from one another, and on further heating the jelly falls into its structural elements. These always have a less total surface than the disperse phase of the freshly prepared solution from which the jelly was produced.

J. F. S.

Colloidal Solutions. II. The System Tannic Acid–Water–Acetic Acid. Emanuele Paterno and G. Salimei (*Kolloid. Zeitsch.*, 1913, **13**, 81—88.* Compare this vol., i, 409).—Freezing-point deter-

* and *Gazzetta*, 1913, **43**, ii, 245—263.

minations have been made of solutions of tannic acid in water, acetic acid, and mixtures of the two solvents. It is shown that the presence of tannic acid does not modify the freezing-point diagram acetic acid–water. A concentration up to 4% of tannic acid in dilute acetic acid brings about a gradual rise in the freezing point of about 0·2° for solutions containing up to 30% acetic acid, and further additions of tannic acid effect no further change in the freezing point. The addition of tannic acid even up to 20% causes no change in the freezing point of a 46·48% acetic acid solution. When the quantity of acetic acid in the mixed solvent exceeds that of the water, the addition of about 10% of tannic acid produces a lowering of the freezing point of about 0·3°. The authors explain these changes by the high absorptive property of the tannic acid, both for water and acetic acid, and they conclude that tannic acid is equally insoluble in both solvents, but forms in both cases colloidal suspensoids. J. F. S.

Colloid-chemical Action of Diuretic Salts. MARTIN H. FISCHER and ANNE SYKES (*Kolloid. Zeitsch.*, 1913, **13**, 112—121).—The authors have injected a number of salt solutions into the blood of rabbits and rats, and measured the quantity of urine expelled during the following two hours. The salts injected were sodium chloride, magnesium chloride, strontium chloride, calcium chloride, and mixtures of these salts all in $N/4$-solutions. Further experiments were carried out with various sodium salts, including nitrate, bromide, acetate, phosphate, iodide, and sulphate; magnesium sulphate was also employed. It is shown that the diuretic action of the various salts runs parallel with their dehydrating action on protein colloids, a fact which points to the conclusion that their action in the first place is due to their influence on the substances as a whole, and that they act as diuretics only so far as they supply free water, extracted from the colloids, to the kidneys. The order of the action in increasing degree is sodium, magnesium, strontium, and calcium, and for anions, chloride, bromide, nitrate, iodide, acetate, sulphate, and phosphate. It is shown that the addition of bivalent metals, such as calcium, magnesium, and strontium, has no antagonistic effect on the action of sodium chloride, but, on the other hand, is additive to it. The osmotic theory of the action of diuretic salts is considered in the light of the present experiments. J. F. S.

Phenomena of "Clot" Formations. I. Clotting of Milk. SAMUEL B. SCHRYVER (*Proc. Roy. Soc.*, 1913, *B*, **86**, 460—481).—When solutions of calcium salts and sodium cholate are mixed a clot is formed on heating. In the case of those salts which raise the surface tension of water, the greater the concentration of salt the shorter is the time required for clot formation. Salts which lower the surface tension decrease the clotting time only up to a certain limit of concentration. Above this limit, the clotting time is increased or the clot formation inhibited entirely. The inhibi-

tion of clotting is attributed to the adsorption of simple molecules by the more complex colloids, which are thereby inhibited from aggregation to form a clot. In milk the materials necessary for clot formation pre-exist, but the adsorption of simple molecules from the solution prevents aggregation. The conception is advanced that the ferment clears the surface of the colloid from adsorbed substances, and allows aggregation to take place.

The solubility in half-saturated lime water is used as a criterion of caseinogen preparations. Products allowed to remain a short time only in contact with acetic acid during preparation give opaque, milky fluids containing 8% of caseinogen. When heated at 37° or allowed to remain with acetic acid a less soluble metacaseinogen is obtained, forming opalescent solutions. Solution of this in sodium hydroxide and precipitation with acetic acid reconverts it into the more soluble form.

The addition of calcium chloride to solutions of caseinogen in sodium hydroxide gives a precipitate only within certain definite limits of concentration of the calcium salt. The addition of rennet to a mixture in which precipitation is inhibited by an excess of the salt immediately causes precipitation. When the optimal amount of calcium salt is present, precipitation may be inhibited by adding milk serum, peptone, or glycine. Rennet only causes precipitation in these cases when too much inhibitor is not present. The final result of the reaction depends on the relative quantities of the various products present in the system. Evidence is quoted to prove that the clot is formed from caseinogen, and not from the calcium salt.

The clot produced by rennet alone is formed from metacaseinogen; that produced by calcium chloride alone is formed from caseinogen. The rennet clot cannot be converted into natural caseinogen. The rennet does not in any way effect proteoclastic digestion in the clot. In milk the clot formation depends on the presence of four series of substances in the system, namely, simple inhibitory substances, colloids, enzymes, and calcium salts.

E. F. A.

Passivity of Metals in the Light of the Theory of Allotropy. ANDREAS SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 191—192).—The author advances a theory of passivity, which assumes that metals are built up of different kinds of molecules of different reactive power. In such a case the internal equilibrium of the surface layer will be disturbed by chemical action, and on the rapidity with which equilibrium is re-established will depend whether passivity is observed or not. J. F. S.

Equilibria in Ternary Systems. VIII. FRANS A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 99—113).—A mathematical paper, in which the composition, entropy, and volume relationships of a liquid, in which two solids are dissolved, with its vapour and the solid phases are considered. J. F. S.

Equilibria in Certain Organic Systems. NIKOLAI A. PUSCHIN and I. V. GREBENSCHTSCHIKOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 741—745).—The following melting-point diagrams have been traced:

(1) Diphenylamine and *p*-nitroanisole. This consists of two branches meeting in a eutectic point at 20·5°, corresponding with 51·5 mol. % of *p*-nitroanisole. The liquid phases exhibit an orange-red coloration. Solid solutions of appreciable concentration are not formed.

(2) Urethane and diphenylamine. This consists of two straight lines meeting in a eutectic point, 32·2°, which corresponds with 39 mol. % of diphenylamine. No solid solutions of marked concentration are observed.

(3) Urethane and *p*-nitroanisole. The eutectic point here is at 34·2°, whereas Mascarelli (*Gazzetta*, 1909, **39**, i, 280) gave 33·2°. Urethane has m. p. 48·3°, that given by Mascarelli being 47·3°. Solid solutions are not formed to an appreciable extent.

(4) *m*-Nitroaniline and naphthalene. The diagram comprises two branches, the eutectic point being 68° and the composition 75 mol. % of naphthalene. Solid solutions were not observed.

T. H. P.

Distribution of a Suspended Substance Throughout Two Liquid Phases, and its Practical Signification. WILLEM REINDERS (*Chem. Weekblad*, 1913, **10**, 700—709).—A theoretical investigation of the conditions governing the distribution of a substance in suspension in two immiscible liquids, and a discussion of the bearing of the problem on Elmore's method for the separation of ores, the cleansing action of soap, and the moist preparation of paints.

A. J. W.

The Systems Phosphorus and Cyanogen. ANDREAS SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 27—33).—The two systems red phosphorus–yellow phosphorus, cyanogen–paracyanogen are considered. It is shown that both systems are alike and comparable in all respects, and probably belong to the ether–anthraquinone type. It is shown that no connexion can be deduced between yellow phosphorus and violet and red phosphorus, or between cyanogen and paracyanogen, although there obviously must be some connexion, since the phases are respectively convertible into one another.

J. F. S.

The Displacement of the Critical Points of Iron by Addition of Silicon. GEORGES CHARPY and ANDRÉ CORNU (*Compt. rend.*, 1913, **157**, 319—322. Compare Vigouroux, this vol., ii, 512).—A study of the variation in the three critical points, a_1, a_2, and a_3, of iron on the addition of increasing amounts of silicon, these points being determined by the rates of cooling of the various alloys. The point a_3 diminishes in intensity as the proportion of silicon increases, whilst passing slightly up the temperature scale, and disappears entirely in alloys containing 1·5% or more of silicon.

The point a_2 passes slowly down the temperature scale as the percentage of silicon increases, but retains its intensity. In alloys containing little carbon, the decrease is 10° to 12° for each 1% of silicon. The point a_1 passes slightly up the temperature scale with increase in silicon, but diminishes in intensity as the carbon becomes converted into graphite, owing to the presence of the silicon, and disappears when the silicon content is above 5%. On account of the opposite natures of the variations of the points a_1 and a_2, the positions of these two points coincide for an alloy containing 3·16% Si, above which they become inverted. W. G.

The Pseudo-system Methyl Thiocyanate–Methyl Thiocarbimide. ANDREAS SMITS and H. VIXSEBOXSE (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 33—39).—It was shown by Walden (A., 1906, ii, 336) that the solution of salts in methyl thiocyanate brought about a lowering of the boiling point, and not raising, as was to be expected. The authors show that this abnormal change is due to the conversion of the thiocyanate into the thiocarbimide, as indicated by $CH_3{\cdot}S{\cdot}C{\vdots}N \longrightarrow CH_3{\cdot}N{:}C{:}S$. The thiocarbimide has a lower boiling point than the normal ester, which consequently explains the lowering of the boiling point. Quantities of methyl thiocyanate were kept in contact with cadmium iodide for prolonged periods, and then fractionally distilled. It was found that the first portion distilled at 123·6°, and that the temperature continually rose as the distillation proceeded until the last fraction had a boiling point of 136·5°. The boiling point of the *iso*- and normal esters are respectively 119° and 130·5°; consequently the experiment shows that an internal change occurs in the solvent, and the boiling point is influenced in the normal manner.

J. F. S.

Binary Systems of Thallous Chloride with the Chlorides of Some Bivalent Metals. CARLO SANDONNINI (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 20—27. Compare this vol., ii, 588).—The paper deals with the thermal analysis of the systems $TlCl$–$PbCl_2$, $TlCl$–$SnCl_2$, $TlCl$–$HgCl_2$, and $TlCl$–$CdCl_2$.

Thallous chloride and lead chloride are completely miscible in the solid state. The curve shows a minimum at about 370° and 40 mol. % of lead chloride.

Thallous chloride and stannous chloride form solid solutions in all proportions. There is a minimum at 185° and 82 mol. % of stannous chloride.

Thallous chloride and mercuric chloride form two compounds. One of these, $TlCl,HgCl_2$, melts unchanged at 224°; the other, probably $4TlCl,HgCl_2$, decomposes on fusion, its temperature of formation being 250°. Both form solid solutions with each other and with the simple salts between very wide limits. The eutectic mixture of $HgCl_2$ and $TlCl,HgCl_2$ lies at about 64 mol. % of mercuric chloride and 183°, the limits of existence of saturated solid solutions being 53—76 mol. % of mercuric chloride. The

eutectic mixture of $TlCl,HgCl_2$ corresponds with about 32 mol. % of mercuric chloride and 205°.

Thallous chloride and cadmium chloride form a compound, $TlCl,CdCl_2$, m. p. about 426°. The eutectic mixtures of this compound with the two salts correspond with 27 mol. % of cadmium chloride and 259°, and 66 mol. % of cadmium chloride and 400° respectively. R. V. S.

The Dissociation of the Molecules into Atoms Considered as one of the Factors of the Velocity of Reaction. E. BRINER (*Compt. rend.*, 1913, **157**, 281—284. Compare this vol., ii, 21).—A theoretical discussion of the above question, in which the author considers that the velocity of a reaction is largely controlled by the atoms, arising from the dissociation of the molecules, and on these grounds he explains the inactivity of nitrogen at moderate temperatures, the molecules of nitrogen being very stable, and giving but few free atoms. W. G.

The Thermal Decomposition of Symmetrical Diarylhydrazines. A Reaction of the First Order. GEORGE O. CURME, jun. (*J. Amer. Chem. Soc.*, 1913, **35**, 1143—1173).—The author has investigated the velocity of decomposition of hydrazobenzene, *p*-hydrazotoluene, and *p*-methylhydrazobenzene, the products being mixtures of azobenzene and aniline, azotoluene and toluidine, and benzeneazotoluene, aniline, and toluidine respectively.

From the results the decompositions are reactions of the first order, and the author inclines to the view that a series of changes occurs, namely, $NHR{\cdot}NHR \longrightarrow 2NHR \longrightarrow NR\colon + NH_2R$, concluding with a coupling of the $NR\colon$ residues to an azo-compound; the first stage is supposed to be slow in comparison with the others, and so determines the unimolecular nature of the reaction.

The ease of decomposition falls in the order hydrazotoluene ($k = 0{\cdot}00160$ at 110·25°), methylhydrazobenzene ($k = 0{\cdot}00146$ at 125·30°), hydrazobenzene ($k = 0{\cdot}00145$ at 140·35°, 0·00253 at 145·35°, 0·00436 at 150·35°). This order appears to agree with that of the sensitiveness towards acids, for on treatment with excess of iodine in alcoholic solution for the purpose of estimation of the respective bases by oxidation to the azo-compound, it is found that about 1% of hydrazobenzene, 3% of *p*-methylhydrazobenzene, and 10% of hydrazotoluene undergoes rearrangement on account of the influence of the acid formed; the amount of iodine used up is therefore not strictly equivalent to the quantity of hydrazo-compound applied. D. F. T.

Catalysis. ISIDOR TRAUBE (*Pflüger's Archiv.*, 1913, **153**, 309—322).—A theoretical paper, in which catalysts are discussed; the author considers them in three groups: (*a*) negative catalysts (bradyatysts), (*b*) positive catalysts (tachysts), and (*c*) Eklysts, catalysts which bring about the reaction. In the first two cases it is shown that the substances included under these headings may, under different conditions, act positively or negatively. The pres-

ence and influence of catalysts are considered in the case of disease, and the action of medicines on the catalysts is considered. In the case of the eklysts the author criticises Ostwald's definition of a catalyst, and deduces evidence to show that catalysts can, and do, bring about reactions which could otherwise not occur even very slowly. The examples put forward to support this assertion are of a medical nature. J. F. S.

A Case of Iron Light Catalysis. H. STAFFORD HATFIELD (*Zeitsch. Elektrochem.*, 1913, **19**, 617).—The author shows that the liberation of iodine from a solution of mercuric iodide in potassium iodide in sunlight does not take place if the materials are entirely free from iron. Consequently, he shows that the reaction $2KI + O + Hg = 2KOH + HgI_2$, which takes place in sunlight, is strongly catalysed by iron compounds. J. F. S.

The Univalent Atom Cannot be a Simple Doublet. MARCEL BRILLOUIN (*Ann. Chim. Phys.*, 1913, [viii], **29**, 473—490. Compare this vol., ii, 493).—A mathematical paper, in which the author demonstrates that the conception of a univalent atom as a simple doublet is inadmissible. H. W.

Some Thermometric and Optical Constants as Functions of the Atomic Weights. WILHELM BILTZ (*Zeitsch Elektrochem.*, 1913, **19**, 613—617).—The author gives very complete curves, which show that the hardness, boiling point, melting point, electric conductivity, light absorption, and index of refraction of the elements are all functions of the atomic weight. The relationships between these various properties are discussed. J. F. S.

Chemical Papyri of the Third Century (The New Stockholm and the Leyden Papyri). EDMUND O. VON LIPPMANN (*Chem. Zeit.*, 1913, **37**, 933—934, 962—964, 1002—1004, 1014—1015).—An account of a chemical papyrus discovered at Thebes in 1828, and now preserved at Stockholm. This papyrus amplifies, in a most fortunate manner, the Leyden papyrus, since whilst the latter deals chiefly with the noble metals, the former deals chiefly with precious stones and pearls and with dyeing, in particular purple dyeing; only a small portion relates to the metals. T. S. P.

Improved Method for the Extraction of Powdery Material. M. KARDOS and W. SCHILLER (*Chem. Zeit.*, 1913, **37**, 920).—A perforated glass tube, sealed at the lower end and funnel-shaped at the upper end, is put down the centre of the powder to be extracted, which is contained in a Soxhlet apparatus. The liquid from the condenser falls into the tube, and then percolates uniformly through the powder, the extraction being completed in a much shorter time than if no tube were present. To prevent the perforations of the tube becoming stopped up by the powder, it is provided with a closely-fitting cloth sheath. T. S. P.

Jacketted Fractionating Column. HENRI VIGREUX (*Bull. Soc. chim.*, 1913, [iv], **13**, 868—869. Compare A., 1904, ii, 611).—The previously-described fractionating column has been improved by slightly increasing its diameter (22—23 mm. instead of 15—16 mm.), which permits the introduction of eight points at each stage instead of four. Further, for liquids of b. p. above 100°, the column is now sealed into a glass jacket at a point just below the side-tube. With this apparatus it is claimed that liquids of high b. p. can be fractionated without overheating even when a long column is used. H. W.

Distillation of Petroleum Distillates Under Normal Pressure. A. SCHELLER (*Chem. Zeit.*, 1913, **37**, 917).—The author describes an apparatus for maintaining a constant pressure, for example, normal pressure, during the distillation of petroleum distillates. The pressure is maintained constant by means of a Bunte pressure regulator (compare Bunte, A., 1873, 1103). The necessity for such an apparatus arises from the fact that the relative proportions of the various fractions vary with the pressure. T. S. P.

A Simplified Modification of the Skita Hydrogenation Apparatus. H. HEINRICH FRANCK (*Chem. Zeit.*, 1913, **37**, 958).—The author describes a simple apparatus, which can be readily built up from material usually found in a chemical laboratory, for carrying out hydrogenations according to Skita's method.
T. S. P.

A Water Pump. HENRI VIGREUX (*Bull. Soc. chim.*, 1913, [iv], **13**, 869—870).—The pump consists of a glass tube, 15 cm. long and 7—8 mm. wide, constricted at two points in such a manner that the lower constriction has a slightly greater diameter than the upper one. Between the constrictions a bulb is blown, which is subsequently flattened in such a manner as to bring the narrowed portions of the tube as closely together as possible. A side-tube is blown on to the bulb.

When the position of the constrictions is correctly adjusted, the apparatus is stated to give as good a vacuum as can be obtained with the most complicated pumps, whilst, even when this is not the case, it is still sufficiently powerful to bring about rapid filtration. H. W.

Tube for Emptying a Kipp Apparatus. A. FRIEDMANN (*Chem. Zeit.*, 1913, **37**, 929).—Through a two-holed stopper in the top of the apparatus are fitted a siphon tube leading to the bottom, and a right-angled tube which reaches a short way below the stopper. By blowing through the second tube the acid is forced out through the siphon. T. S. P.

A Dilution Colorimeter and the Error of Colorimetric Comparison. ROBERT V. STANFORD (*Zeitsch. physiol. Chem.*, 1913, **87**, 159—170).—A form of colorimeter is described and figured,

based on the principle of the dilution of a stronger solution of known concentration of the same substance until both solutions have the same colour. E. F. A.

Simple Ultrafiltration Apparatus. RICHARD ZSIGMONDY (*Zeitsch. angew. Chem.*, 1913, **26**, 447—448).—The apparatus consists of three parts, namely, a flanged funnel, perforated disk, and ring; the disk is clamped between the funnel and the ring, the latter forming a receptacle for the liquid to be filtered. The holes of the perforated plate are covered with a filter paper, on which, and covering the whole surface of the plate, is placed a thin collodion film before the several parts of the apparatus are clamped together. With this apparatus, and using a vacuum pump, it is possible to filter colloidal solutions, such as colloidal solutions of gold and iron oxide, very quickly. The apparatus is also of great value in the estimation of gelatinous precipitates. W. H. G.

Application of Ultrafiltration Apparatus. HEINRICH BECHHOLD (*Zeitsch. angew. Chem.*, 1913, **26**, 472).—The apparatus described by Zsigmondy (compare preceding abstract) permits of filtration under a pressure of only one atmosphere. In cases where higher pressures must be employed, the apparatus described by the author previously (compare A., 1908, ii, 24) is suitable.

W. H. G.

Lecture Experiments with Rare Gases. GEORG GEHLOFF (*Physikal. Zeitsch.*, 1913, **19**, 838—841).—Six lecture experiments are described to demonstrate (1) the absorptive property of strongly cooled cocoanut charcoal, (2) the preparation of helium from the air, (3) the presence of the rare gases in the air, (4) preparation of argon from the air, (5) the presence of neon in the air, and (6) the presence of helium in radioactive minerals. The experiments all make use of the absorption of the commoner gases by cocoanut charcoal, and the preparation of argon makes use of molten potassium. J. F. S.

Inorganic Chemistry.

Apparatus for the Preparation of Hydrogen Bromide. ANTONIO GARCÍA BANÚS (*Anal. Fis. Quim.*, 1913, **11**, 363—364).—Bromine is dropped, by means of a tap-funnel, on to molten naphthalene at 40—50° contained in a distilling flask, the side-tube of which is sealed to a U-tube containing a few c.c. of water, potassium bromide, and red phosphorus. G. D. L.

The Sulphur Set Free in the Action Between Sulphurous Acid and Water. ÉMILE JUNGFLEISCH and LÉON BRUNEL (*Compt. rend.*, 1913, **157**, 257—262. Compare this vol., ii, 581).—If the

interaction of sulphurous acid and water takes place at a temperature above the melting point of octahedral sulphur, the sulphur is precipitated in a liquid form, which on cooling crystallises in a form depending on the temperature. At 98—100° the sulphur is precipitated sometimes in masses, crystallised after fusion, sometimes in liquid globules, which slowly crystallise on keeping, the sulphur thus being molten at a temperature below its melting point. This is explained on the grounds that the sulphur is produced in the plastic form, which at 100° is converted into the octahedral form with the development of heat, thus raising the temperature of the mass to above 113°. At lower temperatures the sulphur is precipitated in the plastic form. Diagrams are given showing the appearance of the sulphur as precipitated under different conditions. W. G.

Sulphur, Selenium, and Tellurium. ERNST BECKMANN (*Sitzungsber. K. Akad. Wiss. Berlin*, 1913, 886—894).—Cryoscopic measurements on solutions of naphthalene, diphenyl, aniline, quinoline, etc., in sulphur gave a value of 213 for the freezing-point constant, from which the latent heat of fusion is calculated to be 14·1 cal. Utilising the results of Smith and Holmes (A., 1903, ii, 284), the molecule of amorphous sulphur is then found to be $S_{5\cdot1}$, that is, it is probably S_6. From various considerations the author comes to the conclusion that the molecule S_6 is dark brown, and hence he gives an explanation of the colour assumed by molten sulphur at different temperatures. The explanation involves the assumption of the formation of a complex between crystalline sulphur (S_8) and amorphous sulphur (S_6).

Boiling-point determinations on solutions of sulphur in liquid chlorine prove the existence of the chloride, S_2Cl_2. When the light yellow solution of this compound is allowed to assume room temperature in a sealed tube, it becomes dark brown after a few hours, owing to the formation of the chloride, SCl_2.

Cryoscopic and ebullioscopic determinations on solutions of sulphur in bromine do not point to the formation of molecules containing only one atom of sulphur; only the bromide, S_2Br_2, exists. Similar experiments in iodine solution show that no combination takes place between sulphur and iodine.

Selenium and chlorine give only the monochloride and tetrachloride, of which the latter is the most stable. Ebullioscopic experiments with solutions of selenium in bromine indicate the formation of a mixture of the compounds Se_2Br_2 and $SeBr_4$. In iodine as solvent, selenium exists as the molecule Se_1 to Se_2, whereas in solvents such as diphenyl and anthraquinone the molecule is Se_8. The application of various physico-chemical methods does not indicate the formation of any compound between selenium and iodine, and the dissociating effect of iodine on the molecule of selenium still awaits an explanation.

Tellurium dissolves in molten iodine with considerable evolution of heat, and the resulting compounds formed contain 1—2 atoms of tellurium in the molecule. T. S. P.

The Molecular Weight of Sulphur Trioxide. Henri Giran (*Compt. rend.*, 1913, **157**, 375—376).—Assuming the molecular weight of sulphur trioxide as 80, and determining the heats of vaporisation and solidification of liquid sulphur trioxide, the author calculates the constant in de Forcrand's modification of Trouton's law to be 35·8, which is sufficiently close to the value 30, given by de Forcrand, to confirm the exactness of the molecular weight, whilst at the same time pointing to a commencement of polymerisation during liquefaction. W. G.

The Mechanism of the Formation of Sulphuric Acid in the Lead Chambers. Emil Briner and A. Kuhne (*Compt. rend.*, 1913, **157**, 448—450. Compare this vol., ii, 21).—The authors consider that the formation of sulphuric acid in the lead chambers is due primarily to the direct oxidation of the sulphur dioxide by the atomic oxygen arising from the dissociation of the nitrogen peroxide, the sulphur trioxide formed then combining with the water. They have obtained sulphur trioxide by the interaction of pure dry sulphur dioxide and nitrogen peroxide at temperatures below 60°. W. G.

Volatility of Sulphuric Acid when Used in Vacuum Drying. H. C. Gore (*J. Biol. Chem.*, 1913, **15**, 259—261).—The total loss of sulphuric acid in a Hempel desiccator was 0·00656 milligram per sq. cm. per day. Lime is recommended instead. W. D. H.

The Chemical Affinities of Nitrogen. Geoffrey Martin (*Chem. News*, 1913, **108**, 49—52).—A recapitulation of views already put forward by the author in his book ("Researches on the Affinities of the Elements," 1905), in which he claims priority for expression of the view that from its position in the periodic system nitrogen must be an element possessing strong affinities, and also for clearly indicating on what elements these affinities would be most strongly exerted. Solid curves are given showing how the affinities of the successive elements vary, passing from lithium through boron, etc., on to fluorine. W. G.

Chemical Reactions at Very Low Pressures. II. The Chemical Removal of Nitrogen in a Tungsten Lamp. Irving Langmuir (*J. Amer. Chem. Soc.*, 1913, **35**, 931—943. Compare this vol., ii, 209).—When a tungsten lamp containing nitrogen at low pressures is run for some time, the nitrogen gradually disappears. Investigation has shown that the disappearance is brought about in three ways, namely: (1) Chemically.—The nitrogen combines with the tungsten vapour to form the brown nitride, WN_2. (2) Electrochemically.—When an electric discharge passes through nitrogen and a hot tungsten cathode is used, the nitride WN_2 is formed at the cathode. (3) Electrically.—At very low pressures and high voltages there seems to be a reversible removal of limited quantities of nitrogen, in which the nitrogen is driven on to the glass in such a form that it can be recovered by heating.

In the present paper the chemical removal is alone considered in detail. From zero pressure up to about 0·001 mm. the rate of removal of the nitrogen is proportional to the product of the rate of evaporation and the pressure of nitrogen. From about 0·003 mm. up to about 1 mm. the rate is directly proportional to the rate of evaporation, and independent of the pressure; above pressures of 2 mm. there is still direct proportionality between the rate of removal and the rate of evaporation, but the latter is materially reduced by the presence of the gas.

The nitride, WN_2, in thin layers is a clear, brown colour, very different in appearance from finely divided tungsten. It is stable in a vacuum at 400°, but is decomposed at 2400° (abs.). It is decomposed by water, giving ammonia and probably the oxide WO_3.

The electrochemical removal takes place at much lower temperatures [1900° (abs.)] than the chemical, when potentials much over 40 volts are used in such a way that a perceptible discharge takes place through the gas. The electrical removal occurs at pressures of 0·005 mm. and less, with 250 volts voltage and high filament temperatures; part, at least, of the nitrogen is easily recovered by heating the bulb.

Nitrogen does not, at any temperature, react perceptibly with solid tungsten. The behaviour of nitrogen towards solid tungsten and tungsten vapour is similar to that of oxygen towards platinum and platinum vapour.

The mechanism of the chemical removal is discussed, the discussion being based on the vapour tension of tungsten and the kinetic theory of gases. The equations developed give the vapour pressure of tungsten as 0·080 mm. at the melting point, 3540° (abs.); the boiling point is about 5000° (abs.). The heat of evaporation of tungsten is very high, namely, $218{,}000 - 1{\cdot}8T$ gram cals. per gram atom.

T. S. P.

Colloidal Boron. ALEXANDER GUTBIER (*Kolloid. Zeitsch.*, 1913, **13**, 137—143. Compare Ageno and Barzetti, A., 1910, ii, 500).—Colloidal solutions of boron have been prepared from boron obtained by the act on of magnesium, potassium, and sodium respectively. on boron trioxide. The products in each case were extracted with hydrogen chloride and then with water until the aqueous filtrate acquired a decided colour. Then the residues were further extracted with 50—100 c.c. of distilled water and filtered; the coloured filtered solutions constituted the boron sols. From the magnesium preparations two sols were obtained: (1) a relatively unstable sol, and (2) a comparatively stable sol. The former sol had a dark brown to reddish-brown colour, and had a petroleum-like fluorescence in reflected light. This substance could be preserved for three to four weeks in a closed vessel, after which it coagulated rapidly. Attempts to concentrate the solution brought about coagulation, and the addition of electrolytes immediately precipitated the colloid. Dilute nitric acid oxidised the colloid immediately to boric acid, and 7·5% hydrogen peroxide in alkaline solution was immediately decomposed, with the formation of boric

acid. Shaking with charcoal or barium sulphate brought about immediate coagulation, and all attempts to purify the solution by dialysis failed. The solution contained 0·06% of boron, and when coagulated the gel so formed was completely insoluble in water. The relatively stable sol is similar to the foregoing, except that it may be preserved for sixty-four days unchanged and allows of purification by dialysis. Two sols were obtained from the product obtained by the action of potassium; these corresponded in all particulars with the foregoing sols, except that they were somewhat darker in colour. Three sols were obtained from the product of the action of sodium; these differ from the foregoing in their colour, which is deep blue. Two of these are unstable, but a third is stable, and may be dialysed; it coagulates to a deep blue, slimy gel, which is readily soluble in distilled water. J. F. S.

The Hydrothermal Formation of Silicates. A Review. GEORGE W. MOREY and PAUL NIGGLI (*J. Amer. Chem. Soc.*, 1913, **35**, 1086—1130).—In the hydrothermal method of the formation of silicates the components are subjected to the action of water, at temperatures generally near, although often considerably above, the critical temperature of water, in closed bombs, and therefore under the corresponding high pressures developed by such solutions. The authors give a review of all the work which has hitherto been done in connexion with hydrothermal reactions, and append a complete bibliography of the subject. T. S. P.

Reactions Between Sodium Silicate and Ferric Chloride Solutions. RAPHAEL E. LIESEGANG (*J. pr. Chem.*, 1913, [ii], **88**, 358—360. Compare A., 1912, ii, 166).—Under certain conditions the reaction between sodium silicate and ferric chloride may give rise to silicic acid and ferric hydroxide only, no ferric silicate being produced.

When an aqueous solution of sodium silicate (40° Bé.) is covered with a 20% ferric chloride solution in a beaker, the latter solution gradually works its way in a thin layer down the sides of the vessel, and finally completely encloses the silicate solution. Between the two solutions a thin, wrinkled skin is formed, which consists of silicic acid, and is irregularly streaked with ferric hydroxide, enclosed in small folds of the silicic acid membrane.

It is possible that the results obtained by Jordis and others (A., 1908, ii, 291; 1910, ii, 416) may be due to the reaction proceeding to some extent in this direction. F. B.

Technical Preparation of Baryta. IV. Preparation of Baryta by Electrolysis of Aqueous Solutions of Barium Sulphide. LUIGI MARINO and U. GIGLI (*Gazzetta*, 1913, **43**, ii, 1—25. Compare Marino, this vol., ii, 592; Marino and Danesi, this vol., ii, 593).—The authors describe a considerable number of experiments undertaken to discover the effect of various alterations in the experimental conditions on this process, which was suggested by Brochet and Ranson (A., 1903, ii, 478). In the work here

recorded, a diaphragm of high resistance is employed in all cases. In certain conditions the yield of barium hydroxide is almost theoretical. The nature of the electrodes is of importance, the best results being obtained with copper. The solution should contain about 20% of barium sulphide, and the electrolysis should be continued for about two-thirds of the time theoretically required for decomposition of the sulphide, using a current density at the anode of 1—3 amperes per sq. dcm. In this case the yields are good, and oxidation products do not amount to more than 4—5%. The barium hydroxide at the anode increases as long as the concentration of the sulphide does not fall below 5%. The quantity of barium hydroxide which can be produced by hydrolysis of the sulphide in concentrated solutions at 70—80° amounts after twenty hours to about 13 grams per litre. The formation of barium hydroxide at the anode in electrolysis is not due to physical phenomena, but to interaction of hydroxyl ions and barium sulphide.

R. V. S.

Action of Various Waters on Lead. HARRI HEAP (*J. Soc. Chem. Ind.*, 1913, **32**, 771—775, 811—815, 847—856).—A historical and critical survey of the work already done is first given. In the author's experiments two methods were used: (1) Coils of lead pipes, 10 yards in length, were completely filled with the water under examination, and stoppered so that air was excluded. (2) Pieces of bright lead foil (99·7% Pb) were immersed in water contained in glass cylinders, which were stoppered in such a way that no air remained in the cylinder. Most of the experiments were carried out in a cellar, the temperature of which was fairly constant.

Pure distilled water, free from dissolved gases, exerts but a very slight action on lead; the amount of lead dissolved is so small as to be only just recognisable by the method used (hydrogen sulphide test in Nessler cylinders). Hydrogen, carbon dioxide, oxygen, and air, when dissolved in water, play a part in causing the lead to dissolve, the most potent being oxygen. In the presence of both oxygen and carbon dioxide a reaction takes place which is comparable with that of many natural waters; the lead passes into solution as the hydroxide, and is then precipitated as basic carbonate by the carbon dioxide; the lead has the appearance known as "eroded lead."

Distilled water made slightly acid and then allowed to act on lead produces a liquid which gives no precipitate with carbon dioxide.

Ordinary distilled water behaves very similarly to the distilled water mentioned above, the amount of lead taken into solution being only slightly increased. Distilled waters containing dissolved atmospheric gases attack lead with increased activity as the temperature rises from 5° to 50—60°; at higher temperatures the action diminishes, being the same at 100° as at 5°.

Calcium and sodium phosphates, present in solution, prevent any lead dissolving; ranking next to the phosphates, as regards this

preventive action, are the carbonates and hydrogen carbonates of the alkali and alkaline earth metals. Nitrates attack lead very vigorously, and sulphates, chlorides, and acetates only slightly, with certain exceptions. Ammonium nitrate has a very marked action, ammonium chloride a much less, and ammonium sulphate still less. Aluminium sulphate, and especially calcium hydroxide, dissolve quite large amounts of lead.

The purer natural waters, for example, rain water, exert actions which are comparable with those of ordinary distilled water; lake waters have a much weaker action than distilled water, and differ from the latter in that the amount of lead passing into solution increases continuously with rise in temperature up to the boiling point. The addition of various substances to lake water modifies its action on lead in a manner very similar to that observed with distilled water.

In seeking an explanation of the action of peaty waters on lead, various types of water were subjected to the action of fresh peat. Both distilled water and rain water exerted less action on lead after such treatment than before, although in some cases they showed increased acidity. Soft upland lake water and a hard spring water were rendered more active by such treatment. Certain hard waters, however, especially those in which the hardness is permanent, are not rendered more active by treatment with peat.

T. S. P.

The Cupric Hydroxides and the Heat of Formation of Copper Nitrate; Comparison with Uranyl Nitrate. ROBERT DE FORCRAND (*Compt. rend.*, 1913, **157**, 441—444).—A study of the various hydrates of cupric oxide. Peligot's blue hydrate, CuO,H_2O, is stable up to 80° for several hours. At 85° it rapidly changes colour to green without loss in weight, but dehydration then commences, and continues progressively; this may be followed by the changes in colour. The author has determined the heat of solution of the various hydrates formed, in the equivalent quantity of dilute nitric acid, and from his results finds that the isomeric change from the blue to the green hydrate is exothermic, and corresponds with 0·261 Cal. From his results, using the figures obtained by Guntz and Martin (A., 1909, ii, 1019) for the heat of solution of anhydrous copper nitrate, the author obtains the value 71·49 Cal. for the heat of formation of this anhydrous salt from its elements and 81·96 Cal. in the dissolved state. These figures are in close accord with the values for uranyl nitrate, starting from uranium dioxide.

W. G.

Preparation and Properties of a Basic Copper Sulphate, $CuSO_4,CuO$. MARIUS EMMANUEL POZZI-ESCOT (*Bull. Soc. chim.*, 1913, [iv], **13**, 816—817).—*Basic copper sulphate*, $CuSO_4,CuO$, is obtained as a heavy, crystalline, greenish-white precipitate when potassium hydrogen sulphite is added to a hot saturated solution of copper sulphate in commercial formaldehyde which is in contact with a quantity of finely powdered crystals of copper sulphate.

The substance does not possess reducing power. On exposure to moist air, it readily absorbs a molecule of water, forming the green, crystalline compound, $CuSO_4,Cu(OH)_2$. It is insoluble in water, readily soluble in dilute acids. Hot water slowly decomposes it into oxide and sulphate of copper. When heated in a glass tube it becomes yellow, and subsequently melts to a clear, red liquid; it can be maintained at this temperature for a long time without undergoing decomposition. H. W.

The Critical Temperature of Mercury. ALAN W. C. MENZIES (*J. Amer. Chem. Soc.*, 1913, **35**, 1065—1067).—Transparent quartz glass tubes, 7 cm. long and 0·2 mm. in bore, were charged with mercury and then sealed after exhausting to 0·03 mm. pressure. On heating in a muffle, the temperature of which could be kept remarkably uniform, it was observed that the liquid phase disappeared at 1275°. This was not due, however, to the critical temperature being attained, but to the blowing out of the quartz tube, with consequent enlargement of its volume; in no case was the quartz tube ruptured.

Königsberger (A., 1912, ii, 1134) has stated that the critical temperature is in the neighbourhood of 1270°, but in view of the above experiments the author doubts that the critical temperature was ever attained by Königsberger. Theoretical calculations, for example, one based on the relation between the densities of a liquid at different temperatures, as put forward by Thorpe and Rücker (T., 1884, **45**, 135), lead the author to the conclusion that the critical temperature for mercury lies above 2600°. T. S. P.

The Products of the Incomplete Reduction of Ceric Oxide. A. DAMIENS (*Compt. rend.*, 1913, **157**, 335—338).—The author considers that the oxycarbide of cerium described by Sterba (A., 1902, ii, 399) is not formed by the incomplete reduction of ceric oxide with carbon, but that the reduction takes place in three stages:

$$2CeO_2 + C = Ce_2O_3 + CO,$$
$$Ce_2O_3 + 9C = 2CeC_3 + 3CO,$$
$$CeC_3 = CeC_2 + C.$$

The carbide, CeC_3, is isolated in the form of red crystals, very slowly attacked by water, and yielding acetylenic hydrocarbons under the influence of water. W. G.

Ultramarine. L. WUNDER (*Chem. Zeit.*, 1913, **37**, 1017—1018). A re-statement, for the most part, of results already published (compare this vol., ii, 54). The reduction of ultramarine to a leuco-compound by the action of yellow phosphorus in the presence of carbon tetrachloride is not a direct action of the phosphorus, since a solution of phosphorus in carbon disulphide does not act in the same way. The phosphorus takes chlorine from the carbon tetrachloride, which is at the same time oxidised by the ultramarine to carbonyl chloride: $CCl_4 + O = COCl_2 + Cl_2$. Sulphur chloride acts in a similar way, gases rich in sulphur dioxide being formed.

Blue ultramarine, when heated with phosphorus trichloride in an autoclave, gives a red product, which becomes blue on heating in the air.

The author does not agree with the view that the blue colour of ultramarine is due to sulphur being present in solid (colloidal) solution (compare *loc. cit.*). T. S. P.

Preparation of Anhydrous Manganese Iodide. F. DUCELLIEZ (*Bull. Soc. chim.*, 1913, [iv], **13**, 815—816).—Anhydrous manganese iodide can be readily obtained by the addition of iodine to finely divided manganese covered with anhydrous ether. A vigorous reaction occurs, which is rendered complete by gentle warming on the water-bath. Excess of iodine and iodide of iron may be removed by washing the product with ether, whilst, if an excess of manganese is employed, it can be separated from the precipitated iodide by washing away the latter in a stream of ether.

When prepared in this manner, manganese iodide is a white substance, which soon becomes discoloured. It is completely soluble in water, and combines energetically with gaseous ammonia.

H. W.

Solubility of Sodium Dichromate in Alcohol. B. REINITZER (*Zeitsch. angew. Chem.*, 1913, **26**, 456).—Sodium dichromate is soluble in alcohol to the extent of 5·13 grams of hydrated salt per 100 c.c. of solution at 19·4°; the solution decomposes very rapidly, with the production of acetaldehyde. Ammonium and magnesium dichromates are also soluble in alcohol. W. H. G.

The Action of Sodium Paratungstate in Fusion on Salts of the Halogen Acids and Oxy-halogen Acids. SIMON BOGHOS KUZIRIAN (*Amer. J. Sci.*, 1913, [iv], **36**, 301—304. Compare Gooch and Kuzirian, A., 1911, ii, 657).—In the case of fluorides, chlorides, and bromides, fusion with sodium paratungstate does not lead to complete expulsion of the halogen, since the simple elimination of that element will not leave an oxide to combine with the acidic oxide of the flux. Any expulsion of halogen taking place is due to atmospheric oxygen entering into reaction. Owing to the higher susceptibility of iodides to atmospheric action, fusion with the tungstate gives a quantitative expulsion of iodine. Iodates also give a quantitative loss of iodine (and oxygen), whereas chlorates and bromates are only partly decomposed. T. S. P.

Haloid Bases of Columbium. HERBERT S. HARNED (*J. Amer. Chem. Soc.*, 1913, **35**, 1078—1086).—By the reduction of columbium pentachloride with sodium amalgam, using the method and apparatus described by Chapin in the investigation of the haloid bases of tantalum (A., 1910, ii, 303), a *chlorocolumbium chloride*,

$$(Cb_6Cl_{12})Cl_2,7H_2O,$$

is obtained, which is analogous to chlorotantalum chloride (*loc. cit.*). It forms black, shining crystals, which give an olive-green powder, insoluble in cold water, but soluble in hot water

to an olive-green solution. As in chlorotantalum chloride, only two of the chlorines are ionic. When treated with the equivalent quantity of sodium hydroxide, *chlorocolumbium hydroxide*, $(Cb_6Cl_{12})(OH)_2,8H_2O$, is formed as a black, microcrystalline precipitate, and from this the *bromide*, $(Cb_6Cl_{12})Br_2,7H_2O$, is readily obtained. The hydroxide is soluble in excess of sodium hydroxide, and from the solution excess of concentrated hydrochloric acid precipitates a brown powder, which has a composition corresponding with the formula $Cb_6Cl_{14},9H_2O$. Evidence, which is not yet complete, was obtained that this chloride is probably different in constitution from the green chloride. T. S. P.

The Absorption of Active Hydrogen by Platinum. A. E. FREEMAN (*J. Amer. Chem. Soc.*, 1913, **35**, 927—931).—During the course of some experiments in which the pressure in a tungsten incandescent lamp was measured by means of a Hale-Pirani manometer (A., 1912, ii, 230) attached to it, it was found that after the lamp had been lit for some time the manometer readings gave what was apparently a negative pressure. Investigation of the various sources of error which would cause such an abnormality has led the author to give the following explanation: During the burning of the lamp atomic hydrogen is produced by the action of the hot filament on the water-vapour present (compare Langmuir, A., 1912, ii, 1162; this vol., ii, 209); this hydrogen alloys with the platinum of the manometer, increasing its resistance, and thereby causing an error in the calculated pressures. T. S. P.

Removal of Spots on Platinum Utensils Used in Leather Analysis. CRISTO D. MANZOFF (*Ann. Chim. anal.*, 1913, **18**, 316—317).—A mixture is made of 1 gram of sodium carbonate and 0·5 gram of borax, and placed on the spot to be cleaned. The whole is heated, first over a bunsen burner and then over the blowpipe. The fused mass is then removed with hot water; if necessary, the operation is repeated. L. DE K.

Mineralogical Chemistry.

Fractionation of California Petroleum by Diffusion Through Fuller's Earth. J. ELLIOTT GILPIN and P. SCHNEEBERGER (*Amer. Chem. J.*, 1913, **50**, 59—100. Compare Gilpin and Cram, A., 1909, i, 1; Gilpin and Bransky, A., 1910, ii, 963).—In continuation of this investigation of the effect on petroleum oils of diffusion through Fuller's earth, it is found that with a specimen D^{20} 0·912 no fractionation is effected by filtration at the ordinary temperature; on working at 75°, however, a certain fractionation is observable, the

earth tending to retain the sulphur compounds, whilst the issuing oil is not only freer from sulphur, but lighter than the original oil.

Working with a less dense oil (D 0·8890) at the ordinary temperature, results were obtained again indicating a preferential absorption of the heavier constituents of the oil, and at the same time of nitrogen compounds present in the original oil.

When paraffin oil to which benzene has been added is made to diffuse through a tube of fuller's earth, there occurs selective absorption of the benzene.

The important factor in determining the extent to which certain ingredients of an oil will be removed, is not the duration of contact, but the amount of earth with which the oil comes in contact. Indications are obtained supporting the view that the bitumen in the oil investigated was in the form of a colloid, and that the fuller's earth, in exerting the effect of a dialysing septum, caused coagulation and adsorption of the bituminous material with the sulphur and nitrogen compounds and the benzene hydrocarbons, whilst allowing free passage to the paraffin oil. D. F. T.

Ferriferous Dolomite from the Simplon Tunnel. MARIO DELGROSSO (*Jahrb. Min.*, 1913, ii, *Ref.* 14; from *Riv. Min. Crist. Ital.*, 1912, **41**, 56—64).—The white rhombohedra have a cleavage angle of 73°48′ and D 2·96. They contain a few enclosures of liquid carbon dioxide. The following analysis corresponds with the formula $4CaCO_3,3MgCO_3,(Fe,Mn)CO_3$:

CaO.	MgO.	FeO.	MnO.	CO_2.	Total.
28·78	15·69	9·33	0·26	46·18	100·24

L. J. S.

Some Segregates of Platiniferous Chromite in the Ural Dunites. LOUIS DUPARC and SANTIAGO PIÑA DE RUBIES (*Anal. Fis. Quim.*, 1913, **11**, 367—374).—Analyses of the chromites show proportions of olivine varying from 2·40 to 5·12%. The associated platinum metal has 64·65—81·94% of platinum, together with iron, 8·93—15·16%, osmium, rhodium, iridium, and ruthenium. G. D. L.

"Chillagite," a New Mineral. A. T. ULLMANN (*J. Roy. Soc., New South Wales*, 1912, **46**, 186).—The mineral was found in Christmas Gift North Mine, Chillagoe, associated with cerussite in a gossan formation, some of the crystals being studded with small crystals of pure cerussite. The crystallisation appears to be tetragonal; the form is tabular, and the diaphaneity translucent. The mineral is lamellar and straw- or lemon-yellow, sometimes brown, in colour. Hardness 3·5; D 7·5. It contains PbO, 54·25%; WO_3, 28·22%; MoO_3, 17·52%; and thus has the formula

$$PbOWO_3,PbOMoO_3.$$

H. W.

Solid Solution in Minerals: Composition of Amorphous Minerals as Illustrated by Chrysocolla. HARRY W. FOOTE and WALTER M. BRADLEY (*Amer. J. Sci.*, 1913, [iv], **36**, 180—184. Compare this vol., ii, 717).—The tabulated ratios for previously-

published analyses show a considerable range, and only few of them agree with the usually accepted formula, $CuSiO_3,2H_2O$. New analyses are given of homogeneous material from Arizona (anal. I and II) and Montana (anal. III). The material was selected under the microscope, as it was found that heavy liquids (potassium mercuric iodide solution and acetylene tetrabromide) had some action on the mineral:

	SiO_2.	CuO.	H_2O.	Al_2O_3.	CaO.	Total.	Ratios. SiO_2 : CuO : H_2O.
I.	38·14	36·74	18·73	5·66	0·90	100·17	1·36 : 1·00 : 2·25
II.	38·32	39·98	19·87	0·98	0·78	99·92	1·26 : 1·00 : 2·19
III.	50·45	37·94	11·11	—	—	99·50	1·75 : 1·00 : 1·29

These analyses also lead to no definite formula, and the conclusion is drawn that chrysocolla represents a solid solution of copper oxide, silica, and water. L. J. S.

Mordenite from Tyrol and the Faroe Islands. STANISLAUS J. THUGUTT (*Jahrb. Min.*, 1913, ii, *Ref.* 33; from *C. R. Soc. Sci. Varsovie*, 1912, **5**, 76—79).—Mordenite from the Seiser Alpe, Tyrol, has the form of rose-coloured needles with an oblique extinction of 7—8°; analysis I corresponds with the formula $RAl_2Si_9O_{22},6H_2O$. Fibrous, silky, colourless material from Osterö, Faroe Islands, gave II and III; the difference here is attributed to the presence of enclosed fibrous silica in the material analysed:

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.
I.	66·86	12·13	0·03	3·86	0·17	0·67	2·41	13·87	100·00
II.	78·70	7·22	—	1·99	—	0·30	2·08	9·71	100·00
III.	74·34	8·84	trace	2·18	—	0·43	2·74	12·05	100·58

L. J. S.

Baueritisation. O. DREIBRODT (*Jahrb. Min.*, 1913, ii, *Ref.* 24—26; from *Diss., Leipzig*, 1912, 39—47).—The natural or artificial process of the bleaching of biotite and its alteration to an end-product consisting mainly of hydrated silica ("bauerite") has been called baueritisation by F. Rinne (*Ber. sächs. Ges. Wiss.*, 1911, **63**, 445). Biotite from Brevig, Norway (anal. I, D 3·0417), was digested in water charged with carbon dioxide for five weeks at 30°; it was then found to be slightly altered in colour, and to have the composition given under II. Digested with concentrated hydrochloric acid for six hours at 80—85°, the biotite is completely bleached, and the residue has the composition III, D 2·3484. Bleaching is also effected by dilute sulphuric acid in eight hours at the ordinary temperature; the residue has the composition IV, D 2·3488:

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	MnO.	Na_2O.	K_2O.	H_2O.	Total.
I.	35·05	1·95	16·18	8·34	24·56	3·67	trace	1·00	2·41	5·09	2·36	100·61
II.	39·02	2·23	15·46	10·39	18·74	1·89	—	0·62	1·37	4·50	6·46	100·68
III.	91·85	—	1·01		—	0·45	—	—	—	—	7·34	100·65
IV.	85·10	—	1·06		—	0·36	—	—	—	—	12·99	99·51

The amount of water present in the residual bauerite is variable, depending on the temperature and on the method of drying.

L. J. S.

Pyroxmangite, a New Member of the Pyroxene Group, and its alteration Product, Skemmatite. WILLIAM E. FORD and WALTER M. BRADLEY (*Amer. J. Sci.*, 1913, [iv], **36**, 169—174).—These minerals were found four-and-a-half miles east of Iva, Anderson Co., South Carolina. Pyroxmangite occurs as brown cleavage masses with a cleavage angle of 91°50′, hardness 5½—6, and D 3·80; the optical characters suggest triclinic symmetry. In composition (anal. I, agreeing with $R''SiO_3$) the mineral differs from the manganese pyroxenes, schefferite and rhodonite; and it is regarded as a new triclinic member of the pyroxene group:

	SiO_2.	MnO.	O.	FeO.	Fe_2O_3.	Al_2O_3.	CaO.	H_2O.	Total.
I.	47·14	20·63	—	28·34	—	2·38	1·88	0·33	100·70
II.	—	31·84	6·53	—	43·95	1·96	—	15·56	99·84

A black alteration product of the pyroxmangite has a metallic lustre and a dark chocolate-brown streak; hardness, 5½—6. It is soluble in hydrochloric acid, and analysis II corresponds with the formula $3MnO_2,2Fe_2O_3,6H_2O$. This appears to differ from previously-described oxides of manganese and iron, and it is provisionally named skemmatite.

L. J. S.

Two Vanadiferous Ægirites from Libby, Montana. ESPER S. LARSEN and W. F. HUNT (*Amer. J. Sci.*, 1913, [iv], **36**, 289—296).—The two pyroxenes described were collected in the Rainy Creek mining district, about seven miles N.E. of Libby, Lincoln County, Montana. The one (*A*) is an ægirite, and the other (*B*) an ægirite-augite, and they occur in veins associated with quartz, calcite, microcline, sulphides, and other minerals. The ægirite contains nearly 4% of V_2O_3, but otherwise its chemical composition is that of ordinary ægirite, with which also its crystal measurements are in close agreement. It is deep brown in colour, and its optical properties differ from ordinary ægirite in the lower index of refraction, weaker birefringence, smaller extinction angle and larger axial angle. The ægirite-augite was found only in fibrous aggregates; it contains nearly 3% of V_2O_3, and its optical properties are not greatly different from those of ordinary ægirite-augite:

	SiO_2.	TiO_2.	Fe_2O_3.	V_2O_3.	Al_2O_3.	CaO.	MgO.	FeO.
A.	51·91	0·91	21·79	3·98	0·38	5·53	3·08	1·48
B.	53·32	0·38	12·38	2·86	1·40	12·18	7·01	3·70

	MnO.	Na_2O.	K_2O.	Cr_2O_3.	S.	CO_2.	H_2O −.	H_2O +.
A.	0·58	10·46	0·22	—	0·13	trace	0·06	—
B.	0·45	6·26	0·26	trace	—	—	0·07	0·13

T. S. P.

Meteoric Iron from Paulding County, Georgia. THOMAS L. WATSON (*Amer. J. Sci.*, 1913, [iv], **36**, 165—168).—The date of find

and exact locality of this iron are not known. It is mostly rusted away, and only 134 grams of fresh iron now remain. This shows a coarse octahedrite structure. Analyses by W. M. Thornton, jun., of (I) the fresh iron, and (II) of the oxidised portion. In the latter the chlorine is unusually high; another determination gave: Cl, 1·99; H_2O at 110°, 3·34%:

	Fe.	Ni.	Co.	Cu.	P.	Cl.	S.	Si.	C.	Total.	Sp. gr.
I.	93·26	6·34	0·50	trace	0·23	0·01	nil	nil	—	100·34	7·886

	Fe_2O_3.	FeO.	NiO.	CoO.	CuO.	SiO_2.	P_2O_5.	Cl.	H_2O at 110°.	H_2O over 110°.	Total.
II.	36·12	41·26	6·57	0·48	trace	0·26	0·48	2·21	2·77	9·23	99·38

L. J. S.

Analysis of the Gases Spontaneously Evolved from the Spring of Alange. FAUSTINO DÍAZ DE RADA (*Anal. Fis. Quim.*, 1913, **11**, 364—367).—The gas contains carbon dioxide, 8·09; oxygen, 6·59; nitrogen and rare gases, 85·32%. The rare gases in two determinations amounted to 1·102 and 1·89% respectively, and consisted of 1·51% of helium and neon and 98·49% of argon, with traces of krypton and xenon. G. D. L.

A Gas Efflux Rich in Helium. E. CZAKÓ and L. LAUTENSCHLÄGER (*Chem. Zeit.*, 1913, **37**, 936).—The gas issuing from the thermal springs of Wildbad (württemberg. Schwarzwald) is found to contain 2·79% CO_2, 94·94% N, 1·56% A, and 0·71% He, that is, 2·27% of the rare gases. This result agrees with the previous measurements of Kayser in 1895. T. S. P.

Manganese in Drinking and Mineral Waters. F. JADIN and A. ASTRUC (*Compt. rend.*, 1913, **157**, 338—339).—The authors have determined the amounts of manganese present in a number of samples of drinking and mineral waters from different sources. The majority of the drinking waters show no sign of manganese, whilst the mineral waters from Vichy and Boulou contain it in amounts varying from 0·09 to 0·20 mg. per litre. W. G.

Analytical Chemistry.

Criticism of a Recent Contribution to the Theory of Indicators. ARTHUR G. A. MILLER (*Chem. News*, 1913, **108**, 73—74).—A criticism of views put forward by Waddell (this vol., ii, 522) explanatory of the behaviour of methyl-orange towards weak acids and phenolphthalein towards weak bases. In his arguments the author supports the present views on the behaviour of indicators

(compare Tizard, A., 1912, ii, 598). He has shown that dry hydrogen chloride passed into a solution of methyl-orange in absolute alcohol immediately turns it red, thus refuting another of Waddell's statements. W. G.

Improvement in Gravimetric Analysis. Ignition of Precipitates. GEORGES RAY (*Ann. Chim. anal.*, 1913, **18**, 306—309).—Cylindrical tubes with round bottom and furnished with a small spout, made of fused quartz, and holding 45—85 c.c. are recommended for precipitation, washing, ignition, and weighing in analytical work. The tubes and contents are centrifugalised for a few minutes in a suitable machine at the rate of 2000—2500 revolutions per minute. In order to assist the drying of the precipitate, this may be centrifugalised finally with a little absolute alcohol. L. DE K.

Convenient Device for Analytical Ignitions. EDWARD D. CAMPBELL (*J. Ind. Eng. Chem.*, 1913, **5**, 675—677).—A piece of apparatus which serves as a support for crucibles is described. It consists of a fire-clay cylinder, 7·5 cm. internal diameter and 10 cm. high; slits are provided in the upper end, so that the triangle carrying the crucible may be arranged at about one-half the height of the cylinder. The cylinder is wrapped round with asbestos sheeting, and its lower end is secured to an asbestos board, the centre of which is pierced with a hole of such diameter as will admit the tube of a Mèker burner. The apparatus is particularly suitable for the conversion of calcium carbonate into calcium oxide, etc. W. P. S.

The Use of Benzoic Acid as a Standard Material. E. R. WEAVER (*J. Amer. Chem. Soc.*, 1913, **35**, 1309—1311).—Benzoic acid absorbs traces of moisture on exposure to the air. Before the pure substance is used as an acidimetric standard (compare Morey, A., 1912, ii, 986) it should be fused at a temperature not higher than 130°. If fusion takes place at 150—160°, small quantities of a brown, resinous substance are formed; this impurity is also formed at lower temperatures, even at temperatures below the melting point, if the benzoic acid is subjected to prolonged heating. The fused product should be quite colourless.

The test for traces of moisture in benzoic acid was made by dissolving the latter in anhydrous ethyl acetate, shaking the solution with calcium carbide, and then decanting it into an ammoniacal solution of cuprous chloride. The formation of a precipitate of copper acetylide indicated the presence of moisture in the benzoic acid; the delicacy of the test was such that 0·07% of moisture could be detected. T. S. P.

Determination of Hydrogen, Nitrogen, and Methane in Gas by Combustion in a Quartz Tube. MATHERS and IRA E. LEE (*Chem. News*, 1913, **108**, 80—82).—A description of a new form of combustion apparatus for the estimation of mixtures of hydrogen,

nitrogen, and methane. The authors replace the standard combustion pipette by a narrow quartz tube, filled with scrap platinum, and heated by a flat-flame bunsen burner. The gas residues mixed with oxygen are passed through this tube at a suitable rate, and the issuing gases are collected in a gas burette and their volumes measured. Care must be taken to make due corrections for all temperature changes, and also for the carbon dioxide which remains in the quartz tube after the combustion.

W. G.

A Macro- and Micro-chemical Method for Estimation of Chlorine in the Blood. H. ROGÉE and C. FRITSCH (*Biochem. Zeitsch.*, 1913, **54**, 53—58).—The proteins are precipitated from the blood by the method of Michaelis and Rona, namely, the diluted blood is mixed with a colloidal iron preparation and magnesium sulphate is then added, the iron precipitate carrying down all the proteins. In the filtrate the chlorine is estimated by titration with silver nitrate in the presence of potassium chromate. The dialysed iron preparation contains a little chlorine; hence a blank analysis must be made. The microchemical method can be carried out with 1 c.c. of blood, and correspondingly small amounts of reagents. In this case $N/25$-silver nitrate is used for titration.

S. B. S.

An Electrochemical Indicator for Oxidising Agents. ERIC K. RIDEAL and ULICK R. EVANS (*Analyst*, 1913, **38**, 353—363).—The apparatus, which is intended more in particular for the detection of free chlorine or hypochlorites in treated effluents, consists of a copper tube 3·5 cm. long and 4 mm. internal diameter. Within this, running axially through it, is a platinum rod 1 mm. in diameter, which is insulated at the two ends from the copper tube by ebonite caps. Liquid is allowed to enter the tubes at the lower end at the rate of 230 c.c. per minute (temp. 13°) and to flow out at the top. The copper and platinum are joined to the two poles of a sensitive current-detector of high resistance; the instrument used by the authors had a resistance of 200 ohms, and registered 0·000004 ampere per degree. No visible deflexion of the pointer over the dial is noticed unless the meter contains free chlorine or hypochlorite, even in cases when these cannot be any more detected by the chemical methods, such as the potassium iodide–starch test.

L. DE K.

The Use of Sodium Paratungstate and the Blowpipe Flame in the Estimation of the Acid Radicles of Chlorides, Chlorates, Perchlorates, Bromides, Bromates, and Fluorides. SIMON BOGHOS KUZIRIAN (*Amer. J. Sci.*, 1913, [iv], **36**, 305—312).—The author has shown (compare this vol., ii, 685) that the action of fused sodium paratungstate on fluorides, chlorides, bromides, chlorates, and bromates under ordinary atmospheric conditions leads to only partial expulsion of the halogens. He has now found that if the fusion takes place in the presence of superheated steam,

a quantitative reaction takes place, which, in the case of chlorides, for example, may be expressed by the equation:

$$5Na_2O,12WO_3 + 14NaCl + 7H_2O = 12Na_2WO_4 + 14HCl.$$

In the case of the oxy-acids, oxygen is also expelled. The method of using the superheated steam is to apply the blowpipe flame, which contains steam as a product of reaction, directly to the surface of the fused mass. The time necessary for the reaction to become complete is comparatively short, being only five to eight minutes, when 0·2—0·3 gram of the halogen compound is used.

The sodium paratungstate, of which 3 grams are used, is easily prepared by fusing sodium tungstate with an equal weight of tungsten trioxide; it is readily fusible, not volatile under the conditions of experiment, and can easily be kept dry in a desiccator containing sulphuric acid. T. S. P.

Reaction of the Iodine Ion. RICCARDO CIUSA and ALFREDO TERNI (*Gazzetta*, 1913, **43**, ii, 86—90).—The production of oxydimercurammonium iodide, which is the basis of Nessler's reaction, can also be used for the detection of iodine. A solution containing 10 grams of mercuric nitrate, 50 c.c. of water, 5 c.c. of nitric acid, and 60 c.c. of concentrated ammonium hydroxide forms the most sensitive reagent for the iodine ion, giving a coloration with potassium iodide at concentrations less than 1×10^{-6}. Chlorides give a white precipitate (of the double salt of the type $Hg_2NCl,3NH_4Cl$), which does not interfere with the detection of iodides. Bromides give a white precipitate (probably of analogous composition), which changes spontaneously into the bright yellow substance, Hg_2NBr. The behaviour of a solution containing bromides and iodides towards the reagent depends on their relative amounts, but after boiling it is possible in most cases to recognise the orange-red coloration due to the iodide. R. V. S.

Estimation of Total Sulphur in Antimonium Sulphuratum. FRANK HARRIS ALCOCK (*Pharm. J.*, 1913, **91**, 213).—The addition of sodium potassium tartrate in the oxidation of antimonium sulphuratum keeps the antimony in solution, and a clear liquid is obtained in which the resulting sulphuric acid may be estimated in the usual manner. When the oxidation is completed, the nitric acid may be expelled by evaporation with hydrochloric acid before the sulphuric acid is precipitated as barium sulphate, and it is advisable to add a small amount of potassium nitrate at the commencement of the oxidation in order to fix the sulphuric acid as it is formed.

W. P. S.

Estimation of Small Quantities of Hydrogen Sulphide in Waters. LUDWIG WILHELM WINKLER (*Zeitsch. anal. Chem.*, 1913, **52**, 641—645).—The testing is preferably done at the source of supply. The water is allowed to flow through a 100 c.c. flask until the first portions, which have been affected by contact with the air, have been completely expelled. At the bottom of the flask, now quite filled, is introduced by means of a long-stem pipette 5 c.c. of

the lead reagent. In a 200 c.c. beaker are now put 100 c.c. of pure water and 5 c.c. of the lead reagent; the darkened contents of the flask are transferred to a similar beaker, and to the colourless mixture is then added drop by drop from a burette a solution of sodium sulphide until the required colour is obtained. The calculation will be readily understood.

The lead reagent is prepared by dissolving 10 grams of Rochelle salt, 10 grams of ammonium chloride, and 0·1 gram of lead acetate in 5% ammonia up to 100 c.c. The sodium sulphide solution is prepared by dissolving an accurate weight (about 0·1 gram) of the pure crystallised salt in 100 c.c. of a strong solution of sodium nitrate containing a few drops of ammonia just before use.

The presence of iron does not interfere with the test provided some Rochelle salt is first added to the sample. Coloured waters cause trouble. L. DE K.

Estimation of Thiosulphates in the Presence of Sulphites. A. A. BESSON (*Chem. Zeit.*, 1913, **37**, 926).—In one portion of the amount of solution the sulphite and hydrogen sulphite is estimated according to Bosshard and Grob's method (this vol., ii, 428). To another portion of the solution are added 25 c.c. of $N/10$-alkali, 20 c.c. of hydrogen peroxide solution (5 c.c. of Merck's "perhydrol" diluted to 100 c.c.), after which it is heated for ten minutes on the water-bath, and then, after cooling, the excess of alkali determined by titration with standard acid, using methyl-orange as indicator (compare A., 1907, ii, 811). Only the hydrogen sulphite and the thiosulphate require alkali during the oxidation, as shown by the equations: $NaHSO_3 + NaOH + H_2O_2 = Na_2SO_4 + 2H_2O$; $Na_2S_2O_3 + 2NaOH + 4H_2O_2 = 2Na_2SO_4 + 5H_2O$. The amount of alkali used up by the hydrogen sulphite is known, and consequently the amount of thiosulphate present is readily calculated. T. S. P.

Determination of Ammonia and Nitrogen. A. J. VAN EYNDHOVEN (*Zeitsch. angew. Chem.*, 1913, **26**, 472. Compare Knublauch, this vol., ii, 789).—The forms of apparatus usually described for use in the determination of ammonia in gas-works products are needlessly complicated. Perfectly accurate results are obtained by distilling the ammonia from a flesk fitted with a stopper through which passes a thistle funnel and a glass tube, bent twice at right angles, and dipping into standard acid. W. H. G.

The Diphenylamine Reaction for Nitric Acid. D. J. DE JONG (*Pharm. Weekblad*, 1913, **50**, 992—993).—A criticism of the method of Tillmans and Sutthoff (A., 1911, ii, 767) for the detection of nitric acid. The author finds that the more concentrated the diphenylamine solution is, the less sensitive is the reagent.

A. J. W.

A Rapid Method for the Estimation of Phosphorus in Steel. HARIPADA BHATTACHARYYA (*J. Soc. Chem. Ind.*, 1913, **32**, 738—739).—The yellow ammonium phosphomolybdate precipitate obtained

from steel in the usual manner is washed with 1% nitric acid until free from iron, and the nitric acid then eliminated by washing with a 1% solution of potassium nitrate. The filter and precipitate are transferred bodily to a 200 c.c. flask, 20 c.c. of $N/10$-sodium hydroxide solution and 2 drops of phenolphthalein are added, and the excess of alkali titrated with $N/10$-hydrochloric acid. The reaction taking place is expressed by the equation: $(NH_4)_3PO_4,12MoO_3 + 24NaOH = (NH_4)_3PO_4 + 12Na_2MoO_4 + 12H_2O$. The results are accurate. T. S. P.

Mocagno's Method for the Volumetric Estimation of Phosphorus in Steel. HENRYK WDOWISZEWSKI (*Chem. Zeit.*, 1913, **37**, 1069—1071).—A modification of the original method. Two grams of steel turnings are placed in a 300 c.c. flask and dissolved in 30 c.c. of nitric acid (D 1·2) at the boiling temperature, when 5 c.c. of permanganate solution (40 grams per litre) are added. After boiling until a separation of manganese peroxide takes place, this is redissolved by adding 1 c.c. of a saturated solution of ammonium oxalate. When cold, 5 c.c. of concentrated ammonia are added, when a dark brown jelly is formed; 25 c.c. of nitric acid are now added, and the liquid is heated almost to boiling until the iron precipitate has redissolved. Fifty c.c. of the usual molybdate solution are added, and after thorough shaking for five minutes the flask is kept for ten minutes in a warm place. The yellow precipitate is then collected and washed first with dilute (1%) nitric acid and then three times with cold water to remove the free acid. The funnel is replaced in the flask, and the contents dissolved by means of a 4% ammonium solution. The filter is washed with hot water until the filtrate amounts to about 30 c.c. To the solution are then added 80—100 c.c. of dilute sulphuric acid (1:4), 10 grams of pure zinc are introduced, and the whole heated on a sand-bath for forty-five to fifty minutes short of boiling, although the reduction is generally complete within thirty-five minutes. The reduced, green, and quite clear solution is now poured into a known volume (10—15 c.c.) of standard permanganate, the flask and zinc are washed with hot dilute sulphuric acid (1:10), and the excess of permanganate is titrated with oxalic acid (1 c.c. = 1 c.c. permanganate). In the author's experiments the strength of the permanganate was such that 1 c.c. represented 0·00818% of phosphorus. L. DE K.

Estimation of Phosphorus in Steels Containing Vanadium. JOHN R. CAIN and F. H. TUCKER (*J. Ind. Eng. Chem.*, 1913, **5**, 647—650).—Phosphoric acid may be precipitated as phosphomolybdate in the presence of vanadium salts, provided that the vanadium is reduced previously to the quadrivalent state. This reduction is best attained by the action of ferrous sulphate and sulphur dioxide, and, if care is taken to prevent the temperature rising above 15° during the precipitation of the phosphomolybdate in the presence of nitric acid, the excess of ferrous sulphate is not oxidised by this acid. The details of the method are as follows:

From 1 to 2 grams of the steel are dissolved in 100 c.c. of nitric acid (D 1·135), the solution is oxidised by boiling with a slight excess of permanganate, sulphur dioxide is then added, and, after cooling, 40 c.c. of ammonia (D 0·96) are added. The mixture is now cooled to 15°, 5 c.c. of a saturated ferrous sulphate solution and 3 drops of concentrated sulphurous acid are added, followed by 40 c.c. of molybdate reagent. The whole is stirred or shaken for ten minutes, and the precipitate is then collected, washed, and titrated by the alkalimetric method. Nickel, copper, chromium, molybdenum, or aluminium when present in the steel do not interfere with the method, but tungsten, titanium, arsenic, tin, etc., must be removed. W. P. S.

Estimation of Phosphoric Acid in Basic Slag. Max Popp (*Zeitsch. angew. Chem.*, 1913, **26**, 480).—The author states that the "citrate process" is a compensation method, the precipitation of the phosphoric acid not being complete, but loss is prevented by the co-precipitation of calcium triphosphate. The magnesium mixture may also deposit some magnesium oxide, so that the composition of the precipitate is no longer true ammonium magnesium phosphate.

The Lorenz method when applied to basic slags gives results which are a trifle too low. L. de K.

Estimation of the Phosphoric Acid Soluble in Citric Acid in Basic Slag. Max Popp (*Chem. Zeit.*, 1913, **37**, 1085—1087. Compare this vol., ii, 336).—In order to oxidise the hydrogen sulphide it is found better to employ 1 c.c. of 3% hydrogen peroxide than 10 c.c. of 0·3% solution. It is occasionally necessary to add more than 1 c.c. The hydrogen peroxide is most conveniently measured by means of the burette employed by Gerber for measuring the amyl alcohol in estimating milk fat.

N. H. J. M.

Estimation of the Phosphoric Acid, Soluble in Citric Acid, in Basic Slag by the Citrate Method and by Lorenz's Method. Hugo Neubauer (*Landw. Versuchs-Stat.*, 1913, **82**, 465—475).—Lorenz's method gives correct results, and is not affected by the citric acid. The citrate method gives high results, even when iron citrate is employed, owing chiefly to the precipitation of some mg. of calcium as tricalcium phosphate, which is not compensated for by incomplete precipitation of the phosphoric acid.

The error in the citrate method, due to the lime, is greater in the case of the citrate-soluble phosphoric acid in basic slag than in estimating the water-soluble phosphoric acid in superphosphates.

N. H. J. M.

Quantitative Analysis of Mineral Phosphates and Ashes by the Carbon Tetrachloride Method. Paul Janasch and Robert Leiste (*J. pr. Chem.*, 1913, [ii], **88**, 273—292).—Having shown previously that metallic phosphates are completely decomposed and

the phosphoric acid quantitatively volatilised by heating them with quartz powder in a stream of carbon tetrachloride, the authors have now applied this method of decomposition to the analysis of mineral phosphates. Full details of the analysis of triphyline, vivianite, pyromorphite, and fluorapatite are given. F. B.

A Simple Method for the Determination of Carbon in Organic Materials. EDWIN BRET HART and K. J. WOO (*J. Amer. Chem. Soc.*, 1913, **35**, 1056—1061).—The method depends on the oxidation of the carbon and fixation of the carbon dioxide by the use of sodium peroxide, the oxidation being effected in an ordinary iron, nickel, or, less satisfactorily, porcelain crucible. Six grams of sodium peroxide and 0·1 gram to 2 grams of the substance for analysis are well mixed in the crucible, which is then fitted with a tight lid; the larger limit to the quantity of substance is for ordinary soils, whilst the lower limit is for peat soils and organic substances containing more than 40% of carbon. To prevent the absorption of carbon dioxide from the heating flame, the crucible is enclosed in a larger iron or nickel crucible of 120 c.c. capacity, which is also covered, and as a further precautionary measure is fitted in a hole in a piece of asbestos board. Gentle heating is then applied, and should be continued for three to five minutes after the first vigorous action has subsided. When cool, the contents of the crucible are transferred to a flask by carbon dioxide, free water, and distilled with 25% sulphuric acid, the evolved carbon dioxide being collected in a measured volume of sodium hydroxide solution of known strength (compare Browser, A., 1912, ii, 995; Brubaker, this vol., ii, 433).

The method gives accurate results, and is especially suitable for routine carbon determinations, for example, in soils, but it can also be applied to the analysis of organic substances. D. F. T.

Modified Platinichloride Method for the Estimation of Potassium. W. B. HICKS (*J. Ind. Eng. Chem.*, 1913, **5**, 650—653). —The following method is applicable to the estimation of potassium in the presence of all other salts with the exception of those of ammonium, cæsium, and rubidium; organic compounds must also be absent. The solution containing the potassium is acidified with hydrochloric acid and evaporated with an excess of chloroplatinic acid solution to a syrupy consistence. After cooling, 80% alcohol is added, and the precipitate is collected on a filter and washed with alcohol in the usual way. The precipitate is then dissolved in hot water, the solution is acidified with 1 c.c. of concentrated hydrochloric acid, and a quantity of magnesium ribbon sufficient to effect complete reduction of the platinum is added. The excess of magnesium is dissolved by the addition of hydrochloric acid, and the flocculent platinum is collected, washed, ignited, and weighed. W. P. S.

Estimation of Lithium in Mineral Waters. LUDWIG WILHELM WINKLER (*Zeitsch. anal. Chem.*, 1913, **52**, 628—640).—Mainly on account of hygienic reasons, *iso*butyl alcohol is recommended

instead of amyl alcohol for the separation of lithium chloride from the chlorides of potassium and sodium; 10 c.c. of this solvent dissolves only 0·5 mg. of alkali compounds (weighed as sulphate).

Lithium has a tendency to precipitate when the water is mixed with sodium hydroxide and carbonate. Hence, the water, if its hardness exceeds 100° (German), should be suitably diluted; even then a double precipitation of the calcium, etc., is advisable.

Sulphates are decomposed in the acidified filtrate by cautious addition of barium chloride. In order to concentrate the lithium it is advisable to evaporate the filtrate to a small bulk, and to precipitate most of the alkali chlorides by adding a large excess of alcohol. After removing the last traces of calcium, magnesium, barium, and aluminium by means of a successive treatment with alkali and ammonia, and then again completely expelling the latter by evaporation with a little alkali, the solution is acidified with hydrochloric acid and evaporated to dryness. After heating at 120° the mass is powdered and exhausted with *iso*butyl alcohol, using in all 10 c.c. As, however, a portion of the lithium chloride is retained in the residue, it is necessary to again dissolve this in a little water and a drop of hydrochloric acid; the residue on evaporation is then treated as before; a third treatment may even be advisable. The author prefers weighing the three results separately. Finally, the lithium chloride is converted into sulphate by ignition with about 0·05 gram of ammonium sulphate. Allowance is then made for the traces of alkali sulphates. L. DE K.

Detection of Small Quantities of Silver. G. MALATESTA and ETTORE DI NOLA (*Boll. chim. Farm.*, 1913, **52**, 533—535).—Meneghini's reaction (compare A., 1912, ii, 390) can be employed as a sensitive test for silver. When a solution of a silver salt is treated with a solution of a chromium salt and then rendered alkaline with potassium or sodium hydroxide, a black precipitate (Ag_4O) is produced, and the liquid becomes yellow from formation of chromate. The reaction is more sensitive than precipitation of silver chloride, for 0·000005 gram of silver per c.c. is recognisable. R. V. S.

Volumetric Estimation of Calcium. THEODOR DÖRING (*Zeitsch. angew. Chem.*, 1913, **26**, 478—480).—The time honoured process of titrating calcium by precipitation as oxalate and titrating this, after thorough washing, with standard permanganate in the presence of dilute sulphuric acid at 70°, gives excellent results when the liquid contains at most 0·2 gram of the metal. With larger quantities much manganous sulphate accumulates during the titration, and this has an injurious effect. Moreover, large precipitates require much washing, and calcium oxalate is not absolutely insoluble in pure water.

When applying the "residue method" (titrating the excess of the oxalic acid added) the calcium oxalate which includes ammonium oxalate, should be thoroughly washed with hot water, and the washings added to the main filtrate. This is then made up

to a definite bulk, and an aliquot part of it taken for the titration. This modification, however, renders the process more complicated, so the first method is to be preferred. L. DE K.

Observations and Proposals Regarding the Chemical Testing of Plaster. ALFREDO CAVAZZI (*Gazzetta*, 1913, **43**, ii, 71—86).—The author discusses methods which have been proposed for this purpose, and describes modifications of them. R. V. S.

Colour Reactions of the Alkaline Earths with Tannic and Gallic Acids and Pyrogallol. OMER SCHEWKET (*Biochem. Zeitsch.*, 1913, **54**, 285—290).—A number of colour reactions given by the above-mentioned phenolic substances (called by the author oxygallols) with salts of the alkaline earths in presence of alkalis are described and tabulated. Certain of these are applicable to qualitative analysis. Calcium may be detected in the presence of barium and strontium by the addition of a few crystals of pyrogallol to a 2% solution of the mixture, followed by the addition of a few drops of alkali; an intense violet colour is thereby produced. If the solution containing alkaline earths is diluted with half its volume of alcohol, and a few drops first of 1% gallic acid and then alkali hydroxide solution are added, a pink precipitate and then gradually a blue coloration of the fluid ensue. The former indicates the presence of calcium. After separation of calcium by the ordinary alkaline reactions, strontium can be detected in the presence of barium by the following reaction. The salts are converted into sulphates, and then treated with water, in which strontium sulphate is sufficiently soluble, to yield the colour test. This consists in the addition of a little solid tannin, followed by the addition of a few drops of alkali hydroxide solution. A bright green colour forms in the presence of strontium. S. B. S.

Separation of the Alkaline Earth Metals. J. L. M. VAN DER TORN VAN DEN BOS (*Chem. Weekblad.*, 1913, **10**, 665—666. Compare A., 1911, ii, 228; this vol., ii, 153).—In the author's method the presence of ammonium acetate must be avoided, since it increases the solubility of the strontium chromate. The weighing of the chromates of barium and strontium can be avoided by dissolving them in cold hydrochloric acid, adding potassium iodide, and titrating the liberated iodine with thiosulphate. A. J. W.

Estimation of Small Quantities of Lead Obtained During Extraction with Lead-glazed Pans. P. A. MEERBURG (*Chem. Weekblad*, 1913, **10**, 752—758).—A comparative investigation of the methods for estimating lead described in *Centr. Gezondh. Raad Maandblad.*, 1908, 155, and *Arb. Kais. Ges. Amte*, 1910, **33**, II., 203. The results obtained by the first method were found to be inaccurate. A. J. W.

Estimation of Copper with Sodium Hypophosphite. JOS. HANUŠ (*Zeitsch. anal. Chem.*, 1913, **52**, 616—618).—A criticism of Windisch's paper (this vol., ii, 247). The author has made a sub-

stantial improvement in the estimation of copper by means of hypophosphite. A sensible source of error is caused by the oxidation of the precipitated copper by atmospheric oxygen in presence of free acid. The author now neutralises this acid by means of normal alkali, with phenolphthalein as indicator; no copper is then redissolved, even after a long interval before collecting it.

The process, however, although very convenient, cannot lay claim to great accuracy, and is not suitable when other metals have to be estimated in the filtrate. L. DE K.

Estimation of Copper by means of Hypophosphorous Acid. RICHARD WINDISCH (*Zeitsch. anal. Chem.*, 1913, **52**, 619—628).—The author states that the amount of copper found becomes less when the precipitate is left in contact with the acid liquid for a considerable time before filtering. Filtration without delay is therefore advisable.

The copper obtained proved to be of great purity. L. DE K.

The Use of Tantalum Electrodes for the Electro-analytical Estimation of Copper and Zinc. GUSTAV WEGELIN (*Chem. Zeit.*, 1913, **37**, 989).—In contradistinction to Brunck (A., 1912, ii, 1128), the author finds that tantalum cathodes give unsatisfactory results in the estimation of copper from copper sulphate solutions at 70°, and of zinc from either alkali zincoxide or sodium acetate electrolytes. The results for copper are satisfactory at room temperature. T. S. P.

Analysis of Bauxites. ERNEST MARTIN (*Ann. Chim. anal.*, 1913, **18**, 297—305).—The author objects to the processes based on fusion as these cause an undesirable accumulation of alkali salts in the filtrate. One gram of the mineral is heated in a flask with 15 c.c. of nitro-hydrochloric acid (equal volumes) and 30 c.c. of dilute sulphuric acid (1 : 1 by volume) until dense, white fumes appear and solid sulphates begin to separate. The residue is then dissolved in 50 c.c. of water. The silica is collected, but before weighing it must be purified by fusion with at most 0·5 gram of potassium pyrosulphate; the aqueous solution is then united with the main filtrate, which is now made up to 500 c.c.

In 200 c.c. of this the joint oxides of iron, titanium, and aluminium are precipitated by ammonia; the filtrate contains only calcium. In another portion of the original liquid the iron and titanium are estimated by the usual gravimetric, volumetric, or colorimetric (titanium) processes; alumina is taken by difference. A table is appended, giving the composition of a large number of French bauxites. L. DE K.

Colorimetric Estimation of Small Quantities of Manganese in Water. E. SCHOWALTER (*Zeitsch. Nahr. Genussm.*, 1913, **26**, 104—108).—In the estimation of manganese by converting it into permanganate by means of nitric acid and ammonium persulphate it is necessary to remove previously any chloride which may be present. This may be done by the addition of silver nitrate, but

the turbidity produced interferes with the subsequent colorimetric estimation; at the same time, the hydrochloric acid cannot be expelled by heating the water with sulphuric acid and persulphate. Silver nitrate, however, appears to enter into the reaction taking place when the permanganate is formed, and the author recommends the following procedure: 100 c.c. of the water are treated with 10 c.c. of nitric acid, and evaporated; the dry residue is moistened with 10 c.c. of nitric acid, again evaporated, then dissolved in 5 c.c. of nitric acid and 10 c.c. of water, and filtered. The insoluble residue is washed with water, and the filtrate, measuring about 35 c.c., is heated to boiling after the addition of 5 c.c. of nitric acid and 1 gram of ammonium persulphate. Ten drops of a 5% silver nitrate solution are now added, and the mixture is boiled for ninety seconds after the first appearance of a pink coloration. The solution is then cooled, and the coloration compared with $N/100$-potassium permanganate solution. (NOTE.—If 100 c.c. of $N/100$-potassium permanganate solution be diluted to 110 c.c., each c.c. will correspond with 0·0001 gram of manganese.)

W. P. S.

Analysis of Ferro-titanium. A. R. SCOTT (*Chem. News.* 1913, **108**, 52—53).—The finely-powdered alloy (0·25 gram) is fused with potassium hydrogen sulphate (10 grams) until all grit has disappeared. The residue is cooled and extracted with warm dilute sulphuric acid, and filtered. The residue is again fused, extracted, and filtered, the two filtrates being mixed.

The residue is ignited and weighed, the silica removed with hydrofluoric acid, and the residue again weighed. From this the ferric oxide is extracted with hydrochloric acid and precipitated with ammonia, any remaining residue being titanium oxide.

The original combined filtrates are boiled, made just alkaline with ammonia, and then just acid with hydrochloric acid; the titanium is precipitated by the addition of sodium thiosulphate, and is collected, ignited, and weighed as the oxide. The filtrate is evaporated to small bulk, oxidised with bromine water, any titanium oxide that may have passed through the filter being filtered off, and the iron and aluminium precipitated by ammonia and weighed as the mixed oxides, in which the iron is estimated by solution in hydrochloric acid, reduction with stannic chloride, and titration with potassium dichromate. The manganese is estimated in the filtrate from the mixed hydroxides by precipitation with bromine and ammonia.

W. G.

Detection of Chromium. ALFREDO TERNI (*Gazzetta*, 1913, **43**, ii, 63—65).—When a solution of a chromic salt containing nitric acid is boiled with lead peroxide, oxidation to chromate occurs, and the yellow colour due to this can be recognised even with 0·1 milligram of chromium; or the chromate may be detected with hydrogen peroxide and ether, 0·005 milligram of chromium being then still evident. The test may be used for the examination of the precipitate obtained in the third group of the ordinary analytical scheme.

In this case, if iron is present, the lead chromate may be precipitated by the addition of sodium acetate, or may be detected by means of hydrogen peroxide and ether. When the substance to be analysed contains manganese, permanganic acid is also formed, and masks any yellow coloration; in this case, addition of hydrochloric acid to the warm liquid decomposes the permanganic acid, and any yellow coloration can then be seen.

Chromic salts in acid solution can also be oxidised by means of potassium permanganate, but the reaction in this case is not so sensitive. Volhard's reaction for manganese (oxidation to permanganic acid by means of lead peroxide) is not trustworthy when traces of manganese are accompanied by considerable quantities of chromium. R. V. S.

The Quantitative Separation of Chromium and Aluminium. Analysis of Chromite FRANÇOIS BOURION and A. DESHAYES (*Compt. rend.*, 1913, **157**, 287—289).—The method employed for the separation of the oxides of chromium and iron, by chlorination with a mixture of sulphur dichloride and chlorine, and treatment of the chlorides by water, the anhydrous chromic chloride being insoluble (compare this vol., ii, 626), can be used for the separation of the oxides of aluminium and chromium. This method is applicable for a complete analysis of chromite. The powdered mineral is first heated gradually to a red heat with mercuric sulphate, and then, thus prepared, it is chlorinated. The residue in the tube contains the unattacked silica and the chlorides of magnesium and calcium. Of the volatile chlorides, the chromic chloride alone is insoluble in water, and can be filtered off, the iron and aluminium being estimated in the filtrate by the usual methods. W. G.

A Delicate Test for Molybdenum. A. KOMAROWSKY (*Chem. Zeit.*, 1913, **37**, 957).—The colour test for molybdenum by means of the formation of ammonium permolybdate (Melikoff, A., 1912, ii, 693) is exceedingly delicate; it is sensitive to 0·006 mg. of molybdenum. T. S. P.

Quantitative Precipitation of Tungstic Acid by Aromatic Amines. ERWIN KAFKA (*Zeitsch. anal. Chem.*, 1913, **52**, 601—606).—To 50 c.c. of sodium tungstate (= about 0·25 gram of the solid salt) are added, respectively, 15 c.c. of ψ-cumidine, 10 c.c. of tetramethyldiaminodiphenylmethane, or 10 c.c. of tetramethyldiaminobenzophenone reagent. When the precipitate has completely settled, it is collected and washed with water containing 5 c.c. of the reagent per 100 c.c., and then ignited to tungstic oxide.

The reagents are, respectively, prepared as follows: 5 grams of ψ-cumidine are mixed with 10 c.c. of water, dissolved by means of 5 c.c. of hydrochloric acid, and diluted to 100 c.c.; 6 grams of tetramethyldiaminodiphenylmethane are dissolved in 4 c.c. of hydrochloric acid and diluted to 100 c.c.; 7·5 grams of tetramethyldiaminophenone are dissolved in 10 c.c. of hydrochloric acid, and diluted to 100 c.c.

The precipitates obtained with the two last reagents have the compositions $WO_3,C_{17}H_{22}N_2$ and $2WO_3,3C_{17}H_{20}ON_2$ respectively.

L. DE K.

Solution and Oxidation of Tin in Dilute Nitric Acid. CURT BUNGE (*Pharm. Zentr.-h.*, 1913, **54**, 845—846).—When assaying commercial tin, the author finds that this may be readily oxidised and dissolved by heating 2 grams of the sample free from grease with 30 c.c. of dilute nitric acid and a drop of a concentrated solution of mercuric chloride. On evaporation on the water-bath a transient coagulation of stannic nitrate is noticed. On boiling the dry residue with dilute nitric acid, insoluble stannic acid is again obtained.

L. DE K.

Detection of Gold and Platinum. GIUSEPPE MALATESTA and ETTORE DI NOLA (*Boll. Chim. Farm.*, 1913, **52**, 461—463).—The reagent employed contains 1 gram of benzidine, 10 c.c. of acetic acid, and 50 c.c. of water. It yields, with traces of a gold salt solution, an intense blue coloration, which becomes violet. In the presence of free acetic acid the coloration is green, passing into blue when excess of benzidine is added. The blue coloration is distinct when the gold solution contains only 0·0000035 gram of gold per c.c. The same reagent, when treated with a solution of a platinum salt, yields in the course of ten minutes a blue, flocculent precipitate; the reaction is perceptible with a solution containing only 0·0000125 gram of platinum per c.c. A solution of a ferric salt, when treated with benzidine acetate, gives a blue coloration, which is stable only in the presence of excess of benzidine. When gold or platinum is being tested for, however, the absence of iron may be ensured by a previous treatment of the material with dilute acid.

R. V. S.

Some Anomalies Observed in the Assay of Platinum Ores from the Ural. MAX WUNDER and V. THÜRINGER (*Ann. Chim. Phys.*, 1913, [viii], **30**, 164—168).—Certain anomalies observed when assaying the "Ural ore" have led Holtz (this vol., ii, 144) to the conclusion that an unidentified metal is present in the material. This appears improbable to the authors. The difference in weight between the portion of the "blacks" dissolved by nitric acid (1:1) and the weight of palladium + copper found by Holtz is attributed to the presence of the excess of zinc used in the reduction. The yellow colour of the filtrate from the copper thiocyanate and the dark precipitate formed by the addition of zinc to it are also encountered with solutions containing rhodium. Holtz deduces the absence of rhodium from the fact that the metal, after solution by melting with potassium hydrogen sulphate, yields a brownish-red mass, which does not give a white turbidity with water. The authors do not regard this as characteristic of the metal, and insist on the dependance in behaviour of the sulphate on the temperature at which the fusion has been performed.

H. W.

Separation of Palladium from Gold, Platinum, Rhodium, and Iridium. Application of Dimethylglyoxime. MAX WUNDER and V. THÜRINGER (*Zeitsch. anal. Chem.*, 1913, **52**, 660—664).—*Gold from Palladium.*—Both metals are precipitated on boiling the solution containing a little hydrochloric acid with excess of dimethylglyoxime; the other members of the platinum group (except platinum itself) are not precipitated. After ignition and redissolving the metals in *aqua regia* the gold may be recovered as metal by warming with ammonium oxalate; the separation of the gold is promoted by adding some dilute sulphuric acid; from the filtrate the palladium may then be again recovered by heating with dimethylglyoxime after first neutralising the bulk of the acid with ammonia. The palladium compound is first ignited in the air, then in a current of hydrogen, and allowed to cool in a current of carbon dioxide. *Platinum from Palladium.*—The platinum is separated by saturating the concentrated solution with ammonium chloride, washing with ammonium chloride, and finally igniting the precipitate. From the filtrate the palladium is then recovered by means of dimethylglyoxime. *Palladium from Rhodium.*—The palladium is removed by means of dimethylglyoxime. After destroying the excess of this reagent by means of hydrochloric acid and sodium chlorate, the rhodium may be precipitated by means of metallic magnesium, the last traces of which are removed by means of 5% sulphuric acid. The metal is then ignited in a current of hydrogen, and allowed to cool in a current of carbon dioxide. *Palladium from Iridium.*—The same process as for rhodium is used; the complete destruction of the excess of dimethylglyoxime is of great importance in this case. L. DE K.

Method of Estimation of Pure Caoutchouc in the Crude Product. RAYMOND MARQUIS and F. HEIM (*Bull. Soc. chim.*, 1913, [iv], **13**, 862—866).—When a solution of pure caoutchouc (1 gram) in chloroform (100 c.c.) is violently agitated with pure sulphuric acid (8 grams) during three to five minutes, a clear, yellow, mobile solution is obtained, from which the caoutchouc is quantitatively precipitated as a white, amorphous powder when the solution is poured into alcohol (200 c.c.). The precipitate has the further advantage of being readily filtered, washed, and dried.

The application of this method to the estimation of pure caoutchouc in artificial mixtures of this substance with varying amounts of rubber resin gives satisfactory results when the quantity of acid employed is increased to ten times the weight of the caoutchouc. Nevertheless, in view of the extremely variable character of the resin present even in similar samples of crude caoutchouc from the same locality and also because the presence of resin frequently retards the filtration very considerably, the authors are led to recommend the de-resinification of samples by means of acetone previous to their assay. H. W.

Alcoholometry. ALFRED FRANCIS JOSEPH and W. N. RAE (*J. Soc. Chem. Ind.*, 1913, **32**, 856—857).—In the determination

of the strength of alcoholic liquids by the distillation method the authors have investigated the effect of the temperature of the condenser water on the results obtained, and also the probable errors caused by the use of Sikes' hydrometer. It is found that condensation of the distillate is equally efficient when the temperature of the condenser water varies between 15·5° and 49°. Using the ordinary density tables, a large error is caused when the density is measured with the Sikes' hydrometer; at 37·7° the error may amount to as much as 6% of proof spirit. A great improvement is made if the tables compiled by C. H. Bedford are used in conjunction with Oertling's glass Sikes' hydrometer, or even with the ordinary brass instrument, which, however, is not so good. T. S. P.

New Colour Reactions for Di- and Tri-phenols. Omer Schewket (*Biochem. Zeitsch.*, 1913, **54**, 282—284).—Catechol, when treated with a few drops of 1% iodine solution in potassium iodide and then, after dilution, with a few drops of 5% sodium hydroxide solution, yields immediately a bright green colour. The immediate production of this colour distinguishes catechol from resorcinol. Pyrogallol under the same conditions yields a fugitive violet colour. This substance, when its aqueous solution is diluted with half the volume of alcohol and a few drops of a solution of alkali hydroxides, gradually gives a violet colour similar to that of permanganate solutions. This test serves to distinguish pyrogallol from phloroglucinol. When a hot dilute aqueous solution of the latter substance is treated with a few drops of 0·5% iodine solution in potassium iodide, the iodine is decolorised. On addition of a few drops of alkali solution, a bright, brown coloration is formed, which on heating becomes violet. Phloroglucinol in alkaline solutions yields, on treatment with hydrogen peroxide, a very stable, bluish-violet coloration, which gradually changes into red and then yellow on addition of acids, and is restored again on addition of alkalis.

S. B. S.

The Differentiation of Vegetable and Animal Oils. J. Marcusson and H. Schilling (*Chem. Zeit.*, 1913, **37**, 1001—1002).—The authors make use of the fact that cholesterol and phytosterol form characteristic, sparingly soluble compounds with digitonin (compare Windaus, A., 1909, i, 172). Combination of the precipitation of these compounds with Bömer's phytosteryl acetate test gives a simple method for distinguishing between animal and vegetable oils.

Fifty grams of the oil or fat are shaken for fifteen minutes in a separating funnel with 20 c.c. of a 1% alcoholic solution of digitonin. When the emulsion has cleared, the bottom layer of oil is run off, and then the alcoholic upper layer, which contains the flocculent precipitate of the digitonide, is shaken with 50—100 c.c. of ether. After collecting the digitonide it is washed with ether to remove oil, dried, powdered, and again washed with ether to remove the last traces of fat, after which it is heated in a test-tube with

1·5 c.c. of acetic anhydride for half-an-hour. On cooling, the cholesteryl and phytosteryl acetates crystallise out; they are recrystallised once or twice from alcohol, and then the melting points determined, etc., as in the Bömer test. If desired, the acetates may be hydrolysed and the free alcohols obtained.

It is not necessary to saponify fats, or extract the higher alcohols from them, previously to treatment with the digitonin.

T. S. P.

Quantitative Estimation of the Cholesterol Substances in the Presence of One Another. II. Cholesterol. J. LIFSCHÜTZ (*Biochem. Zeitsch.*, 1913, **54**, 212—235).—Qualitatively as well as quantitatively, both oxycholesterol and cholesterol behave similarly towards Liebermann's "cholestol" reagent, that is, a mixture of acetic anhydride and sulphuric acid. The colours produced by this reaction pass through three stages, namely, a red, a blue, and a green stage. The second (blue) stage is characterised by absorption bands in the yellow, which extend until they include the whole of the orange and the greater part of the green part of the spectrum. The third stage (green) is characterised chiefly by a band in the red between the *B* and *C* lines. It is shown by the author that the bands in the second stage may be most readily obtained if a relatively larger quantity of sulphuric acid is added, whereas the band in the red of the third stage is best obtained if sulphuric acid in smaller quantity (sulphuric acid diluted with ten times its volume of acetic acid) is employed. The bands of either the second or third stage may be employed for quantitative estimation of the combined cholesterol or oxycholesterol content, the solution under investigation being compared with a solution of known content of either of these substances. For this purpose either the necessary dilutions necessary to bring the bands to disappearance or the spectrometric method already described by the author (*loc. cit.*) for the estimation of oxycholesterol by the acetic and sulphuric acid reagent in the presence of iron salts, may be employed. By the latter method the oxycholesterol may be estimated separately, and by the quantitative application of Liebermann's reaction, the total cholesterol and oxycholesterol may be estimated. Liebermann's reaction is only applicable to the estimation of these substances when they are not combined as esters of the higher fatty acids. In the presence of chloroform, however, as in Burchard's modification of the method, the cholesterol and oxycholesterol as fatty esters can also be estimated. By estimating the substances by both the Liebermann and the Liebermann-Burchard methods, both the free and combined "cholestol" substances can be estimated.

S. B. S.

The Action of Sugar Solutions on Glass. J. N. LAIRD (*J. Path. Bact.*, 1913, **18**, 32—33).—When sugar solutions are heated in ordinary test-tubes they extract calcium from the glass, and this accelerates the reaction with Fehling's solution. Of five reducing sugars investigated, galactose is the most sensitive to the presence of calcium hydroxide.

W. D. H.

A Source of Error in the Estimation of the Sugar in the Blood of Frogs and Tortoises. ERNST J. LESSER (*Biochem. Zeitsch.*, 1913, **54**, 252—255).—When attempts were made to estimate the sugar by Bertrand's method, after precipitation with Michaelis and Rona's colloidal iron hydroxide reagent, no copper reduction took place. When, however, the filtrate from the proteins had been treated with mercuric nitrate before the sugar estimation, a certain amount of cuprous oxide was precipitated. The conclusion is drawn that the blood of these cold-blooded animals contains some substance which retains cuprous oxide in solution. S. B. S.

Influence of the Alkali of Ordinary Water on Dextrose. H. J. WATERMAN (*Chem. Weekblad*, 1913, **10**, 739—742).—The results obtained in the polarimetric estimation of dextrose dissolved in ordinary water containing alkali are much too low. A. J. W.

Estimation of Traces of Dextrose in Urine by the Bertrand Method. ELSE HIRSCHBERG (*Zeitsch. physiol. Chem.*, 1913, **86**, 484—493).—Use is made of Oppler's observation (A., 1912, ii, 100) that the addition of alcohol to a sugar determination eliminates the reducing action of the substances which accompany dextrose in urine. To apply the Bertrand permanganate method to the titration of dextrose in urine, the urine was first shaken with charcoal and hydrochloric acid, and diluted. Equal volumes of the diluted urine and alcohol were taken. Quantities of 0·5—0·9% of dextrose were accurately determined; quantities of 0·1—0·5% tended to give slightly low results. E. F. A.

Estimation of Dextrose in Fæcal Matters. L. H. DEJUST (*Ann. Inst. Pasteur*, 1913, **27**, 570—576).—Twenty-five grams of the substance are mixed in a flask with 125 c.c. of 96% alcohol, neutralised with acetic acid, and, after the addition of 5 c.c. of 10% acetic acid, the mixture is boiled for fifteen minutes under reflux. The solution is then filtered, and the insoluble residue is extracted twice again with alcohol in the same manner, the residue being finally washed with about 20 c.c. of alcohol. Two c.c. of 10% hydrochloric acid are added to the alcoholic extract, and this is evaporated under reduced pressure to a syrupy consistence. The syrup is dissolved in water, transferred to a 50 c.c. flask, 12 c.c. of mercuric nitrate solution are added, the mixture is neutralised with sodium hydroxide solution, diluted to the mark, and filtered. The filtrate is shaken for forty-five minutes with an excess of zinc dust (about 5 grams), again filtered, and the reducing power of the filtrate is determined. W. P. S.

Fiehe's Reaction [for Honey]. J. GERUM (*Zeitsch. Nahr. Genussm.*, 1913, **26**, 102—104).—The fact that some samples of genuine honey give an orange or reddish-yellow coloration with this test for invert sugar (A., 1910, ii, 660) is due to the presence of traces of wax substance in the honey. When such a reaction is obtained, a larger quantity of the honey should be extracted with ether, and the

residue obtained on evaporating the ether examined for the presence of beeswax. W. P. S.

Estimation of Oxalic Acid. Iw. Buromsky (*Centr. Bakt. Par.*, 1913, ii, **38**, 506—507).—A reply to Wehmer (this vol., i, 432). Extraction of the fungus with hydrochloric acid was avoided, as it would cause loss of weight.

When the precipitate, obtained by Wehmer's method, contains much calcium phosphate and sulphate it is proposed to titrate with permanganate, as these salts do not readily dissolve in acetic acid after being heated with calcium chloride and ammonia.

N. H. J. M.

[**Estimation of Oxalic Acid.**] C. Wehmer (*Centr. Bakt. Par.*, 1913, ii, **38**, 508).—A reply to Buromsky (preceding abstract).

N. H. J. M.

Estimation of Tartaric, Malic, and Succinic Acids in Wines. Paul Dutoit and Marcel Duboux (*Bull. Soc. chim.*, 1913, [iv], **13**, 832—862).—The authors have previously described a method of volumetric analysis (A., 1910, ii, 342) which is based on the determination of the end-point in a precipitation process by means of conductivity measurements. When successive quantities of a concentrated solution of a precipitant are added to a dilute solution of a precipitable salt and the conductivity after each addition is plotted as a function of the volume of the solution of the precipitant added, two approximately straight line graphs are obtained, the intersection of which corresponds with the point of complete precipitation. The application of this method to the estimation of tartaric, malic, and citric acids in wines is now described.

The use of salts of barium, lead, glucinum, bismuth, cadmium, lanthanum, magnesium, and silver as precipitating agents is discussed, lanthanum nitrate being finally chosen. When, however, this reagent is added to solutions of alkaline salts of tartaric, malic, and succinic acids and the results plotted as above, two straight-line curves are obtained, the inflexion of which only corresponds with the point of complete precipitation, assuming the formation of $La_2(C_4H_4O_6)_3$ when the experiments are performed with aqueous solutions; with aqueous alcoholic solutions, less reagent (up to 8%) appears to be required, so that it is necessary in practice to standardise the lanthanum nitrate solutions against solutions of sodium tartrate and malate of known concentration.

In order to obtain a solution of the sodium salts of tartaric, malic, and succinic acids suitable for titration from a given wine, the total acidity and sulphates in the latter must first be determined (A., 1908, ii, 781); 100 c.c. of the wine are heated to boiling and treated with exactly that quantity of barium hydroxide (or of a barium salt) which is necessary to precipitate the sulphates and with 1 c.c. *N*-uranium nitrate solution; after several minutes sodium hydroxide is added until the mixture is neutral to litmus, followed by a sufficient volume of aqueous-alcoholic silver nitrate

solution to precipitate tartaric, malic, and succinic acids as silver salts. A large excess of silver nitrate is to be avoided as the presence of an excess of sodium nitrate (subsequently formed) interferes with the delicacy of the titration. After filtration, the precipitate is decomposed by agitation with the necessary volume of *N*-sodium bromide solution, and the solution made up to 200 c.c. with an aqueous alcohol containing 50% alcohol (95%).

In one portion of this solution, the sum, tartaric + malic + succinic acid, is determined by titration with lanthanum nitrate solution. The exact volume of solution to be taken and the volume of 50% alcohol to be added to ensure the complete precipitation of the lanthanum salts of the acids depend on the acidity of the wine. Before titration, the solutions are acidified by 0·5 c.c. *N*/10-acetic acid.

In a second portion of the solution, tartaric and malic acids are estimated together, lanthanum nitrate being again used. Precipitation of lanthanum succinate is avoided by performing the titration in a more strongly acidified solution, which also contains a larger proportion of alcohol, the exact proportion of the various solutions depending, as before, on the acidity of the wine.

The estimation of tartaric acid alone is performed in a still more strongly acidified solution and in the presence of a larger proportion of alcohol. Barium acetate solution is used as a precipitant. The results are only accurate if the proportion of tartaric to malic acid exceeds 3·7. If this is not the case, a suitable known volume of sodium tartrate solution must be added, and the determination repeated.

The method gives accurate results with wines which contain less than 3·4 grams of malic acid per litre, that is, in the great majority of cases. Certain wines, such as those of 1912, contain up to 8 grams of malic acid per litre. For these it is preferable to estimate the tartaric acid as potassium bitartrate, and to subtract the value thus found from the sum of tartaric + malic acid determined by the conductivity method. The determination of succinic acid is also less precise in the presence of much malic acid.

Citric acid, if present, is precipitated in each of the determinations described above. In order, therefore, to apply the method to wines containing this acid, a fourth determination is necessary, which may consist in estimating the tartaric acid either as potassium bitartrate or as calcium racemate. H. W.

Increased Sensitiveness of Mylius' Reaction for the Detection of Cholic Acid and for Distinguishing it from the True Bile Acids. Jules Ville (*Bull. Soc. chim.*, 1913, [iv], **13**, 866—868).—Mylius (A., 1887, 606) has shown that when a solution of iodine in aqueous potassium iodide is added to an alcoholic solution of cholic acid and the mixture gradually diluted with water, a brown solution results, which deposits the compound $(C_{24}H_{40}O_5I)_4KI,nH_2O$, fine blue needles with reddish-brown reflex. The author finds that the sensitiveness of this reaction may be greatly increased either by the addition of solid sodium chloride

to the reaction mixture or by dissolving the iodine and potassium iodide in a concentrated solution of sodium chloride. In this manner, 0·0005 gram of cholic acid immediately yields a deposit of blue crystals, whilst the presence of 0·0002 gram acid gives an appreciable reaction. H. W.

Oxidation of Gallic and Tannic Acids in Air in the Presence of Alkalis, and a Colour Reaction for Lead. OMER SCHEWKET (*Biochem. Zeitsch.*, 1913, **54**, 277—284).—If a solution of gallic acid is poured over a solution of alkali, the upper layer is coloured green, and the lowest pink, the intervening layer being yellow. These colours correspond with various stages in the oxidation of the acid. The green colour can be produced by adding a few drops of 10% alkali hydroxide to the gallic acid solution, preferably in presence of alcohol. With excess of alkali, and in presence of air, an orange-red colour is formed. Experiments showing that the formation of these colours represent stages in the oxidation, are given. If to a lead salt solution sufficient sodium hydroxide is added to dissolve the precipitated lead hydroxide, a solution is obtained, which, on addition of a few drops of gallic acid solution, shows on the surface (if the mixture is not shaken) a green zone, and below a carmine-red zone. On shaking, the whole mass becomes carmine red. For this reaction lead must be in excess. Tannin gives the same reaction. If a larger amount of gallic acid is added (1—4 c.c. of a 1% solution to 5 c.c.) a green colour is produced. The production of the red colour is the more delicate test.

A method is also given for the detection of gallic and tannic acids in the presence of one another. The tannic acid is precipitated by caffeine, and in the filtrate the gallic acid can be detected by the following tests: (1) Half the volume of alcohol is poured on to the liquid, and then a few drops of sodium hydroxide solution. A green colour develops in the alcoholic layer. (2) The following reagent can be employed: 5% sodium hydroxide solution, containing 0·2% lead acetate. This is added drop by drop with constant shaking, whereby a green colour is produced, which turns red on addition of acids. (3) The addition of barium chloride, followed by sodium hydroxide, produces a blue precipitate. The tannic acid can be detected in the caffeine precipitate when this is dissolved in alcohol by the following reaction. On addition of a few drops of sodium hydroxide solution a reddish-yellow precipitate is formed, which dissolves in water with a reddish-yellow colour. Gallic acid under the same conditions gives a green solution. S. B. S.

Application of "Activated" Aluminium to the Estimation of Tannin. ÉMILE KOHN-ABREST (*Ann. Chim. anal.*, 1913, **18**, 349—351).—The method depends on the direct precipitation of tannin from its solution by means of aluminium which has been treated with mercuric chloride solution. One hundred c.c. of the tannin solution are brought into contact with a piece of aluminium foil (about 1 mm. in thickness and weighing 3 grams) which has

been immersed for three minutes in a 3% mercuric chloride solution and then washed. About four hours' contact is required to precipitate the tannin completely; if after this time the solution still yields a coloration with ferric chloride, a fresh piece of treated aluminium is introduced. The mixture is then filtered, and an aliquot portion of the filtrate is evaporated. The difference between the weight of the residue obtained and that found on evaporating an equivalent portion of the original tannin solution, gives the weight of the tannin precipitated. A small quantity of aluminium passes into solution, and an allowance may be made for its amount by incinerating the residues and ascertaining the difference between their weights. W. P. S.

Estimation of Tyrosine. EMIL ABDERHALDEN (*J. Biol. Chem.*, 1913, **15**, 357—358).—Polemical. A criticism of Folin and Denis' method. It is stated that tryptophan and other substances give the same colour reaction, and therefore the method is not accurate for the estimation of tyrosine. W. D. H.

Detection of Formaldehyde in Foods. F. RACHEL (*Pharm. Zentr.-h.*, 1913, **54**, 759—761).—Attention is called to some colour reactions recommended by Friese (*Hyg. Inst.*, Dresden, 1907, **1**) for the detection of formaldehyde. On this the author has based the following process for the detection of this preservative in meat, caviare, and fish wares.

The article is acidified with phosphoric acid and heated in a current of steam; 1 or 2 c.c. of the distillate are then mixed with 4 c.c. of milk free from formaldehyde and 10 c.c. of hydrochloric acid (D 1·19), to which has been added 1 drop of nitric acid per 300 c.c. In the presence of formalin a bluish-violet coloration appears; no notice must be taken of any coloration formed after five minutes. In presence of much formaldehyde milk will not give the reaction, so the experiment must be repeated after suitably diluting with pure water. L. DE K.

A Colour Reaction of Hypochlorites with Methylaniline and Ethylaniline. PAUL NICHOLAS LEECH (*J. Amer. Chem. Soc.*, 1913, **35**, 1042—1044).—Contrary to the statement of Hofmann (A., 1874, 807), carefully purified methylaniline gives a navy blue coloration when 1 c.c. of a $N/100$-aqueous solution is treated with a few drops of $6N$-sodium hydroxide solution and $\frac{1}{2}$—2 c.c. of half-saturated solution of bleaching powder. The colour begins to appear in approximately twelve seconds, reaches a maximum in about thirty-five seconds, and after a minute or so slowly fades to a yellow, a precipitate of calcium carbonate being simultaneously produced. It is suggested that the reaction may depend on the primary oxidation of the methyl group (compare Meisenheimer, this vol., i, 447).

Ethylaniline gives an analogous but slower reaction, but the blue colour passes through green and dark brown before changing to yellow. D. F. T.

Estimation of Small Amounts of Caffeine. A Comparison of Methods. B. L. MURRAY (*J. Ind. Eng. Chem.*, 1913, **5**, 668—670).—For the estimation of caffeine in substances containing less than 0·5% of the alkaloid, Görter's method (extraction of the moistened sample with chloroform, evaporation of the extract, separation of fat by adding water and filtration, and again extracting the caffeine with chloroform) yields results which are considerably higher than those obtained by Lendrich and Nottbohm's method (A., 1909, ii, 449). The latter method gives concordant results, and the necessity of the permanganate purification as described by the authors of the method is confirmed. W. P. S.

Colorimetric Estimation of Adrenaline in Desiccated Suprarenal Glands. ATHERTON SEIDELL (*J. Biol. Chem.*, 1913, **15**, 197—212).—Previous methods were tested and found unsatisfactory. The new method proposed consists in the use of manganese dioxide as the reagent for developing a colour with aqueous adrenaline solutions, or extracts of suprarenal glands. The colour is estimated against standards made by mixing cobalt chloride, gold chloride, and water. W. D. H.

Detection of "Saccharin" in Beer. RENÉ LEDENT (*Ann. Chim. anal.*, 1913, **18**, 314).—Beer is allowed to traverse drop by drop a long and narrow column of ether, thus avoiding emulsion and insuring complete extraction of the "saccharin." A modification of Duyk's apparatus (A., 1906, ii, 407) is employed. L. DE K.

New Indican Reaction. ADOLF JOLLES (*Zeitsch. physiol. Chem.*, 1913, **87**, 310—312).—Urine containing thymol gives a violet coloration with potassium indoxylsulphate in presence of an oxidising agent in strongly acid solution. The following test for indican is based on this observation. Urine is precipitated with lead acetate, and filtered. A little alcoholic thymol is added to the filtrate, together with strong hydrochloric acid containing ferric chloride and chloroform. The whole is well shaken, when in presence of traces of indican the chloroform is coloured a deep violet. On shaking with water, the colour changes to a yellowish- or reddish-brown. *p*- and *o*-Xylenols give a similar violet coloration, which, however, is stable towards both water and alkali. E. F. A.

Detection of Hæmatin in Human Blood Serum. OTTO SCHUMM (*Zeitsch. physiol. Chem.*, 1913, **87**, 171—181).—The blood serum is centrifuged and examined in a layer of 4 cm. in a spectroscope. The thickness of the layer is then diminished so as to locate the position of the absorption bands. The hæmatin is then converted by means of ammonium sulphide into hæmochromogen, and the spectrum again examined. The delicacy of the test depends on the transparency of the serum and the presence of other pigments. In some cases hæmatin corresponding in amount with a 1% solution of blood has been detected. E. F. A.

General and Physical Chemistry.

Leisegang's Rings and Related Phenomena. ERNST KÜSTER (*Kolloid. Zeitsch.*, 1913, **13**, 192—194).—The iridescence which makes its appearance when a solution containing alkali metal phosphates and alkali hydroxide is allowed to diffuse into a gelatin jelly containing calcium chloride is shown to be due to the folding of a delicate membrane which is formed at the surface of the gelatin. The original explanation of the phenomenon (Liesegang, this vol., ii, 453) attributed the iridescence to the formation of concentric layers of precipitate, but various observations are described which indicate that this view is untenable.

It is also shown that a periodic variation of the external conditions may lead to the formation of differentiated zonal regions in colloidal systems. H. M. D.

An Oxidisable Variety of Nitrogen. T. MARTIN LOWRY (*Trans. Faraday Soc.*, 1913, **9**, 189—192. Compare T., 1912, **101**, 1152).—Photographs of spectra illustrating the conclusions already published. C. H. D.

Emission and Absorption of Heated Carbon Dioxide. HANS SCHMIDT (*Ann. Physik*, 1913, [iv], **42**, 415—459).—The absorption and emission of layers of carbon dioxide have been determined for a number of temperatures (435—900°) and wave-lengths. With homogeneous heating carbon dioxide gives rise to the emission and absorption band spectrum which was discovered by Paschen. This points to the fact that gases can be made to emit a discontinuous spectrum by raising their temperature. At constant pressure the absorption bands increase on the long wave-length side as the temperature is increased. It is shown that in all probability the Kirchhoff law holds quantitatively for homogeneously heated carbon dioxide. J. F. S.

The Influence of Concentration and of Different Colourless Metal Ions on the [Light] Absorption of Coloured Salt Solutions. ARTHUR HANTZSCH and, in part, C. S. GARRETT and F. GAJEVSKI (*Zeitsch. physikal. Chem.*, 1913, **84**, 321—347).—The absorption spectra and extinction coefficients of aqueous and alcohol solutions of the alkali and alkaline earth salts of chromic acid, hydroferrocyanic acid, chloroplatinic acid, and those of methyloxindone, acetyloxindone, and oxindonecarboxylic ester have been determined. Whilst in the experiments it is shown that the ions of coloured salts are optically identical, or nearly so, with the undissociated salt, still the different solvents exercise an optical effect on the coloured ions. This effect is more marked the less saturated the components are, which may be explained by the formation of solvates. Small divergences from Beer's law are only to be found

in very concentrated alkaline solutions of chromates and possibly ferrocyanides by the extinction method. These divergences are probably to be explained by incomplete hydration rather than by dissociation changes. It is shown that the analogous observations of Jones (A., 1912, ii, 507, 216) for concentrated solutions, and Baly (T., 1913, **101**, 91) for pyridine solutions, are probably not physical changes, but chemical, and due to a shifting of the equilibrium point of different complex ions, or perhaps hydrates. This result is confirmed by the following. All variations of the colorimetric dilution law are due either to experimental errors or to chemical changes of the substances by the solvent. The absorption of saturated and constitutionally unchangeable inorganic coloured anions is so slightly changed by the different cations that the influence of the cation could only be detected by the extinction method. The absorption of unsaturated coloured organic anions of unchangeable structure is only changed by the different cations at the highest concentrations, and then only in non-aqueous solutions; this is brought about by the auxiliary valencies of cations combining with the residual valencies of the anions. The absorption of the coloured alkali and alkaline earth organic salts decreases with the decreasing positive character of the cation, the order being: Cs–Rb–K–Na–Li–Ba–Sr–Ca. The optical effects observed here are relatively small when compared with the changes which the same metals bring about in solutions of polychromatic acids through structural alterations of the anions. As a general result it is shown that the changes in light absorption of coloured substances correspond with constitutional changes, or, in other words, the absorption changes more the more the constitution changes. J. F. S.

The Dependence of the Light Absorption of Some Metallic Salts on the Nature of the Linking. I. Mercuric Salts. HEINRICH LEY and W. FISCHER (*Zeitsch. anorg. Chem.*, 1913, **82**, 329—340).—The ultra-violet absorption of mercuric salts is displaced towards longer wave-lengths in passing from the chloride to the iodide, the bromide being exactly intermediate. The iodide has an absorption band. The undissociated salt in alcoholic solution may be compared with its component ions by using mercuric perchlorate, which is highly dissociated, in a tube placed in series with one containing a solution of the corresponding potassium salt. In this way it is found that salt formation is accompanied by a bathochromic effect, which is greatest in the iodide. Mercuric cyanide is almost as diactinic as water, and much more so than mercuric ions, a result which is explained by the presence of a mercury–carbon linking. In accordance with this, mercury methyl chloride and mercury ethyl chloride absorb less than mercuric chloride. On the other hand, compounds with mercury linked to nitrogen, such as mercury propionamide and mercury succinimide, have a high absorption.

Mercurous perchlorate absorbs more than the mercuric salt,

favouring the view that a bivalent complex ion (Hg·Hg)$^{\cdot\cdot}$ is present. C. H. D.

Quantitative Investigation of the Absorption of Ultra-violet Rays by Saturated and Unsaturated Aliphatic Acids. III. JAN BIELECKI and VICTOR HENRI (*Ber.*, 1913, **46**, 2596—2607. Compare this vol., ii, 263).—The authors have extended their studies from monobasic fatty acids to polybasic saturated and unsaturated acids and their corresponding hydroxy-acids. The molecular coefficients of absorption for different wave-lengths are tabulated, and curves are also given. The results are summarised as follows:

(1) In the case of saturated acids (acetic, oxalic, malonic, succinic, and tricarballylic) a considerable exaltation of the absorption is caused by increasing the number of carboxyl groups, and the exaltation rises faster than the number of these groups.

(2) Saturated acids have about the same absorption as their corresponding hydroxy-acids (propionic and α-hydroxypropionic acids, succinic, malic, *d*-tartaric and racemic acids, tricarballylic and citric acids), but the small exaltation caused by the alcoholic hydroxyl group is much greater than the absorption of the corresponding normal alcohol.

(3) Ethylenic acids (allylacetic, itaconic, α-crotonic, fumaric, maleic, mesaconic, citraconic, and aconitic acids) are much more absorbent than the saturated acids, and the exaltation effect of the double linking is much stronger the nearer it is to the carboxyl group (compare Macbeth, Stewart, and Wright, T., 1912, **101**, 603). The exaltation is much greater in the case of corresponding saturated and ethylenic acids than in the case of corresponding alcohols.

(4) The acetylenic linking (methyl propiolate and ethyl acetylenedicarboxylate) has not such a great influence as the ethylenic linking, but the position of the triple bond with respect to the carboxyl group is of the same importance.

(5) Stereoisomeric acids have different absorptive powers, and *trans*-isomerides show higher values than the *cis*-forms.

(6) As was previously found (*loc. cit.*), the acids are more absorbent in alcohol than in water, with the exception of maleic acid, in which case the converse is true.

(7) Aconitic acid, having three carboxyl groups and a double linking between two carbon atoms, each of which bears a carboxyl group, has an enormous absorption constant, the highest of all the acids studied.

As a general result of their studies in this field the authors come to the conclusion that the effect of different chromophores in a molecule is not additive, but that the absorption constant is equal to the product of the "absorption factors," corresponding with the several chromophores, and the "exaltation factors," which depend on the relative position of the chromophores in the molecule. These factors have different values for different wave-lengths, and appear to be complicated functions of the frequency.

J. C. W.

The Absorption Spectra of White and Yellow Santonin. ARNALDO PIUTTI (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 192—204). —Carbon electrodes which have been alternately heated to redness and immersed in ferric chloride solution a few times, or a carbon and an iron electrode, may be employed with advantage instead of iron electrodes for the arc used as a source of light in these experiments. The curves obtained indicate that the transformation of santonin into photosantonic acid and *iso*photosantonic acid by light proceeds by way of intermediate compounds. Photosantonic acid, and probably also *iso*photosantonic acid, are very transparent to the ultraviolet rays, but santonin is not. No confirmation could be obtained of the alleged re-conversion of yellow santonin into white on boiling. The alleged visible alteration of santonin crystals under the action of light could not be observed.

Asparagine, lactic acid, and carbamide are almost completely transparent to the light of the iron arc. R. V. S.

The Absorption of the Visible and Ultra-violet Rays by the Carotinoid Pigments. CHARLES DHÉRÉ and L. RYNCKI (*Compt. rend.*, 1913, **157**, 501—504. Compare A., 1912, i, 887).—A study of the absorption spectra in the visible and ultraviolet portion of the spectrum of the two pigments, carotine and xanthophyll. Photographs are given of these spectra for the first-named pigment. They exhibit a relatively considerable transparency for all the ultraviolet radiations up to $\lambda = 225\,\mu\mu$. W. G.

The Absorption of the Visible Rays by the Oxyhæmocyanins. CHARLES DHÉRÉ and A. BURDEL (*Compt. rend.*, 1913, **157**, 552—555).—A study of the absorption spectra of oxyhæmocyanins from various sources, in solution in sodium chloride ($N/5$) and sodium carbonate ($N/100$). Reproductions are given of three spectrophotographs, and the results seem to show that there is an absorption band common to all the oxyhæmocyanins. On reducing these substances to hæmocyanins, the band disappears, but is restored by agitating the solution with air. W. G.

Connexion Between Fluorescence and Ionisation. MAX VOLMER (*Ann. Physik*, 1913, [iv], **42**, 485—486).—Polemical. A reply to Stark's criticism (this vol., ii, 743) of the author's paper (this vol., ii, 456). J. F. S.

Connexion Between Fluorescence and Ionisation. WILHELM E. PAULI (*Ann. Physik*, 1913, [iv], **42**, 487).—Polemical. A reply to Stark's criticism (this vol., ii, 743) of the author's paper (this vol., ii, 456). J. F. S.

A Silica-jacketed Silica Polarimeter Tube. T. MARTIN LOWRY (*Trans. Faraday Soc.*, 1913, **9**, 193).—The silica jacket is fused on to the silica tube, with a fused joint where the central tube passes through the jacket. The metal ends are slotted to receive the silica water tubes, and are cemented on. C. H. D.

Investigation of Nitro-celluloses in the Polarisation Microscope. HANS AMBRONN (*Kolloid. Zeitsch.*, 1913, **13**, 200—207).—From an examination of a series of nitrocelluloses by means of the polarisation microscope, the author has found that there is a definite connexion between the nitrogen content of the substance and the optical properties of the fibres. When the percentage of nitrogen is small, the double refraction is positive. As the nitrogen content increases, the refractive power falls to zero, and in the case of the more highly nitrated products the double refraction is negative, becoming more and more negative as the percentage of nitrogen increases. The change in the character of the double refraction appears to vary continuously with the nitrogen content.

Similar changes in the optical properties have been found in the case of nitrated ramie fibre, and for this material it has been observed that the denitrification of the fibre by treatment with ammonium sulphide yields a product which in regard to its optical properties is identical with the original ramie fibre previous to nitrification.

It is suggested that the polarisation microscope may find useful application in the nitro-cellulose industry, and in particular that it may be employed in the estimation of the nitrogen content.

H. M. D.

Optical Superposition. LEO TSCHUGAEV and A. GLEBKO (*Ber.*, 1913, **46**, 2752—2762).—The *l*-menthylurethane of ethyl *d*-tartrate has $[\alpha]_C$ $-58·31°$, $[\alpha]_D$ $-74·34°$, $[\alpha]_E$ $-96·77°$, and $[\alpha]_F$ $-119·97°$ at 22° in acetone ($c=7·80$). The *l*-menthylurethane of ethyl *l*-tartrate has $[\alpha]$ $-31·04°$, $[\alpha]_D$ $-38·76°$, $[\alpha]_E$ $-48·64°$, and $[\alpha]_F$ $-57·44°$ under similar conditions ($c=6·48$). The *l*-menthylurethane of ethyl mesotartrate has $[\alpha]_C$ $-45·14°$, $[\alpha]_D$ $-57·78°$, $[\alpha]_E$ $-74·16°$, and $[\alpha]_F$ $-89·77°$ ($c=7·75$), values which are within 2% of those calculated by van't Hoff's principle of optical superposition. The *dl*-fenchylurethane of ethyl *d*-tartrate has $[\alpha]_C$ $-27·41°$ ($-35·59°$), $[\alpha]_D$ $-35·29°$ ($-45·40°$), $[\alpha]_E$ $-46·76°$ ($-59·47°$), and $[\alpha]_F$ $-58·58°$ ($-74·01°$) at 21° in acetone ($c=5·58$) and chloroform ($c=4·23$), the rotatory powers in brackets being those in the latter solvent. The *dl*-fenchylurethane of ethyl *l*-tartrate has $[\alpha]_C$ $+5·82°$ (1·03°), $[\alpha]_D$ $+7·80°$ (1·91°), $[\alpha]_E$ 11·25° (3·53°), and $[\alpha]_F$ $+13·52°$ (5·59°) in acetone ($c=4·809$) and chloroform ($c=3·397$) at 21°. The *dl*-fenchylurethane of ethyl mesotartrate has $[\alpha]_C$ $-11·24°$ ($-16·51°$), $[\alpha]_D$ $-14·35°$ ($-20·63°$), $[\alpha]_E$ $-18·80°$ ($-26·41°$), and $[\alpha]_F$ $-23·07°$ ($-32·74°$) in acetone ($c=5·159$) and chloroform ($c=3·64$) at 21°; these values are within 6% of those calculated by the principle of optical superposition. The authors assert, therefore, that the principle is tenable, at least as a first approximation (compare Patterson, T., 1905, **87**, 40; 1906, **89**, 1884; 1907, **91**, 705). The calculated values of the rotation dispersion-coefficients, $[\alpha]_F/[\alpha]_C$, of the two urethanes of the mesotartrate agree exactly with those actually observed. The results also show that the abnormally high values of the dispersion-coefficients of the fenchylurethane of ethyl *l*-tartrate are caused by

the superposition of the individual optical effects, thus confirming the view previously expressed (A., 1911, ii, 787) that a relation exists between abnormal rotation dispersion and optical superposition of the partial rotations corresponding with the individual centres of optical activity. C. S.

Spectral Distribution of Light Sensitiveness in Photochemical Reactions. JOH. PLOTNIKOV (*Zeitsch. Elektrochem.*, 1913, **19**, 753—754).—Polemical against Bruner (this vol., ii, 745). It is shown that that author's assertion, which states there is no evidence to show that photochemical reactions are influenced by the wave-length of the exciting light, is not in accord with facts (compare Plotnikov, A., 1911, ii, 4, 452). J. F. S.

Experimental Confirmation of Faraday's Law in Gas Reactions. SAMUEL C. LIND (*Zeitsch. physikal. Chem.*, 1913, **84**, 759—761).—The author points out that Jellinek, in his treatise, "Physikalischen Chemie der homogenen und heterogenen Gasreaktionen," has entirely omitted the case of chemical reactions brought about by radioactive α-rays. These reactions, both from point of priority and from the manner in which they confirm Faraday's law, are equally, if not more, important than the reactions of Krüger and Möller (A., 1912, ii, 1126), which are included. The author cites a number of such reactions which have been studied quantitatively. J. F. S.

Scattering of α-Particles by Gases. ERNEST RUTHERFORD and J. M. NUTTALL (*Phil. Mag.*, 1913, [vi], 702—712).—The scattering of α-particles in gases was investigated by causing α-rays of radium-*C*, from a fine platinum wire coated with the radium active deposit, to pass between two parallel plates of glass kept at various distances apart by mica strips, in a cylindrical chamber which could be filled with the gas under investigation at any pressure desired, and provided with a thin mica window at the other end for the escape of the α-rays into an ionisation chamber. Corrections for the decrease of ionisation due to loss of range of the α-particle in the gas were carried out directly in the same apparatus with the parallel plates removed. Over a certain range of pressure the loss of ionisation due to scattering, when gas at increasing pressure was admitted into the chamber, showed that the unscattered radiation varied exponentially with the pressure of the gas. For different distances between the plates, the scattering varied approximately as the 5/4th inverse power of the distance. The scattering coefficient was found to vary inversely as the fourth power of the velocity, and this, combined with the result that the scattering varies inversely as the pressure of the gas, shows that the effect is mainly due to single rather than compound scattering. The relative scattering per atom of hydrogen, helium, carbon, nitrogen, oxygen, and sulphur are respectively 0·0176, 0·064, *0·40*, 0·48, 0·53, and 1·61, which agree, considering the difficulties of the experiment and the probable divergence between experiment and theory, for

the heavier atoms with the calculated numbers 0·0190, 0·057, *0·40*, 0·53, 0·69, and 2·58. The latter are derived from a formula deduced by Darwin, $\lambda = cn(n+1)$, where λ is the scattering coefficient, c a constant, and n the number of positive charges on the atomic nucleus (1, 2, 6, 7, 8, and 16 respectively for the above atoms). The results confirm the view put forward previously that the atom consists of a positively charged nucleus of small dimensions carrying a number of atomic charges equal to half the atomic weight and surrounded by a compensating distribution of negative charges. F. S.

Range and Ionisation of the Alpha Particle in Simple Gases. THOMAS S. TAYLOR (*Phil. Mag.*, 1913, [vi], **26**, 402—410).—The ranges found for the α-particles of polonium and radium-*C* are shown in the following table:

	Range in cm. at 760 mm.				
	0°		15°.		
	Po.	Ra-*C*.	Po.	Ra-*C*.	Ratio of ranges.
Air	3·57	6·57	3·77	6·93	1·84
Oxygen ...	3·25	5·94	3·43	6·26	1·83
Hydrogen.	15·95	29·36	16·83	30·93	1·84
Helium ...	16·70	30·84	17·62	32·54	1·84

The diminution in the number of α-particles towards the end of the range was found to be relatively more abrupt in air and oxygen than in hydrogen and helium, which is as is to be expected on the view that the heavier the atom through which the α-particle passes the greater the angle through which the particle is liable to be deflected. Ionisation-range curves were taken in helium, hydrogen, and air adjusted in pressure, so that the range in each was the same. The curves were very similar in shape, the area of the helium curve being 5% greater than that of the hydrogen curve, showing that the energy required to ionise a hydrogen atom is 5% greater than that for a helium atom. Geiger's formula (A., 1910, ii, 473) expressed the results well. F. S.

β-Rays of the Radium Family. JEAN DANYSZ (*Ann. Chim. Phys.*, 1913, [viii], **30**, 241—320).—A résumé of work on this subject is given, together with a detailed account of the author's own work already recorded in A., 1911, ii, 840; 1912, ii, 113, 219, 220, 617, 888; 1913, ii, 270. T. A. H.

Analysis of the β-Rays from Radium-*B* and Radium-*C*. ERNEST RUTHERFORD and H. ROBINSON (*Phil. Mag.*, 1913, [vi], **26**, 717—729).—A new method is described for photographing the spectrum of β-rays in a uniform magnetic field. The source of rays (thin-walled tube of emanation, wires coated with radium-*B* + -*C* or -*C* alone) is placed below a slit, and at the side of a lead block on which the plate is laid face upward, the slit being in the plane of the plate, and source, and parallel to the magnetic

field, which must be very uniform. The β-rays are coiled into circles, and strike the plate at different distances from the slit. A comparatively wide slit is used. All rays of the same radius of curvature which pass through even a wide slit intersect in the neighbourhood of the photographic plate, and thus leaving a quite sharp trace. Tables are given of the value of $H\rho$, the velocity β and energy E, calculated from $H\rho$ by the Lorentz-Einstein formulæ, for 16 lines due to radium-*B* and 48 lines due to radium-*C*, but more than 50 lines have been observed from the latter, the intensity of the different lines varying greatly. A plate is given showing diagrammatically the distribution of the lines along scales of $H\rho$ and E, and their relative intensity. For radium-*B*, no lines were observed with $H\rho$ above 2450 ($\beta = 0{\cdot}823$ in terms of the velocity of light). For radium-*C* the highest velocity lines which showed clearly had $H\rho = 8530$ ($\beta = 0{\cdot}9808$), but five faster lines are recorded (up to $H\rho = 9965$, $\beta = 0{\cdot}9858$), and a number still higher could be faintly seen. The lower limit of the complete record is $H\rho = 4840$, but below this the plates are crowded with fine lines, and only a few have been as yet included. These extend right into the low velocity regions where the radium-*B* lines are found. The rays of radium-*C* appear to be very closely homogeneous, the lines being sharp without indication of any widening. The energy of the various lines of radium-*C* appear to be integral multiples of $0{\cdot}4284 \times 10^{13}e$. For the higher groups the average difference is twice this, but between the multiples 24 and 44 all twenty are represented, and no lines are missing. The suggestion is made that the groups of β-rays observed are not due to the original β-particle expelled, which causes the disturbance, but to the emission of β-rays consequent on vibrations of definite systems of electrons within the atom. Below the multiple 24, the difference between the energies of successive lines is much smaller than that given, and the theoretical analysis of these slow velocity electrons presents great difficulties. F. S.

Scattering and Absorption of γ-Rays of Radium. J. A. GRAY (*Phil. Mag.*, 1913, [vi], **26**, 611—623).—The effect of placing radiators of different materials (carbon, iron, lead) to make different angles with a source of radium and an electroscope, screened from the direct γ-radiation, has been studied. The quantity of radiation scattered per unit mass is approximately independent of the nature of the radiator. The reason why lead appears to give much less scattered radiation than carbon and iron, which give about the same, is due to the relatively greater absorption of the scattered radiation in the lead. The quality of the scattered radiation depends on the angle of scattering, and not on the radiator, being the softer the greater the angle. The softer the primary γ-rays the greater the percentage of it scattered by unit mass. The exponential law of the absorption of primary γ-rays is discussed, and it is deduced that γ-rays absorbed exponentially are hardened by any material of higher atomic weight, whereas rays exponentially adsorbed by a heavy material like lead, are softened by substances

of lower atomic weight, due to the production of a larger proportion of scattered radiation. F. S.

Analysis of the γ-Rays from Radium-*D* and Radium-*E*. ERNEST RUTHERFORD and H. RICHARDSON (*Phil. Mag.*, 1913, [vi], **26**, 324—332).—Owing to the minute amount of γ-radiation given by radium-*D* and -*E*, and to the fact that the β-rays excite in heavy elements secondary γ-rays in greater amount than the primary radiation, the active preparations containing the minimum quantity of impurity were tested on filter paper or glass or aluminium. They were separated from old radium preparations by known methods. Radium-*E* was removed from the solution of -*D* and -*E* by nickel, and volatilised on to aluminium, radium-*D* and a few mg. of added lead being precipitated with aluminium by ammonia. The absorption curves of the γ-radiation in aluminium, β-rays being removed by an electro-magnet, were taken in an electroscope filled with a mixture of methyl iodide vapour and hydrogen. The γ-rays of radium-*E* are very weak in intensity compared with those of radium-*D*, and the same curve is obtained for pure -*D* as for -*D* and -*E* together. The greater part of the γ-rays of radium-*D* is exponentially absorbed ($\mu = 45$) in aluminium, and the absorption for this type is complete in about 1 mm. of aluminium. About 7% of the total ionisation is due to a second more penetrating type also exponentially absorbed ($\mu = 0{\cdot}99$). Absorption is similar in carbon, and the proportion of the two types remained the same. The total γ-rays gave about nineteen divisions per minute. From radium-*E* a γ-radiation giving only 0·5 div. per minute was obtained. As nearly as could be seen it was homogeneous, and identical with the softer type given by radium-*D*, but that it was not due to the latter was shown by the fact that it decayed to zero with the period of radium-*E*. For similar β-radiations, the γ-rays of radium-*D* were some two hundred times greater than those of radium-*E*. The soft γ-radiations of radium-*D* and -*E* are probably the characteristic radiations of the *L* series to be expected of an element of atomic weight 210. F. S.

The Spectro-analytical Proof of Molecule Canal Rays. JOHANNES STARK (*Ber. Deut. physikal. Ges.*, 1913, **15**, 813—820).—A method is devised for detecting the presence of molecule canal rays in addition to the atom canal rays. By means of this method the author has been able to detect the presence of H_3 canal rays, and this confirms the existence of H_3 molecules which he is of the opinion are identical with Thompson's X_3. J. F. S.

Uni- and Multi-valent Canal Ray Lines of Aluminium, Argon, and Mercury. JOHANNES STARK, GEORG WENDT, H. KIRSCHBAUM, and R. KÜNZER (*Ann. Physik*, 1913, [iv], **42**, 241—302. Compare this vol., ii, 546).—The canal-ray spectra of aluminium, argon, and mercury are examined with the object of determining the nature of the carriers to which the different lines owe their origin. It is shown that aluminium gives rise to uni-, bi-, and ter-valent positive

atom ions in front of the cathode, and therefore gives rise to canal rays of three different velocity regions. When the potential fall at the cathode is less than about 8000 volts, the number of uni- and bi-valent aluminium atom ions in the canal rays behind the cathode far exceeds that of the tervalent aluminium ions, but above 8000 volts tervalent ions are readily obtainable in the canal rays. The univalent ions are the carriers of the doublet λ 3961·7—3944·2 Å ; the bivalent ions are the carriers of the line λ=4663·5 Å, and the lines λ=4529·7, λ=4513·0, λ=4480·0 Å belong to the tervalent ions. The lines of the red argon spectrum are due to univalent positive argon ions; the visible lines of the blue argon spectrum are mainly due to bivalent positive ions, although a small number are to be attributed to the positive tervalent ions. During the emission of variable intensities, a movable equilibrium is set up between the uni-, di-, and ter-valent argon ions. Slow-moving cathode rays give rise to univalent ions by their collisions; rapidly-moving cathode rays are responsible for bi- and ter-valent argon ions. The mercury doublet λ=2847—2224 Å is caused by the univalent mercury atom ions, whilst the first and second subsidiary mercury series of triplets are occasioned by the positive bivalent mercury ion. The lines λ 4916, 4339, 4347, 4109, and 4078 Å belong to the spectrum of the tervalent mercury ions, and the very intensive lines λ 4797, 4707, 4486, and 4398 A are due to the positive quadrivalent mercury ions. The line λ 2536·7 Å, which is probably the first member of a series of single lines, belongs to the spectrum of the neutral mercury atom. Mercury canal rays in either hydrogen or helium contain chiefly uni- and bi-valent positive rays, and very few tervalent rays when the cathode potential fall is less than 8000 volts. With a cathode potential fall of 15,000 volts and over, there are a large number of tervalent rays and some quadrivalent rays. Under special conditions an equilibrium is set up between the neutral canal rays and the uni-, bi-, ter-, and quadri-valent canal rays. J. F. S.

Electron Affinity at the Collision Ionisation of Atoms in Chemical Compounds. JOHANNES STARK (*Ber. Deut. physikal. Ges.*, 1913, **15**, 809—812).—A theoretical paper, in which it is shown from many examples that when canal rays cause the formation of a positive atom ion by their collision with a chemical compound of an electropositive element with an electronegative element, it is generally the electropositive element which forms the ion.

J. F. S.

The Unstable Nature of the Ion in a Gas. RICHARD D. KLEEMAN (*Proc. Camb. Phil. Soc.*, 1913, **17**, 263—279).—A number of experiments are described on ionisation by collision with negative ions. The experiments were conducted in the vapours of ether, ethyl propionate, methyl butyrate, carbon tetrachloride, ethyl chloride, chloroform, pentane, benzene, acetaldehyde, methyl formate, methyl bromide, methyl iodide, ethyl bromide, ethyl iodide,

and carbon disulphide, and in the gases acetylene, hydrogen, oxygen, nitrous oxide, carbon dioxide, and air. It is shown that the ratio of the number of free ions to clusters is independent of the pressure. The ratio mentioned is obtained from the ratio of the abscissæ at a common ordinate of two curves *A* and *B*. The curve *A* being obtained with the ions drawn through the gauze screen from the space adjacent to its lower side, *B* was obtained after placing a quantity of radium near the chamber. The majority of the gases and vapours mentioned above gave the same value for the ratio, carbon tetrachloride, carbon disulphide, benzene, air, oxygen, chloroform, and hydrogen giving ratios considerably greater. The behaviour of ion clusters in gaseous mixtures is considered theoretically. J. F. S.

The Emission of Electrons by Platinum, and the Origin of the Activity of Oxide Electrodes. KARL FREDENHAGEN (*Ber. K. Sachs. Ges. Wiss. Math.-phys. Kl.*, 1913, **65**, 42—74).—A continuation of work (A., 1911, ii, 571; 1912, ii, 517) on the emission of electrons by heated metals, and the effects of heating platinum and calcium in the presence of an oxidising agent (fuming nitric acid) to a high temperature in a vacuum are now described. F. M. G. M.

Ions from Hot Salts. OWEN W. RICHARDSON (*Phil. Mag.*, 1913, [vi], **26**, 452—457. Compare Abstr., 1911, ii, 9, 10, and 1051; Davisson, 1912, ii, 116).—The salts were examined chiefly to determine e/m, and in consequence the molecular weight of the emitted ions. For zinc iodide freshly heated, the ions had an "electric atomic weight" (atomic weight divided by number of charges) 31·6 corresponding with Zn_{++}, lower values being obtained after prolonged heating. For cadmium iodide there is an emission of Cd_{++} lasting for some hours, followed by the emission of K_{+} and Na_{+} in turn, the temperature being from 500° to 930° Pt. Strontium iodide at about 1200° gave Sr_{+}, ferric chloride at 518° gave only ions corresponding with K_{+}, and manganous chloride between 878° and 962° gave ions of which the electric atomic weight increased from 33·9 to 79·4, and then decreased to 39·2, due probably to a mixture of K_{+} and Na_{+} with $MnCl_{+}$ and possibly Mn_{++}.

The negative ions emitted by salts at relatively low temperatures are mixtures of electrons and heavy ions, whereas all the negative ions from platinum are electrons. For calcium iodide the proportion of the current carried by the negative electrons was 0·375 at 292°, 0·734 at 315°, rising to above 0·9 at 365°. The electric atomic weight of the heavy negative ions was 120, indicating that they were I_{-}. When left cold in a vacuum (0·001 mm.) calcium iodide loses its power of emission of negative ions, although it recovers it when exposed to air at higher pressure, as well in dried air as in ordinary air. Strontium iodide and barium iodide gave results very similar to calcium iodide. Calcium bromide gave a less copious emission than the iodide and fluoride, but the numbers

obtained pointed to Br_- as the ion emitted. Calcium fluoride gave a large proportion of electrons even at low temperature, and the value, 97, obtained for the electric atomic weight of the heavy ions may not be accurate. In every case the deviations from the calculated value for the ions to which the results were attributed were in such a direction as to point to an undiscovered common impurity giving ions of the value of about 100 for the electric atomic weight.

F. S.

The Use of Calcium Hydride for the Autogenous Reduction of "Crude Sulphate" in the Preparation of Radium and Mesothorium. ERICH EBLER and W. BENDER (*Zeitsch. anorg., Chem.*, 1913, **83**, 149—158).—The absolutely dry sulphate, powdered as finely as possible, mixed with equally finely powdered calcium hydride, is pressed into a crucible and fired, as in the thermite process, by magnesium ribbon and a priming mixture. The reaction occurs with violence, and the liberated hydrogen burns off in a few minutes. Since silica is not reduced under these conditions, only the quantity of calcium hydride is added necessary to reduce the sulphates present. The more lead sulphate present the more violent is the reduction, and mixtures with more than 20% are dangerous in large quantity. The product is stirred as quickly as possible into hot dilute hydrochloric acid free from sulphuric acid, and the hydrogen sulphide expelled rapidly by boiling. If lead is present normal acid is used in which lead sulphide is insoluble, the residue being repeatedly re-extracted. In absence of lead, 5*N*-acid is employed. From the solution, the barium–radium chloride is precipitated in pure state by passing in hydrogen chloride, until three-fourths of the barium chloride, containing all the radium, is precipitated. In trials with crude sulphate from carnotite, equal parts of hydride and sulphate were employed, the extracted barium chloride weighed 37% of the raw material, and contained 80·5% of the radium present. In trials with a poor lead-free crude sulphate, from a vanadium and copper containing chalcolite from Ferghana (Turkestan), two-thirds of the weight of hydride was used; the extract weighed 24% of the raw material, and contained 86·2% of the radium present. The reduction of the sulphate is extraordinarily complete, and the method shortens the process of extracting the radium considerably. The calcium hydride (from Elektrochemische Werke, Bitterfeld) is powdered in a steel ball mill, and contains then 80% of calcium hydride. F. S.

Method for the Determination of Radium in Radioactive Substances. ARNOLD L. FLETCHER (*Phil. Mag.*, 1913, [vi], **26**, 674—677).—In this method, by an adaptation of the micro-furnace, a small, splintered and weighed fragment of the mineral or salt (from 0·01 to 0·0001 gram) is placed in a hollow in a thin carbon rod, and raised for ten to thirty seconds to a temperature between 2000° and 3000° inside a small chamber provided with a rubber balloon to allow for the expansion and generation of gas. Afterwards the contents of the chamber are drawn into an exhausted

electroscope in the usual way. Trials with small quantities of different minerals gave concordant results, and the method has the great advantage that it does not require the use of chemicals. Experiments showed that the rapid escape of emanation from heated minerals does not begin until 750°, and de-emanation is complete at bright redness. F. S.

Distribution of the Active Deposit of Radium in an Electric Field. II. EDWARD M. WELLISCH (*Phil. Mag.*, 1913, [vi], **26**, 623—635; *Amer. J. Sci.*, 1913, [iv], **36**, 315—327. Compare Abstr., 1912, ii, 521).—As the result of this investigation, the amount of active deposit settling on the cathode appears to reach a definite limiting fraction of the total with large potentials, but columnar recombination of the positively charged active deposit particles with negative ions reduces the amount for smaller potentials, whilst volume recombination operates for very small potentials. The recoil atom in its passage through the gas produces a great number of ions, and under these conditions the atom may lose its positive charge, but the proportion so discharged is not influenced by the electric field or the pressure of the gas, which affect the columnar and volume part of the recombination. There is evidence that the recoil atoms differ from ordinary positive ions, more readily suffering recombination, which possibly is connected with their larger mass. This is especially the case with moist gases, but the difference is well marked in gases dried with all care. Owing to its larger mass and slower motion of diffusion the recoil atom escapes from the column of ions it produces less readily than the positive ion. The limiting value to the percentage cathode activity depends on the nature of the gas. This is shown by experiment to be specially small (10%) in ethyl ether, which is ascribed to the ease with which the molecules of this substance are ionised. F. S.

The Distribution of the Active Deposit of Actinium in Electric Fields. H. P. WALMSLEY (*Phil. Mag.*, 1913, [vi], **26**, 381—401).—Using special precautions to eliminate dust and the accumulated active deposit products from the gas, it was found that the actinium active deposit distributes itself exponentially along the length of a negatively charged wire, stretched axially through a tube along which an air stream carrying the emanation is passing, and therefore that the ratio of the deposits on the cathode and anode is independent of the concentration of emanation in the gas. By measuring the variation with voltage of the active deposit, both when the wire was charged positively and negatively, it was shown that the anode activity decreases and the cathode activity increases with increase of voltage, and hence that none of the active deposit atoms carry a negative charge. The measurements were found to conform to the view that the actinium-*A* atoms acquire a positive charge during their creation from the emanation, and then are subject, like positive ions, to neutralisation of the charge by recombination with negative ions in the gas.

But in circumstances when the whole of the actinium-*A* is transformed during the passage to the electrode and the whole deposit reaches the electrode as actinium-*B*, recombination continues, which renders it extremely probable that actinium-*B* also acquires a positive charge at the moment of its creation. External ionisation of the gas increases the amount of uncharged active deposit, and the proportion deposited on the anode, as is the case with the radium active deposit. The effects of dust particles and large ions in the gas in increasing the anode activity were also studied. F. S.

Preparation of Radioactive Substances from Thorium. FRITZ GLASER (*Chem. Zeit.*, 1913, **37**, 1105—1106. Compare this vol., ii, 465).—The presence of lead sulphate is an advantage in the separation of thorium-*X* from monazite sand, thorium, etc., as the radioactive substance is absorbed by the lead sulphate. When the lead is subsequently separated as sulphide, the radioactive substance remains in solution. Radioactive substances may also be prepared from mesothorium, barium salts being added before the original monazite sand is decomposed with sulphuric acid in order that the substances may be concentrated with the barium sulphate. W. P. S.

The Distribution of the γ-Rays among the Single Products of the Thorium Series. LISE MEITNER and OTTO HAHN (*Physikal. Zeitsch.*, 1913, **14**, 873—877).—Thorium-*X* was freed from its subsequent products by ignition three times in a platinum dish, and showed initially less than 0·2% of the equilibrium amount of thorium-*C*. The initial radiation was taken in a β-ray electroscope through a variety of thicknesses of aluminium foil. It was found that the ratio of the final equilibrium activity to the initial activity reached a maximum for 0·5 mm. aluminium, which corresponds with the complete absorption of the soft β-rays of thorium-*X*, then diminished as the equilibrium β-rays of thorium-*D* are absorbed, and finally increased for greater thicknesses, namely, 2·5 mm. aluminium, and 0·7 mm. of lead. This indicates that thorium-*X* emits a γ-radiation more penetrating than the β-rays, and less penetrating than the γ-rays of thorium-*D*.

Thorium-*B* was shown to give a γ-radiation by comparing the α- and γ-ray recovery curves of an initially pure preparation. The α-ray curve rose from zero, but the γ-ray curve rose from an initial value about 22% of the maximum activity, as measured without screens, except the 2 mm. thick brass wall of the γ-ray electroscope. These γ-rays are much more easily absorbed than those of thorium-*D*, and are reduced to half-value in about 1 mm. thickness of lead.

Thorium-*C* gives the greater portion of the β-rays of thorium-*C* and -*D*, and these are of a harder type than those of thorium-*D*, but the latter gives practically all the γ-rays (A., 1912, ii, 514). Two preparations of pure thorium-*C*, obtained by deposition on a nickel foil which was cut in half, were examined for the recovery

curve of γ-rays through different thicknesses of lead. The two recovery curves were of the same form, proving that if thorium-*C* emits any γ-radiation at all, its penetrating power, between 0 and 19 mm. of lead, is identical with that of the γ-radiation of thorium-*D*. F. S.

Some Experiments with the Active Deposit of Thorium. Ernest Marsden and R. H. Wilson (*Phil. Mag.*, 1913, [vi], **26**, 354—361).—The question whether thorium-*C* consists of two separate products, or of one product disintegrating dually in two ways, was investigated by finding whether during the decay of the α-radiation of thorium-*C*, separated from a solution by means of a nickel plate, the α-rays of range 4·8 cm. decayed at a different rate from those of range 8·6 cm. This was done by balancing in two ionisation chambers the current due to the latter part of the range of the rays of longer range against the first part of the range of both rays together. No alteration of balance occurred as the radiations decayed, and it was deduced that if thorium-*C* consists of two separate products, their periods must be the same to within 1 part in 570.

A repetition of the experiments of Meitner (A., 1912, ii, 723) confirmed the results, but it was found that thorium-*C*, which, when deposited from the emanation on a wire, is not volatile below 1200° in air, is appreciably volatile when evaporated from a hydrochloric acid solution and heated gently, not above 300°. From a nitric acid solution no volatilisation occurs. In presence of stannous chloride, zinc chloride, or even ammonium chloride, practically the whole may be volatilised with the fumes of the added salt. It appears that the differences observed by Meitner in the α- and γ-ray recovery curves of thorium-*B* are to be ascribed to more complete volatilisation of thorium-*C* from the single drop of α-ray preparation than from the larger quantity of γ-ray preparation. Other experiments showed that no true separation of the two sets of α-rays from thorium-*C* had been effected. Experiments with the β-rays of thorium-*C* showed that the product giving these rays could not be separated from the parent of thorium-*D*.

A soft γ-radiation was found to be emitted by thorium-*B* analogous to that recently discovered for radium-*B*. F. S.

The Position where the Thorium Series Branches. P. Beer and Kasimir Fajans (*Physikal. Zeitsch.*, 1913, **14**, 947—951. Compare preceding abstract).—The absorption curves of the α-rays from thorium-*C* separated by nickel from the solution of the active deposit, both with and without the use of stannous chloride, were found to be identical, whereas if Meitner's explanation were correct, a difference should have been observed. Similarly, the absorption curves of the β-rays were identical. Meitner's results were traced to the volatility of thorium-*C* chloride in presence of stannous chloride. The greater volatility of the *C*-product than the *B*- in form of chloride, and the lesser volatility in form of metal or oxide, is in accord with the fact that the *C*-product is analogous to

bismuth, and the *B*-product to lead. Experiments with radium-*E*, which is chemically identical with thorium-*C*, showed that in absence of stannous chloride it is quantitatively precipitated on nickel; in presence of stannous chloride only 10% is separated. These observations support the scheme of Marsden and Darwin that the branching of the thorium series occurs at the *C*-member, and remove all the objections to it. F. S.

The Branching Relations and Atomic Weights of the *C*-Members of the Three Disintegration Series. KASIMIR FAJANS (*Physikal. Zeitsch.*, 1913, **14**, 951—953. Compare this vol., ii, 660).—It is shown that the products, actinium-*C*, thorium-*C*, and radium-*C*, which disintegrate dually along two branches, conform to the previous generalisation. The separate periods of the α-modes of disintegration are respectively 2·15 minutes, 2·87 hours, 45 days, and the estimated atomic weights, 210·5, 212·4, and 214·5. The separate periods of the β-ray modes of the two latter are 1·55 hours and 19·5 minutes. In the same place in the periodic table is radium-*E*, with atomic weight 210·5, and β-ray period five days, which also conforms. F. S.

Range of the Recoil Atoms from Thorium-*C* and Actinium-*C*. A. B. WOOD (*Phil. Mag.*, 1913, [vi], **26**, 586—597).—In the first method the active deposit on a small platinum disk was placed at the centre of a hemisphere, lined with tin foil, and kept charged positively to the disk. Recoiled atoms of thorium-*D* or actinium-*D* reached the hemisphere at low pressures by virtue of their momentum, whereas those just failing to reach were drawn back to the source by the action of the field, which was not sufficiently intense appreciably to affect the range of the recoil atoms. Dust and moisture had to be eliminated. The amount of recoil product was measured in a β-ray electroscope, and curves plotted of the amount for different pressures of air and hydrogen. The amount fell off with increasing pressure to about 4 mm. pressure (of air), and then remained constant at a small value, due probably to diffusion of recoil atoms which have become discharged *en route*. By extrapolation, it was estimated that the maximum range of the recoil atoms of thorium-*D* is 0·12 mm. in air at *N.T.P.*, and in hydrogen rather more than four times longer. For actinium-*D* the range was found to be almost exactly the same, indicating that thorium-*D* is produced in the change of thorium-*C* in which an α-particle of range 4·8 cm. is emitted (that of actinium-*C* being 5·4 cm.), and not in the change of thorium-*C* in which the α-particle of range 8·6 cm. is expelled, in agreement with the accepted view. The recoil atoms showed marked lack of homogeneity, due either to irregularities in the surface of the plate from which they recoil, or to scattering in their passage through the gas.

In the second method, the ionisation produced by the recoil atoms was measured at different pressures in an apparatus analogous

to that used by Bragg for determination of α-ray ranges. After correction for ionisation due to α-rays and for δ-rays, the curves connecting the ionisation per mm. of pressure and the pressure was found to be of the same form for actinium-C as that connecting the amount of recoil product with pressure in the first method. But for thorium-C a marked difference was observed, indicating that in addition to thorium-D there is a second inactive recoil product of longer range capable of producing ionisation, and corresponding with the change of thorium-C associated with the 8·6 cm. range α-particle. The range of this recoil product was estimated to be 0·175 mm. in air, and 0·74 mm. in hydrogen, in agreement with Wertenstein's conclusion that the ranges of recoil products are proportional to the ranges of the α-particles expelled in the same change. F. S.

Uranium-X_2 the New Element of the Uranium Series. KASIMIR FAJANS and O. GÖHRING (*Physikal. Zeitsch.*, 1913, **14**, 877—884).—Since the product of a β-ray change is electrochemically nobler than its parent, it is to be expected that uranium-X_2 would be easier to separate electrochemically than uranium-X_1. Separation was effected by immersing polished lead plates for a minute in a feebly acid solution of uranium-X containing iron. Decay curves are shown, from which it is deduced that the mean value of the half-period was 1·15 minutes ($\pm$0·01), and the period of average life 100 seconds. Since uranium-X_1 is analogous to thorium and uranium-X_2 to tantalum, the precipitation of tantalic acid by acidifying a solution of potassium hexatantalate was tried to effect the separation. Uranium-X_2 is nearly quantitatively precipitated without uranium-X_1, when an acid solution of uranium-X, containing thorium, is added to an alkaline solution of potassium hexatantalate. With such preparations it was shown that uranium-X_2 emits only the hard type of β-rays given by uranium-X. From the recovery-curve of the β-rays of uranium-X_1, prepared, free from uranium-X_2, by precipitation of thorium-uranium-X in acid solution with hydrofluoric acid, it was shown that uranium-X_2 gives practically no hard β-rays. It could not be shown experimentally that uranium-X_1 gives the soft β-rays and uranium-X_2 the γ-rays, as may reasonably be inferred. F. S.

The Disintegration of Uranium-X. ALEXANDER FLECK (*Phil. Mag.*, 1913, [vi], **26**, 528—535. Compare preceding abstract).—The existence of the uranium-X_2 of Fajans and Göhring has been confirmed. It is deposited from slightly acid solution of uranium-X on lead, in small amount on zinc and magnesium, but not on gold or platinum. The hard β-radiation of the lead plate fell, in six or seven minutes, to the practically constant value of 60 or 80% of the value as first measured, from one and a-half to two minutes after removal from the solution. It is precipitated in excess of the equilibrium amount with lead chloride, bismuth oxychloride, lead or bismuth sulphide, when these precipitates are formed in a solution of uranium-X. On the other hand, a precipitate of lead

sulphate contains initially less than the equilibrium amount of uranium-X_2, and from such a preparation the recovery curve of the hard β-rays was obtained. Precipitates of barium or thorium oxalate appear to be similar. By comparing the hard and soft β-rays from such a precipitate of lead sulphate, it was shown that the soft β-radiation comes from the parent substance, uranium-X_1, of period of average life 35·5 days, whilst the hard β-radiation comes from the product, uranium-X_2. The mean value found for the period of average life was 1·6 minutes, corresponding with the half-period 1·1 minutes. In one experiment with bismuth oxychloride, which could not be repeated, 94·5% of the equilibrium amount of uranium-X_2 was removed. It could not be volatilised at all under any conditions, even when evaporated and ignited with hydrofluoric acid or acid potassium fluoride, although under these conditions tantalum is more volatile than niobium. It has not been found possible to obtain a definite proof that it occupies the predicted place in the periodic table as "eka-tantalum."

F. S.

The Existence of Uranium-*Y*. GEORGE N. ANTONOV (*Phil. Mag.*, 1913, [vi], **26**, 332—333).—Controversial against Fleck (this vol., ii, 464), claiming that the existence of uranium-*Y* has not been disproved.

F. S.

Emission of Electrons from Tungsten at High Temperatures: an Experimental Proof that the Electric Current in Metals is Carried by Electrons. OWEN W. RICHARDSON (*Phil. Mag.*, 1913, [vi], **26**, 345—350; *Physikal. Zeitsch.*, 1913, **14**, 793—796).—The view that the emission of electrons from heated solids is invariably a secondary effect accompanied by traces of chemical action is combated. Tungsten filaments, surrounded by a concentric cylindrical electrode of copper gauze, were heated in a high vacuum, special methods being employed to remove absorbed gases and volatile impurities. The number of electrons emitted by the glowing filament was compared with the number of molecules of gas emitted, as deduced from the rise of pressure of a gauge attached, and found to be from 5 to 200 million times greater. It is also many thousand times greater than the calculated number of impacts of gas molecules upon the filament. The possibility that the emission is connected with the slow evaporation of the tungsten was negatived by the fact that, per atom of tungsten so lost, about a million electrons are emitted. In some circumstances the mass of the electrons emitted exceeds the mass of the tungsten lost, and amounts to 4% of the total mass of the tungsten. The possibility that condensable vapours, not measured by the gauge, may cause the emission is negatived by the fact that liquid air and charcoal do not affect the emission, which is not affected by very considerable changes in the amount and nature of the gases and vapour present. It is not denied that under other circumstances electrons may be emitted from metals by the action of chemical reagents, and that this emission would follow the same

law of dependence on temperature. The experiments prove that the current in metals must be carried by electrons entering the metal from outside points of the circuit. F. S.

The Helium Content and Radioactivity of Natural Gas. EMERICH CZAKÓ (*Zeitsch. anorg. Chem.*, 1913, **82**, 249—277. Compare Cady and McFarland, A., 1907, ii, 949).—Natural gas is examined in a special apparatus, in which hydrocarbons are condensed by liquid air, and other gases are removed by means of cooled charcoal. All the gases examined are found to contain helium, the percentages in natural gas being 0·0014 from Kissármás (Hungary), 0·0063 from Pechelbronn, 0·0089 from Wels (Austria), and 0·0141 from Neuengamme near Hamburg; also 0·0067 in a mine gas from Gneisenau, and 0·38 in gas from a deep boring in Alsace, the last containing 46% of nitrogen, whilst the others are low in nitrogen. Atmospheric air contains about 0·0005% of helium, and calculations are given of the quantity passed daily into the atmosphere from some of the principal thermal springs and sources of natural gas.

The radioactivity of the same gases is determined by means of the fontaktoscope. All the gases examined contain emanation, the quantity being small, and varying within rather narrow limits. The deep boring in Alsace gives a very high activity, the primary rock being reached in this case, whilst the other borings are in sedimentary rocks. An approximate proportionality between activity and helium content is observed. The quantity of helium is, however, far too large to be derived entirely from the recent disintegration of radium, and the greater part must have been present previously in the rocks. C. H. D.

An Occurrence of Radioactive Minerals. W. MIRONOV (*Zeitsch. Kryst. Min.*, 1913, **52**, 619; from *Sitzungsber. Naturf. Ges. St. Petersburg*, 1910, No. 7—8, 286—290).—Radioactive minerals occur in a granular limestone of Devonian age at Tyuya-Muyan, 50 versts south-east of Andijan in Fergana, Russian Central Asia. One of these minerals—ferganite—has a radioactivity of 1·44, compared with thoria as 1, and Joachimsthal pitchblende as 1·82. L. J. S.

Occluded Gases in Geissler Tubes. ROBERT W. LAWSON (*Physikal. Zeitsch.*, 1913, **14**, 938—941).—The author has extracted the gases found in Geissler tubes, some of which were new, and some of which had been used for prolonged periods. He draws the conclusion from the experiments that all the gases observed had been occluded in the electrodes, and that the formation of helium from hydrogen is not confirmed by his experiments. In the same way the synthesis of neon from helium and oxygen is unlikely, since helium was present long after the neon; and oxygen was only observable when the tube had been in use for several hours. The author attributes the relatively large amount of oxygen to the decomposition of neon into helium and oxygen (compare Collie and Patterson, T., 1913, 419). J. F. S.

Electrochemistry of the Halogens, Chlorine, Bromine, Iodine and of Iodine Monochloride, Iodine Bromide, and Iodine Trichloride in Nitrobenzene Solution. LUDWIK BRUNER and ANTONI VON GALECKI (*Zeitsch. physikal. Chem.*, 1913, **84**, 513—557).—A large number of conductivity experiments have been carried out with solutions of the above-mentioned substances and hydrogen bromide in nitrobenzene solution. It is shown that the conductivity differs as absolutely dry nitrobenzene or nitrobenzene which has been exposed to the air is used. The various solutions were therefore in many cases prepared and measured in entire absence of moisture and out of contact with air. In perfectly dry nitrobenzene, chlorine, bromine and iodine do not conduct electricity, whilst iodine trichloride and iodine bromide possess considerable conductivity. In moist solutions of nitrobenzene, iodine, bromine, bromine iodide and iodine trichloride all conduct, the conductivity increasing in the order in which they are written above. Dilution of the solutions causes an increase in the equivalent conductivity. On electrolysis, both in dry and moist nitrobenzene solutions, the halogen is always deposited on the anode in accordance with Faraday's law. The electrodes in these experiments were of silver which had been coated with a silver haloid, and consequently were not affected by coming into the halogen solutions. The amount of electrolysis was determined by an increase in the weight of the anode due to further formation of silver haloid. There was no deposition on the cathode but in some cases a slight reduction occurred. Continued electrolysis caused complete removal of the halogens from the solution. In transport experiments the halogens wandered entirely to the anode, the quantity of the halogen round the anode corresponded with two equivalents for every 96,540 coloumbs passed through the solution except in the case of bromine, where the relationship is smaller, and varied between 1·5—1·7 equivalents. The nature of the conductivity in these cases is discussed, and it is shown that it is not due to the presence of halogen acids or to an ionisation of the halogens $ICl \longrightarrow I^{\cdot} + Cl'$. An explanation is offered based on the formation of additive compounds of the oxonium type with the solvent, thus $C_6H_5 \cdot N \begin{smallmatrix} \nearrow O{=}ICl \\ \searrow O{=}Cl_2 \end{smallmatrix}$. Measurements are also given of the conductivity and transport of hydrogen bromide in dry nitrobenzene solution. J. F. S.

The Variations in the Electrical Conductivity of Nitrobenzene Solutions of Bromine. LUDWIK BRUNER and J. SAHBILL (*Zeitsch. physikal. Chem.*, 1913, **84**, 558—569. Compare preceding abstract).—The influences which may bring about a fluctuating conductivity in solutions of nitrobenzene have been studied. It is shown, in the first place, that the addition of water is not responsible entirely for the changes. On distilling nitrobenzene, four fractions were obtained, each extending over a range of 0·25°; the first of these gave a solution with bromine which had a conductivity value six times as large as that of the last fraction. On freezing a solution

of bromine in nitrobenzene and then raising to the experimental temperature, the conductivity rises permanently. The addition of several oxides (Ag_2O, Al_2O_3, and CdO) reduce the conductivity of a bromine solution about seventy-five times. Other substances, such as silica and barium sulphate, have no action. A hypothesis to explain the changes of conductivity is given. This is based on the formation of conducting additive compounds and an absorption of these conductors by the added oxides. J. F. S.

The Electrical Conductivity and Electrolysis of Solutions of Bromine, Iodine Bromide, Iodine Chloride and Iodine Trichloride in Liquid Sulphur Dioxide. LUDWIK BRUNER and E. BEKIER (*Zeitsch. physikal. Chem.*, 1913, **84**, 570—584. Compare preceding abstracts).—Experiments similar to those of Bruner and Galecki (*loc. cit.*) in nitrobenzene solution have been carried out in sulphur dioxide solution. It is shown that liquid sulphur dioxide which has been carefully dried by distilling over phosphoric oxide has no conductivity. A solution of bromine has no conductivity in the absence of moist air, but as soon as moisture is admitted to the apparatus a considerable conductivity is set up. The conductivities of the halogen compounds mentioned above have been measured in sulphur dioxide solution, and it is shown that the equivalent conductivity in each case is about one hundred times smaller than that given by Walden. In the latter cases the authors attribute the conductivity to the formation of conducting additive compounds with the solvent. From electrolysis experiments it is shown that the halogens are deposited on the anode, and that there is no evidence of the existence of a halogen acting as cation in sulphur dioxide solution. J. F. S.

Electrical Conductivity of Dilute Solutions of Some Sodium Salts in Ethyl Alcohol. NILRATAN DHAR and DEVENDRA NATH BHATTACHARYYA (*Zeitsch. anorg. Chem.*, 1913, **82**, 357—360).—The value of μ_{∞} for sodium benzoate and other organic salts in alcohol is less than 40, whilst for inorganic sodium salts it approaches 45. C. H. D.

Electrical Conductivity of Solutions of Molybdenum Pentachloride. STEWART J. LLOYD (*J. Physical Chem.*, 1913, **17**, 592—595). —Molybdenum pentachloride dissolves in organic solvents, forming solutions which have a greenish- or a reddish-brown colour. The solutions with a green colour show a decrease in molecular conductivity on dilution, whilst the reddish-brown solutions either do not conduct appreciably or show an increase in molecular conductivity when diluted. In the case of the acetone solutions which are of a deep green colour, the conductivity decreases on dilution, passes through a minimum, and on further dilution increases. This change in the character of the conductivity-dilution curve is not accompanied by any corresponding change in the colour of the solutions. Data are recorded for solutions in methyl and ethyl acetate, acetone, benzaldehyde, pyridine, and glycerol. H. M. D.

A General Relation between the Concentration and the Conductivity of Ionised Substances in Various Solvents. CHARLES A. KRAUS and WILLIAM C. BRAY (*J. Amer. Chem. Soc.*, 1913, **35**, 1315—1434).—The authors propose to express the relation between the concentration and the conductivity of electrolytic solutions by the general equation: $(c\gamma)^2/c(1-\gamma)=K+D(c\gamma)^m$, where c is the concentration, γ the conductivity ratio Λ/Λ_0, and K, D, and m are constants. In sufficiently dilute solutions, the term involving $(c\gamma)^m$ becomes negligible in comparison with K, and the equation approaches the simple mass-action law as a limit. In concentrated solutions K becomes negligible in comparison with $D(c\gamma)^m$, and the equation assumes the form of that of Storch. For $m>1$ the molecular conductivity passes through a minimum value, whilst for $m<1$ the molecular conductivity decreases continuously with increasing concentration.

At first glance it may appear that the proposed equation is a purely arbitrary one, involving four constants, Λ_0, D, K, and m (Λ_0 being involved in the determination of γ). The constants, however, are not arbitrarily determined in all respects. K and Λ_0 are, of course, interdependent, but they may in most cases be determined independently of D and m. In many cases m may be determined independently of the three remaining constants. Graphical methods are described whereby the constants may be conveniently evaluated from the experimental data. It is also shown that a method is provided whereby the law of mass action may be tested without assuming a value for Λ_0, a result of very great importance.

The general equation was tested on, and found to apply to, the extensive conductivity data which have been accumulated by Franklin and his co-workers for solutions in liquid ammonia. The deviations from the law of mass action become appreciable at ionic concentrations between $0{\cdot}001N$ and $0{\cdot}0001N$. The smaller the ionisation of the electrolyte the higher the total concentration up to which the law of mass action is sensibly obeyed.

With the aid of the transference data of Franklin and Cady (A., 1904, ii, 466) the ionic velocities of a considerable number of ions in liquid ammonia solutions have been calculated, and these values compared with those of the same ions in water. The former are, on the average, 2·59 times greater than the latter, although the ratio is by no means constant. It is noteworthy that the velocity of the ammonium ion is not larger than that of the other cations in liquid ammonia, and from this result and other considerations the conclusion is drawn that the speed of certain ions in a given solvent is not related to the possible dissociation of this solvent into ions of the same character as those of the dissolved substance.

The general equation is also found to apply to solutions in liquid sulphur dioxide. The influence of temperature on the conductivity of these solutions is readily accounted for by the variation which these constants undergo with change in temperature.

In the case of dilute solutions of strong electrolytes in non-aqueous solvents (including the higher alcohols), conductivity measurements on which have been made by Dutoit and his co-workers, it was found that the law of mass action applies, within the limits of experimental error, up to ionic-concentrations between 0·0001 and 0·001 normal; at higher concentrations the deviations become measurable. This limiting ionic concentration is approximately the same for solutions of a given electrolyte in different solvents, and for different electrolytes, strong or weak, in the same solvent.

In the case of concentrated solutions in solvents of low ionising power, γ may be neglected in comparison with 1, and the general equation simplifies to $c\Lambda^2 = P(c\Lambda)^m$, where P is a constant involving Λ_0. Since Λ_0 does not occur explicitly in this equation, the general equation may be tested without a knowledge of the value of this constant. The equation was found to hold for all cases (sixty-seven solutions and twelve solvents) for which trustworthy data exist.

The general equation is also applicable to aqueous solutions of strong electrolytes, for example, to solutions of potassium chloride varying in concentration from 0·001 to 2·0 normal. The agreement is to within 0·1%, but to obtain this agreement in the more dilute solutions it is necessary to assume $\Lambda_0 = 128·3$ instead of the commonly accepted value 130·1. In all probability the commonly accepted values for Λ_0 for all binary electrolytes are 1—2% too high.

There is reason for believing that salts of higher valence type obey the same general law as do binary electrolytes, but the general equation cannot be tested as yet, owing to the lack of available data and because of complications arising from the formation of intermediate ions.

The relation between the ionising power of a solvent and the values of constants K, D, and m is discussed, and it is shown that, with decreasing dielectric constant, K approaches zero (or, at least, a very small value); D approaches a constant value, 0·35, which undergoes but little change as the dielectric constant falls below 22; and m increases, approaching a value greater than 2. The exceptions to the Nernst-Thomson rule lose their significance in the light of the results obtained in this paper, and when the comparison for a given solute is made between the constants of the general equation instead of between the conductivities directly, no discrepancies appear.

From a theoretical point of view the most important results obtained are: that all solutions of binary electrolytes obey the same dilution law; that the law of mass action is obeyed at high dilutions; that the divergence from the law of mass action at higher concentrations is a function of the ionic concentration; and that for a given electrolyte in different solvents the trend of the conductivity curve is determined by the dielectric constant of the solvent. Finally, it is shown that the fundamental hypothesis of Arrhenius,

according to which the ionisation is measured by the ratio Λ/Λ_0, is in harmony with the observed facts, not only in very dilute solutions, but also in concentrated solutions (up to more than normal when viscosity changes are taken into account). An explanation of the observed deviations from the law of mass action is to be looked for in the interacting forces due to the presence of charged particles (ions) throughout the body of the solution. T. S. P.

Chemical Reactions and Electrical Conductivity of Non-aqueous Solutions. HAMILTON P. CADY and H. O. LICHTENWALTER (*J. Amer. Chem. Soc.*, 1913, **35**, 1434—1440).—Kahlenberg and others (Kahlenberg, A., 1902, ii, 301; Sammis, A., 1906, ii, 835; Gates, A., 1911, ii, 394) have conducted double decompositions in non-aqueous solutions, and state that some instantaneous reactions occur in solutions which show no conductivity, that is, in solutions where dissociation has not occurred. This statement has been disputed by Allen (*Kans. Univ. Sci. Bulletin*, 1905), and the authors have carried out further experiments on the subject.

Benzene, toluene, and light petroleum were used as solvents, the salts employed being silver melissate, copper melissate, lead stearate, barium linoleate, lead erucate, and copper oleate. In all experiments moisture was rigorously excluded.

The benzene and toluene solutions of each of these salts showed some conductivity, which increased when dry hydrogen chloride was passed into the solution. No precipitation occurred with the salts of the saturated acids, that is, with the melissates and stearates, when hydrogen chloride was passed in, but precipitates were formed with the oleates and erucates, that is, with the salts with one double bond, and with the linoleate, which contains two double bonds. In no instance was the reaction found to be instantaneous, although rather rapid; the conductivity of the solution diminished as precipitation took place. The solutions of the salts all showed the phenomenon of polarisation, which indicated that they possessed properties similar to those of an ordinary electrolyte.

It is thus possible, in contradistinction to the opinion of Kahlenberg, that the above reactions may be due to ionisation. An alternative explanation may be that the reactions with the salts of the unsaturated acids take place in two stages, additive products being first formed with the hydrogen chloride, and then breaking down into the metal chloride and the organic acid. T. S. P.

The Volume of Ions in Solution. NILRATAN DHAR (*Zeitsch. Elektrochem.*, 1913, **19**, 748—753).—On the assumption that Stokes' law is applicable to ions, the author deduces the formula

$$6\pi\zeta v/HaN = 29 \times 10^{13},$$

in which a is the radius of the ion, N the number of ions in the gram ion, v the mean velocity of the ion, H the field in which it moves, and ζ the viscosity of the solution. From investigation of this equation with a number of solutions it is shown that the ions occupy a smaller space than the molecules from which they are formed. J. F. S.

The Degree of Dissociation of Binary Electrolytes as a Function of the Normality. CORNELIS VAN ROSSEM (*Chem. Weekblad*, 1913, **10**, 874—876).—A theoretical paper discussing the relation between the degree of dissociation of weak and strong binary electrolytes and the normality. A. J. W.

Electrical Dispersion Bands in Benzene, Toluene, and Petroleum. ANDREI R. COLLEY (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, *Phys. Part*, 249—265).—The author shows that the method employed by Linnitschenko (this vol., ii, 550) in investigating electrical dispersion leads to considerable errors, the accuracy attained being at most one-tenth of that given by the author's method (A., 1908, ii, 909), so that Linnitschenko's criticisms of the author's results are unjustified. T. H. P.

The Potential Due to Liquid Contact. III. ALEXANDER C. CUMMING and ELIZABETH GILCHRIST (*Trans. Faraday Soc.*, 1913, **9**, 174—185).—Whilst Planck's equation applies to boundaries at which mixing does not occur, Henderson's equation applies to continuous transition through a series of mixtures. Experiments show that a "sharp" boundary is not realisable in practice, and Planck's equation is therefore inapplicable. The change of contact potential with time has been measured, and must be attributed to salt migration. In actual measurements, a boundary must be freshly prepared, and capillary tubes must be avoided.

Cells of the type $N/1KCl$|connecting solution|$N/1KCl$ have also been examined, in which the first boundary is at a membrane, and at the second the solutions mix. In all cases a potential is observed, which steadily falls to zero. C. H. D.

Thermal Calculation of Electromotive Forces. JOHANNES N. BRÖNSTED (*Zeitsch. Elektrochem.*, 1913, **19**, 754—757).—The heat of the reactions $Hg + AgCl = HgCl + Ag$ and $\frac{1}{2}Pb + HgCl = Hg + \frac{1}{2}PbCl_2$ have been redetermined, and found to have values 1400 cal. and 10,930 cal. respectively, which are in accordance with the values previously found by the author. Using the Nernst heat theorem, the electromotive force of the two elements represented by the above equations calculates out to $\pi = 0{\cdot}026$ and $0{\cdot}514$ respectively. These numbers agree well with those determined experimentally. It is shown that the heat values used by Pollitzer (this vol., ii, 669) are not in accord with those found experimentally. J. F. S.

Inaccuracy of the Copper Voltameter. NILRATAN DHAR (*Zeitsch. Elektrochem.*, 1913, **19**, 746—748).—The author gives the results of a series of determinations made with a copper voltameter in series with a silver voltameter which show that for small currents, 5—0·5 milliamperes, the copper voltameter gives values which are much too low. The results of a number of other investigators on the same subject are discussed, and it is made evident that the influence of the current density, acid concentration, and presence of air affect the accuracy of the voltameter, but in exactly which way is not clear. J. F. S.

The Electrical Transport of Gels. STANISLAUS GLIXELLI (*Kolloid-Zeitsch.*, 1913, **13**, 194—200).—Measurements have been made of the rate at which particles of stannic acid are transported when under the influence of an electrical field. The stannic acid was prepared by hydrolysis of the halogen salts of tin.

The mobility of the gel is found to be a function of the hydrogen ion concentration of the dispersive medium, the gel behaving as a negative colloid when the hydrogen ion concentration is very small and as a positive colloid at higher concentrations. The isoelectric point corresponds with 0·00011 mol. of halogen acid per litre. The transition from the one electrical condition to the other is a reversible process, and the isoelectric point can be satisfactorily determined either by the gradual addition or by the gradual removal of acid. From experiments in which other acids were added to the dispersive medium, it has been found that the behaviour of oxalic acid is anomalous, and this is attributed to the formation of complex compounds.

An explanation of the varying electrical character of the gel particles is given, in which it is supposed that the amphoteric nature of the stannic acid plays a part. H. M. D.

The Photoelectric Effect. KARL T. COMPTON and OWEN W. RICHARDSON (*Phil. Mag.*, 1913, [vi], **26**, 549—567. Compare A., 1912, ii, 1039).—The relationship between the frequency of the light and the photoelectric emission of electrons is studied in the case of platinum and aluminium by means of an apparatus similar to that previously employed. The results indicate that the photoelectric sensitiveness is the same function of the frequency for all metals, the difference being that the curve is shifted bodily out to the region of short wave-lengths for electronegative metals. This function is evidently not expressed by the equation

$$N = Ah/R^2v^2(1 - e/300 \,.\, w_0/hv),$$

which it was proposed to test in the investigation. The equation, however, accurately predicts the values of λ_0 and $\lambda_{max.}$ and seems to express part of the truth. It had previously been shown that this equation is only one of the solutions of the theoretical equations. The present results point to the existence of another term in the solution, which would probably be found in N being equal to the sum of two terms. The first term would be the right member of the equation, and would provide the first maximum and the "selective" effect. The second term would provide the second maximum, and account for the "normal effect." J. F. S.

Photoelectric Researches on Some Liquids. Apparent Loss of Positive Electricity Caused by the Ultraviolet Rays. MICHELE LA ROSA and V. CAVALLARO (*Nuovo Cim.*, 1913, [vi], **6** ii, 39—47).—When photoelectric observations are made on feebly active substances placed very near the source of ultraviolet rays, the Hallwachs effect and the Lenard effect are superposed, so that some substances may appear active in the usual way (most rapid dispersion of the negative charge), some inactive and some active

in the opposite way (most rapid dispersion of the positive charge). The result depends on the nature of the substance and on the conditions of experiment. Water, ethyl alcohol, and ethyl acetate show the Hallwachs effect more than the other. Ethyl ether is inactive or very feebly so; methylene bromide is feebly active; in both cases the Lenard effect is greater than the other effect.

R. V. S.

Magnetic Susceptibility of Binary Alloys. KÔTARÔ HONDA and TAKÉ SONÉ (*Sci. Rep. Tôhoku Univ.*, 1913, **2**, 1—14. Compare A., 1910, ii, 686).—The magnetic susceptibility of the alloys of antimony–bismuth, antimony–zinc, antimony–aluminium, antimony–tellurium, tin–tellurium, tin–lead, and bismuth–tellurium have been determined. It is shown that compounds of these elements have a susceptibility value which cannot be deduced from the values of the constituents, and that in the susceptibility concentration curve the existence of a compound is most markedly shown. The curves are straight lines between the compounds and the single constituent when there is no miscibility. When there is miscibility the curves have rounded course. Complete diagrams are given of the cases investigated. J. F. S.

Magneton and Stere Numbers of Magnetic Cations. ADOLF HEYDWEILLER (*Ber. Deut. physikal. Ges.*, 1913, **15**, 821—825).—From investigations on the ion refraction of salts of manganese, iron, cobalt, nickel, copper, and chromium, the relationship between the stere numbers and the magneton numbers are compared, the latter values being taken from the measurements of Weiss (*Verh. Deut. Physikal. Ges.*, 1911, **13**, 736). It is shown that the stere number (p) of the bivalent cations are not very different, whilst those of the tervalent cations are also similar, but about 3/2 times as large as those of the bivalent cations. In all cases the stere numbers and magneton numbers (n) are of the same dimensions. In four cases, $p \gtreqless n$, Cr''', Fe''', Ni'', and Cu'', in the case of Fe''' and Ni''' $p \triangleq n$, in three cases, Fe'', Mn'', and Co'' $p < n$. It is also shown that in those cases where there is approximately the same space-filling, the true ion volume is changed considerably when there is a change in the valency. The amount of the change is approximately in the ratio of the two valencies. J. F. S.

New Formulæ for Calculating the Cubic Expansion of Water. P. H. HOFBAUER (*Zeitsch. physikal. Chem.*, 1913, **84**. 762—763).—The author deduces two formulæ which give values for the cubical expansion of water that agree with the experimentally-determined values to the fifth decimal place. The first formula covers the temperature range 0—40°, and has the form

$$v = (e^{1/e} \cdot r^{1/r})^{e(e/r \cdot e^{1/e})}$$

and the second covers the range 50—100°, and has the form

$$v = {}^{\log_e r}\left[(e^{1/e} \cdot r^{1/r})^3\right]$$

in which r has the value $e\theta/277$, θ the absolute temperature of the water, v the corresponding volume, and e the base of natural logarithms. J. F. S.

Discontinuity of Temperature at the Limit of a Gas and an Absorbing Wall. K. LEONTIEV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, *Phys. Part*, 210—218).—The author has investigated, by von Smoluchovski's method (A., 1900, ii, 63), the manner in which the discontinuity of temperature of a gas at a glass wall depends on the temperature. The gases employed were ammonia, methylamine, ethylamine, methyl and ethyl chlorides, methyl bromide, and methyl ether, which undergo considerable adsorption at a glass surface.

The forms of the curves obtained for the relation between discontinuity and temperature may be explained on Lazarev's assumption (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 69) that the adsorption of the gas on the wall of the vessel influences the magnitude of the discontinuity. At low temperatures the gaseous lamina formed has a considerable effect, with the result that the conditions are excellent for the equalisation of temperature between the wall and the adjacent gas molecules; consequently, the extent of the temperature discontinuity diminishes. When the temperature is raised the adsorbed layer becomes lessened, and the discontinuity more marked; at a certain temperature of the wall the efficiency of the gaseous layer is determined solely by the general number of the molecules, and the conditions are then analogous to those prevailing with gases, such as air, which are only slightly adsorbed. Indeed, the curve for the discontinuity-coefficient in air possesses the same general form as the upper portions of the curves for the gases mentioned above.

That the variation of the discontinuity with temperature cannot be regarded as due exclusively to change of the coefficient of thermal conductivity is evident from the essentially different forms of the curves expressing the relations of these magnitudes to temperature.

T. H. P.

An Improved Method for the Determination of the Specific Heat and the Heat of Dilution of Liquids with Details in the Cases of Dilute Hydrochloric, Hydrobromic, Hydriodic, Nitric and Perchloric Acids, and Lithium, Sodium and Potassium Hydroxides. THEODORE W. RICHARDS and ALLAN W. ROWE (*Zeitsch. physikal. Chem.*, 1913, **84**, 585—610. Compare A., 1905, ii, 677; 1908, ii, 806).—The specific heats of the above-mentioned solutions have been determined by a modification of the method previously described (*loc. cit.*). It is shown that an uncertainty crept into the value of the determinations in previous experiments owing to undetermined temperature changes during the pouring of the alkali into the acid, and as the heat liberated in this reaction is the basis of the determination, the results were not as accurate as they might have been. The present experiments were carried out adiabatically in the usual manner, the liquid under investigation being placed in a platinum calorimeter. The acid which was to be neutralised was placed in a platinum vessel and sunk in the liquid in the calorimeter, and the alkali was contained in a smaller platinum vessel, which in its turn was sunk in the acid.

Both platinum vessels could be rotated, and so serve as stirrers. When the temperature of the whole system had become constant the vessel containing the alkali was opened at the bottom and the acid and alkali allowed to mix, and the heat thus generated, which was known exactly, used to heat up the surrounding liquid. The first experiments were carried out with water at a number of temperatures, and from them, assuming the specific heat of water had the value unity, the temperature-coefficient of the neutralisation of sulphuric acid by sodium hydroxide under the experimental conditions was $-49·5$ cal. per degree rise of temperature. The carefully prepared solutions of alkalis and acids were substituted for water and the specific heat determined. The results are shown to be correct to 0·0001. The following mean values are given for the temperature range 15·9—20·1°: $HCl,200H_2O$, 0·9814; $HCl,100H_2O$, 0·9634; $HBr,100H_2O$, 0·9433; $HI,100H_2O$, 0·9213; $HNO_3,100H_2O$, 0·9584; $HClO_4,100H_2O$, 0·9466; $KOH,100H_2O$, 0·9568; $NaOH,100H_2O$, 0·9664; $NaOH,200H_2O$, 0·9827; and $LiOH,100H_2O$, 0·9813. The molecular heats of the solutions are calculated, and it is shown that on dilution of $HCl,100H_2O$ to $HCl,200H_2O$ the added heat capacity of the gram-molecular weight is slightly less than the heat capacity of the added water; the same applies to the dilution of sodium hydroxide. From the molecular heats of the solutions of the type $MX,100H_2O$ it is shown that the value increases with increasing molecular weights for the halogen acids, and falls for the alkali hydroxides; perchloric acid has a somewhat larger value than nitric acid. J. F. S.

Specific Heat of Solids. HANS VON JÜPTNER (*Zeitsch. Elektrochem.*, 1913, **19**, 711—720).—A mathematical paper in which an expression is evolved, giving the relationship between specific heat and temperature for solid substances. The expression is applied to the known values for a number of substances. J. F. S.

Specific Heats of Some Binary Liquid Mixtures. ADOLFO CAMPETTI (*Atti R. Accad. Sci. Torino*, 1913, **48**, 968—977).—The binary mixtures of alcohol with diphenylamine, nitronaphthalene, α-naphthylamine, and salol have specific heats greater than those calculated from the law of mixtures (compare Schultze, A., 1912, ii, 624). Diphenylamine and α-naphthylamine show a rapid change of specific heat in passing from the solid to the liquid state, but the mixtures studied do not exhibit this behaviour. In the case of mixtures at a temperature below the m. p. of one component, this component has a specific heat corresponding with that which it would have in the superfused, not in the solid, state. R. V. S.

Cryoscopic Investigations of Solutions of Diethyl Ethylene Ether and Water. (Mlle.) V. A. UNKOVSKAJA (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1099—1108).—It was found by Makovecki that, with dilute solutions of diethyl ethylene ether in water, the lowering of the vapour pressure of the water is approximately twice as small as it should be according to Raoult's law. Since

Trouton's constant for this ether has the value 21·2, which is that given by non-associated liquids, the author has investigated the molecular freezing-point depressions of dilute aqueous solutions of diethyl ethylene ether.

It is found that, with increasing concentration of the ether, the molecular depression at first diminishes, but remains constant at a mean value of 18·63° for depressions lying between 0·3 and 1·6°. The initial diminution of the molecular depression is shown to be due to the supercooling influence of the bath. The results of this and a further series of measurements with solutions of higher concentration show that as the mol. % of the ether increases from 0·0506 to 15·18, the molecular depression of the freezing point diminishes only from 18·63 to 15·18. Hence, within the range of concentration investigated by the author, it seems impossible that the diminution of the vapour pressure of water by diethyl ethylene ether should be only one-half as great as that required by Raoult's law.

The molecular depressions for solutions of water in diethyl ethylene ether have also been investigated. On the assumption that the curves connecting the molecular depression with the logarithm of the concentration of the water give, throughout their whole course, a partial indication of the extent to which the water molecules are associated, it is seen that with increasing concentration association proceeds at first slowly and then rapidly; if the concentration is raised approximately to the cryohydrate point, association again slackens, and the curve becomes asymptotic to the log.-concentration axis. The greatest observed value for the molecular depression of the freezing point of diethyl ethylene ether is 41·4, and the mean value calculated from van't Hoff's formula, 39·05. Measurements of the specific heats of the liquid and solid ether gave the mean values 0·4203 and 0·2839 respectively.

T. H. P.

Synthesis of Natural Fats from the Point of View of the Phase Rule. II. The Ternary System: Tripalmitin–Stearic Acid–Palmitic Acid. ROBERT KREMANN and H. KLEIN (*Monatsh.*, 1913, **34**, 1291—1311. Compare A., 1912, ii, 1152).—A purely physical paper, forming the second of a series in which the freezing-point curves of systems approximating in composition to the mixtures of glycerides and fatty acids present in natural fats will be recorded and discussed. In the present paper tables and curves of the melting points of mixtures of the three substances mentioned in the title, taken two at a time, are first given, and then similar data are given for ternary systems in which two of the components are present in constant amount, with varying proportions of the third.

T. A. H.

Connexion between Boiling Point and Molecular Weight of Substances. J. C. THOMPSON (*Chem. News*, 1913, **108**, 189—191. Compare A., 1912, ii, 1136).—In an attempt to find a relationship between the boiling point and molecular weight of organic sub-

stances, it has been found that the expression $T/\rho^{0\cdot235}.M^{0\cdot5}$ affords an approximate constant for a large number of hydrocarbons. By means of several examples it is shown, however, that the value of the function increases slightly as the proportion of double and triple bonds increases. An attempt is made to explain the observed influence of unsaturation in terms of the attractive forces acting between the carbon atoms. H. M. D.

New Formulæ for Calculating the Vapour Pressure of Water Vapour. P. H. HOFBAUER (*Zeitsch. physikal. Chem.*, 1913, **84**, 764. Compare A., 1912, ii, 735; this vol., ii, 556).—In a previous paper the author deduces the formula

$$\log P/p = c \log \sqrt{\rho\delta \cdot \rho'\delta'} + \log(1/\theta + 1/\Theta).$$

In the present paper the value of the constant c in the above expression is given, for the conditions $\Theta = 373°$ absolute, $P = 760$, ρ the heat of evaporation, and δ the density at the normal boiling point, and $m = 0{\cdot}434294$ as

$$c = \log(m \cdot \Theta^2 dP/P \cdot d\Theta) \cdot \log \rho\delta.$$

If this value is inserted in the above expression, the formula then takes the form:

$$P/p = e^{\Theta - \theta\sqrt{dP \cdot dp/P \cdot p \cdot d\Theta d\delta}}.$$

J. F. S.

Vapour Pressure of Saturated Solutions. III. The Determination of the Vapour Pressure of Solutions of Sodium Chloride by the Boiling-point Method. ALEXANDER SPERANSKI (*Zeitsch. physikal. Chem.*, 1913, **84**, 160—188. Compare A., 1909, ii, 378; 1911, ii, 1065).—A continuation of previous work, in which the author had shown the expression $T \log_e p_0/p$ for concentrated solutions between 20° and 60° is a linear function of the temperature; p_0 represents the vapour pressure of the pure solvent, and p that of the solution at the temperature T. The present paper deals with the vapour pressure of sodium chloride solutions at higher temperatures. This was determined in a manostat in which the pressure could be kept constant to 1·5 mm. A full description of the apparatus is given. It is shown that for sodium chloride the value of $T \log_e p_0/p$ is not a linear function of the temperature, but rises to a maximum at about 60° and then falls. It is shown that if the molecular weight of sodium chloride is calculated from the vapour-pressure determinations a value of 20·4 is obtained between 30° and 100°, which indicates that sodium chloride dissociates into 2·87 ions, that is, 58·5/20·4. This seems to point to the formation of hydrates in the solution. J. F. S.

Determination of the Vapour Pressure of Saturated Solutions by the Boiling-point Method. P. PAVLOVITSCH (*Zeitsch. physikal. Chem.*, 1913, **84**, 169—178. Compare preceding abstract).—The vapour-pressure curves of saturated aqueous solutions of copper sulphate, potassium nitrate, potassium chlorate,

and sodium sulphate have been determined, using the apparatus designed by Speranski (*loc. cit.*). It is shown that in the region 60—100° the vapour-pressure curve does not bend toward the temperature axis. The Bertrand formula $p=K(T-l)^{50}/T^{50}$ holds for saturated solutions of substances which have a solubility that changes but little with temperature. For solutions of salts the solubility of which changes rapidly with temperature, the formula holds if a suitable smaller index than 50 is chosen; the formula of Dupré-Hertz, however, holds even better. The formula of Speranski, $\log p = a \log C + b$, in which C is the concentration in grams per 100 grams of solvent, holds for solutions of copper sulphate and sodium sulphate, but not for potassium chlorate and nitrate. The value of $T \log_e p_0/p$ increases in a linear manner with the temperature for copper sulphate solutions; with sodium sulphate it increases in a less rapid manner; and with potassium chlorate and nitrate in a more rapid manner. The vapour-pressure curves of solutions of copper sulphate, sodium sulphate, and potassium chlorate are practically coincident, whilst that of potassium nitrate lies considerably beneath them. J. F. S.

Higher Valencies in Oxygenated Organic Compounds. I. Oxonium Compounds of Aliphatic Alcohols. VLADIMIR V. TSCHELINCEV (*J. Russ. Phys. Chem. Soc*, 1913, **45**, 844—864).—The author has measured the heat effects accompanying the formation of complexes of the three types PrOMgI,R·OH, PrOMgI,2R·OH, and PrOMgI,3R·OH, R representing methyl, ethyl, propyl, *iso*propyl, butyl, *iso*butyl, *sec.*-butyl, *tert.*-butyl, *iso*amyl, amyl (amylene hydrate), heptyl, or octyl.

The amounts of heat developed during the combination of successive molecules of the alcohol show that the formation of complex depends on the length and structure of the carbon-atom chain of the alcohol radicle and on the position of the hydroxyl group. Union of 1 mol. of ethyl alcohol corresponds with a slightly larger development of heat than that of 1 mol. of methyl alcohol, but, in general, for primary, secondary, and tertiary alcohols, the heat effect diminishes in passing from methyl to ethyl to propyl; the diminution is then arrested, and the heat effect remains virtually constant as far as the octyl group.

The influence of the methyl group gradually weakens as its distance from the hydroxyl group increases. Thus, although the heat effects are greater for *iso*butyl than for *n*-butyl alcohol, with the amyl alcohols no such differences are observable.

The heat effects for secondary alcohols are sometimes greater and sometimes less than for primary alcohols. For tertiary alcohols the effects are generally less than for the primary or secondary alcohols; with *tert.*-amyl alcohols the higher valency of the oxygen is so weak that they give with the magnesium alkyl complexes only compounds containing 1 mol. of the alcohol.

These results may be compared with those of Ostwald's investigations of the dissociation constants of organic acids and of

Menschutkin's measurements of the velocities of esterification of organic acids (compare also Michael, A., 1909, ii, 219). T. H. P.

Higher Valencies in Oxygenated Organic Compounds. II. Oxonium Compounds of Phenols. VLADIMIR V. TSCHELINCEV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 864—880).—Similar measurements have been made to those previously described (see preceding abstract), using, in place of the monohydric alcohols, phenol, *o*-, *m*-, and *p*-cresols, thymol, carvacrol, *o*-, *m*-, and *p*-chlorophenols, *p*-bromophenol, *s*-trichloro- and tribromo-phenols, and *α*- and *β*-naphthols.

The results show that the position of the substituent in the benzene nucleus and, to a less degree, its character, exert a substantial influence on the manifestation of increased valency by the oxygen of a hydroxyl group united to an aromatic ring.

Substitution by an alkyl radicle in the ortho-position of phenol lowers the heat-effect of combination of the first complex molecule, and, in the case of *o*-cresol, the development of heat by the reactions, $PrOMgI,C_6H_4Me{\cdot}OH + C_6H_4Me{\cdot}OH$ and $PrOMgI,2C_6H_4Me{\cdot}OH + C_6H_4Me{\cdot}OH$, is zero. When the substitution takes place in the meta-position, very slight lowering is produced in the heat-effect for each molecule of the phenol added. With para-substitution, the heat-effect is raised, lowered, and almost unchanged respectively for the first, second, and third molecule combined. With more complicated substitution, as in thymol or carvacrol, the heat-effects are intermediate to those of *o*- and *m*-cresols.

When an acid radicle, such as chlorine, is introduced into the ortho-position in phenol, the amounts of heat developed on combination of the first and second molecules with the magnesium complex are considerably diminished, and union with a third molecule does not take place. But if the acid substituent enters in the meta- or para-position, marked increases are observed in the heat-effects accompanying combination of the first two molecules, and the heat-effects due to the third molecule are virtually unchanged and slightly raised with *m*- and *p*-chlorophenols respectively. Replacement of the chlorine in *p*-chlorophenol by bromine produces but slight changes in the amounts of heat developed. Analogous results are obtained with two acid radicles in the two ortho-positions of phenol, either alone or with a third acid radicle in the para-position.

With the naphthols, the thermal changes are quite small in comparison with those obtained with phenol. Further, the higher valency of oxygen is, in general, manifested in weaker degree in aromatic compounds than in the corresponding aliphatic compounds.

An alcohol, such as ethyl alcohol, which forms complexes with development of considerable quantities of heat, displaces phenol from its complexes almost completely.

Parallelism exists between the heats of formation of these complexes and the velocities of esterification, both with aliphatic alcohols and with phenols. T. H. P.

Exact Vapour Density Determinations of Some Liquid Organic Substances. ALFRED SCHULZE (*Physikal. Zeitsch.*, 1913, **14**, 922—926).—A modified Dumas method for the determination of vapour densities is described. The apparatus usually employed is modified by having a small bulb of about 5 c.c. capacity blown on to the bottom of the Dumas bulb. It is connected by means of a short capillary tube. In making a determination, the small bulb and about one-third of the large bulb are filled with the liquid under investigation. The whole is then placed in a thermostat until the last trace of liquid has disappeared, when it is sealed in the usual way. The apparatus is then removed from the thermostat and the small bulb dipped into liquid air, when the whole of the vapour is condensed in it. When this has happened, the small bulb is removed from the the larger by melting the capillary. The small bulb, on weighing, gives the weight of the vapour, and on filling the large bulb with water, the volume of the vapour is easily obtained. From determinations with a number of substances the author shows that the results obtained reach an accuracy of 99·7%. It is shown incidentally that carbon disulphide and nitrobenzene are associated to a small extent in the vaporous condition. J. F. S.

Compressibilities of Dilute Solutions of Certain Inorganic Salts. WILLIAM WATSON (*Proc. Roy. Soc. Edin.*, 1913, **33**, 282—291. Compare A., 1911, ii, 793).—The compressibility of solutions of sodium carbonate, sodium hydroxide, potassium hydroxide, magnesium sulphate, and zinc sulphate have been determined in dilute solutions up to a pressure of 1000 atmospheres. The values of $\Delta K/C$ have been compared with those obtained by Tammann from the thermal expansion, where it is shown that there is a good agreement between the two. It is shown that a small molecular volume or a large contraction on solution is associated with a small compressibility of the solution. J. F. S.

The So-called Laws of Tate. THEODOR LOHNSTEIN (*Zeitsch. physikal. Chem.*, 1913, **84**, 410—418).—Polemical against Morgan's work on the weight of a falling drop, and the laws of Tate (A., 1911, ii, 372, 384, 584, 699, 857, 1064); see also Lohnstein (A., 1909, ii, 25). J. F. S.

The Weight of a Falling Drop and the Laws of Tate. XII. The Drop Weights of Certain Organic Liquids and the Surface Tensions and Capillary Constants Calculated from them. J. LIVINGSTON R. MORGAN and EDWARD C. STONE (*J. Amer. Chem. Soc.*, 1913, **35**, 1505—1523).—The drop weights, and hence the surface tensions and capillary constants, at various temperatures of the following organic liquids have been determined: methyl propyl ketone, paracetaldehyde, ethyl nitrate, nitromethane, butyl alcohol, *iso*butyl alcohol, allyl alcohol, formic, propionic, butyric, *iso*butyric, and *iso*valeric acids, *o*-toluidine, *p*-toluidine, formamide, dimethylnitrosamine, acetophenone, benzophenone,

ethyl propyl ether, acetal, furfuraldehyde, and anethole. Of these, only acetal, ethyl propyl ether, and *o*-toluidine were found to be non-associated.

In some cases the calculated critical temperature increased with the temperature of observation, the meaning of which is not obvious.

Benzophenone was investigated at temperatures as much as 39° below its melting point, but no abnormalities were observed in the supercooled liquid.

Ortho-compounds have a higher surface tension than para-compounds. T. S. P.

The Constants *a* and *b* of the van der Waals' Equation. PAUL FUCHS (*Zeitsch. physikal. Chem.*, 1913, **84**, 755—758. Compare Bose, A., 1909, ii, 989).—Bose (*loc. cit.*) puts forward the hypothesis that the attraction between molecules of equal mass will be greater the more complex the molecules. It is shown that this is not the case; for example, the *a* value for methane is 1·88, whereas that of ammonia is 4·10. It is also shown that in a series of gases containing an equal number of molecules the *a* value decreases with increasing molecular weight, whereas according to the Bose theory it ought to increase. The conclusion is drawn from the discussion of the values that the constant *a* of the van der Waals' equation is not to be represented only by the force of the attraction between the molecules, that it is not absolutely constant, and that it is influenced by other conditions. J. F. S.

Total Surface Energy and Chemical Constitution. G. M. BENNETT and ALEC DUNCAN MITCHELL (*Zeitsch. physikal. Chem.*, 1913, **84**, 475—497).—A theoretical paper, in which it is shown that the total molecular surface energy in normal liquids is independent of the temperature, and that $(\gamma - t\,.\,d\gamma/dt)(Mv)^{2/3} = K$. This expression is shown to be an atomic function, $K = \Sigma(a)$. In associated liquids the value of K increases, but $(\gamma - t\,.\,d\gamma/dt)(Mxv)^{2/3} = K'$ should be constant, where x is the association factor of the liquid, and from this the value of K' can be calculated by the formula $x = (K'/K)^{3/2}$. J. F. S.

Viscosity and Surface Tension of Suspensions and Solutions of Muscular Proteins Under the Influence of Acids and Alkalis. FILIPPO BOTTAZZI and E. D'AGOSTINO (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 183—192).—The experiments relate to the product myosin (compare Bottazzi and Quagliariello, this vol., i, 1132), which yields with water a suspension which gradually passes into a solution when treated with acid or alkali. When potassium hydroxide is added, the viscosity rises in course of time to a maximum, and then decreases again. When a given suspension is treated with increasing amounts of potassium hydroxide or hydrochloric acid, the viscosity first attains to a maximum, and then diminishes. Lactic acid gives a similar result, but the maximum was not reached in the experiments quoted. If the viscosity of the suspension has already been augmented by the addition of lactic

acid, further addition of sodium chloride produces a considerable diminution in the viscosity of the liquid. The surface tension of the myosin suspension differs little from that of water, but the addition of acid or alkali causes a diminution of the surface tension of the solution. A solution of myoprotein (*loc. cit.*) has a low surface tension which is not much influenced by the addition of potassium hydroxide, but is diminished by addition of hydrochloric acid, protein being simultaneously precipitated. R. V. S.

Internal Friction of Liquids. ALEXIUS J. BATSCHINSKI (*Ann. Soc. d'Encour. Sci. Exp., Suppl.* 3, 1913, *Reprint*, 1—68).—Since with gases the internal friction is conditioned principally by the transference of motion as a result of molecular impacts, whilst in the case of liquids it is due to the action of molecular forces, the viscosity of liquids must differ essentially from that of gases. Unsuccessful attempts have been made by various investigators to express analytically the dependence of the viscosity of liquids on the temperature, and it would seem probable that such viscosity can be expressed more simply as a function of the specific volume. With the single exception of water, the viscosity is a diminishing function of the specific volume, and the author deduces the expression $\eta = c/(v-\omega)$, where v represents the specific volume, and c and ω are constants characteristic of any particular liquid. Hence the curves connecting the fluidity, $1/\eta$, and the specific volume should be rectilinear. Such curves have been constructed for a series of eighty-seven substances investigated by Thorpe and Rodger (*Phil. Trans.*, 1894, **185**, *A*, 574), for mercury and carbon dioxide; also for ether, ethyl acetate, and benzene at temperatures higher than the ordinary boiling points.

It is found that the law $\eta = c/(v-\omega)$ holds for all non-associated liquids over wide limits of variation of the co-ordinates; with ethyl acetate, for example, over a temperature-interval exceeding 180°. This law is not obeyed by associated liquids, but in the case of very dense gases it seems to be applicable to the same extent as with liquids. With sixty-six of the liquids the values of c and ω have been calculated, and the values of η then obtained from the above formula compared with the observed values; the differences are mostly very small, and only in rare cases exceed 1%.

That the law holds also when η and v undergo alteration as a result of change of pressure is shown for carbon dioxide, ether, and benzene. From the formula $\eta = c/(v-\omega)$ is derived $\omega/v_1 + \beta/\alpha = 1$, where v_1 is the specific volume of the liquid at a pressure of one atmosphere, β is the coefficient of compressibility, and $\alpha = 1/\eta \,.\, d\eta/dp$.

The constant ω may be defined as the specific volume corresponding with infinitely great viscosity of the liquid. It is hence termed the "limiting volume," and $v-\omega$ the "free volume." The value of ω is found to be intermediate to those of the liquid and solid at the solidifying temperature. The constant c may be regarded as the value of the viscosity coefficient for a free volume of 1.

When the free volume is relatively very small, marked divergence

from the law $\eta = c(v - \omega)$ appear, so that the law loses in accuracy when the molecules approach one another too closely.

For all substances which obey the law, the limiting volume, ω, equals approximately 0·307 times the critical volume, and is very nearly the parameter b of van der Waals' equation.

The molecular limiting volume, $M\omega$, is additive in character. The increments, ϵ, of this magnitude have been calculated for the separate elements in a compound and, in fifty-three out of sixty-six cases, the observed values of $M\omega$ and those calculated from the increments differ by less than 2%.

Consideration of the dependency of the constant c on the critical constants or on the parameters of van der Waals' equation leads to the conclusion that c is proportional to the square root of the specific molecular attraction, a. The relation between the author's law and the viscosity formulæ of other authors is discussed.

T. H. P.

Internal Pressure of Liquids. ALBERT P. MATHEWS (*J. Physical Chem.*, 1913, **17**, 603—628. Compare this vol., ii, 300, 494).—A number of methods are described which have been employed in the computation of the internal pressure of liquids. In these methods the value of "a" of the van der Waals' equation is derived respectively: (1) from the surface tension, on the assumption that the thickness of the surface layer is $T_c/(T_c - T)^{2/3}$ molecular diameters; (2) from Eötvös's law by a modification of Young's method; (3) from van der Waals' equation as applied to the critical temperature, the assumption being made that $b_c = 2V_c/S$, where S is the critical coefficient, and is given by $S = RT_c/V_cP_c$; (4) from the internal heat of vaporisation at temperatures in the neighbourhood of the critical temperature; and (5) from the molecular weight M and the number of valencies N by means of the formula $a = 1·259 \times 10^{11}.(MN)^{2/3}$ (compare previous papers, *loc. cit.*).

All five methods give practically the same results, but the values are uniformly higher than those obtained previously, with the exception of Lewis's values calculated from the latent heat of expansion. The data for pentane and ethyl ether are also found to afford values for the internal pressure, which remain constant over a wide range of temperature. This seems to show that in the absence of association, the molecular cohesion is independent of the temperature.

H. M. D.

Pressure of Flow and Hardness of Plastic Substances. NIKOLAI S. KURNAKOV and SERGEI F. SCHEMTSCHUSHNI (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1004—1076).—The authors first give a summary of previous work on the hardness and pressure of flow of plastic substances, which behave like liquids of high internal friction under slow deformation, and like elastic, brittle solids under rapid deformation. They have devised a special apparatus for measuring the pressure of flow for such substances, and have applied it to the investigation of a large number of them.

Under constant conditions, the curves representing the pressures

on the piston of the vessel from which flow takes place as ordinates and the times as abscissæ are of four principal types: (1) After an initial period of increase, the pressure reaches a limit, and then remains constant as the flow continues. (2) The pressure first increases, then diminishes, and finally remains constant; in a particular form of this type, the initial increase is followed by continuous increase during the period (0·5—6 hours) of the observation. (3) The rising curve exhibits a bend corresponding with the initial pressure of flow; the establishment of flow lies outside the limits of pressure measured by the apparatus. Such diagrams are obtained with metals. (4) With this type, characteristic of substances brittle under the experimental conditions, the curve first rises rapidly, and then assumes a sharp zigzag form, indicating sudden rises and falls in the pressure within the vessel. A diagram of this kind is given by the double compound of silver chloride and thiocarbamide, $AgCl,2CS(NH_2)_2$. Many intermediate forms of diagram exist to these four types.

At constant temperature the pressure of flow for all types of diagram increases with the velocity of deformation. The latter increases more slowly than the pressure.

The phenomenon of relaxation or diminution of the pressure while the flow remains constant (see type 2, above) is considered analytically, and it is shown that investigation of the diagram of flow affords a general mechanical method for measuring the time of relaxation, which is a fundamental magnitude in establishing the different conditions of solids. The time of relaxation, T, is, indeed, a measure of the brittleness, whilst its reciprocal, $1/T=k$, represents the characteristic of plasticity. With constant rate of flow, the pressure of flow is proportional to the coefficient of viscosity.

Results are given of the investigation of the flow of a large number of elements, salts, and organic compounds, some of the conclusions drawn from these being as follows. In general, the accumulation of oxygen in a molecule, for example, by the conversion of potassium iodide into iodate or of potassium or silver nitrite into nitrate, increases the pressure of flow and favours brittleness. Among organic compounds, marked plasticity and low pressures of flow are observed with derivatives of the terpene group, for instance, camphene, camphor, pinene hydrochloride, borneol, and menthol.

The data obtained with binary systems show that: (1) The formation of solid solutions and isomorphous mixtures is accompanied by increase in the hardness and pressure of flow. (2) The variation of the hardness of a continuous series of solid solutions is expressed by a continuous curve exhibiting a maximum. (3) The hardness of systems formed by the mechanical superposition of the components is a linear function of the composition. (4) The formation of solid solutions of plastic substances is accompanied by increase in the temperature-coefficient of hardness (or viscosity). (5) For metallic alloys, the diagrams of hardness and its temperature-coefficient in relation to the composition possess the

inverse or antibatic (compare Luther, *Zeitsch. Elektrochem.*, 1906, **12**, 97) forms of those of the corresponding diagrams of electrical conductivity and of the temperature-coefficient of electrical resistance.

It is shown that the hardness number and the pressure of flow may serve as characteristics of the purity of metals. Increase of the hardness and of the viscosity coefficient of solid solutions possessing maximum hardness is not merely dependent on increase of the molulus of elasticity E in the equation, $\eta = ET$, but is also related to increase in the time of relaxation T. This conclusion is confirmed by the results obtained with an extensive series of solid solutions of copper and iron (brass, bronze, steel, etc.) of wide industrial application. Thus, tempered steel, distinguished by its great hardness, possesses a lower modulus of elasticity than soft iron. Since the time of relaxation may be taken as a measure of brittleness, it follows that increase in the hardness of solid solutions due to increased time of relaxation should be accompanied by increased brittleness. Such a conclusion receives complete experimental confirmation. Of great technical interest are metallic solid solutions, the increased hardness of which is conditioned chiefly by increase in the modulus of elasticity; such substances, which should be hard without greatly augmented brittleness, are to be investigated later.

In many cases in which the formation of definite chemical compounds is accompanied by loss of internal energy from the reacting substances, increase in the hardness occurs, in some instances to that of the hardest component. Contrary to what is observed with solid solutions, the increased hardness and pressure of flow with definite compounds formed with considerable development of heat depends on simultaneous increase of the times of relaxation and of the moduli of elasticity of the components. Comparison of the moduli of elasticity serves as a new means of distinguishing solid solutions from chemical compounds, since, with a substance of the former class, the modulus of elasticity is either equal to or less than the arithmetic mean of those of the components.

T. H. P.

Variation of the Resilience of Some Industrial Alloys of Copper as a Function of the Temperature. LÉON GUILLET and VICTOR BERNARD (*Compt. rend.*, 1913, **157**, 548—550. Compare this vol., ii, 710).—A study of the variation in resilience with temperature of some seven bronzes containing from 3·5 to 20% of tin and varying proportions of lead and zinc, four brasses, and one aluminium bronze. The results are expressed by curves giving the breaking strain in kilograms/sq. cm., and show that lead acts unfavourably as regards resilience. The aluminium bronze shows rapid decrease in resilience with rise in temperature. W. G.

Weight Relations Occurring when Liquids are Imbibed by Absorbent Paper. I. P. KRAIS (*Zeitsch. angew. Chem.*, 1913, **26**, 598—600).—Strips of dry filter paper were arranged so that

the bottom part was immersed in a given liquid. After a given time sections of the filter paper above the surface of the liquid were cut out, and the amount of liquid absorbed by them was determined by weighing. It was found that the amount of liquid absorbed diminished as the height above the surface of the liquid increased.

The experiments are only preliminary, since great difficulties have been experienced in obtaining filter paper uniform in quality, and in determining the exact conditions under which comparative experiments can be made. T. S. P.

Dissociation of Mercuric Oxide. GUY B. TAYLOR and GEORGE A. HULETT (*J. Physical Chem.*, 1913, **17**, 565—591).—The dissociation pressure of mercuric oxide has been measured at temperatures between 360° and 480° by static and dynamic methods. The rate of decomposition of the oxide is very slow, but the equilibrium pressures can be attained in presence of suitable catalysts. The decomposition is accelerated by finely divided platinum, ferric oxide, manganese dioxide, and cadmium oxide, whilst aluminium and stannic oxides are without effect. The total dissociation pressure amounts to 90 mm. at 360°, 141 mm. at 380°, 231 mm. at 400°, 387 mm. at 420°, 642 mm. at 440°, 1017 mm. at 460°, and 1581 mm. at 480°. From these numbers the heat of dissociation of the oxide is calculated to be 76,400 cal., which is in good agreement with the calorimetric data.

From the variation of the dissociation pressure with the temperature it is shown that mercuric oxide is stable in the air at the ordinary temperature in presence of mercury, and that this is the case even under greatly reduced partial pressure of oxygen. The data show further that mercury may oxidise under ordinary atmospheric conditions; the rate is very small, but may be greatly accelerated by catalysts.

Measurements have also been made with the yellow oxide, and these show that the dissociation pressure curve is identical with that of the red oxide, indicating that these do not represent different modifications of the oxide. H. M. D.

Examination of Dolezalek's Gas Solubility Theory with Radium Emanation. RICHARD SWINNE (*Zeitsch. physikal. Chem.*, 1913, **84**, 348—352).—The Dolezalek theory of gaseous solubility (A., 1910, ii, 184) has been examined for several liquids with radium emanation. It is shown that for normal liquids the theory holds approximately. With strongly associated liquids a great divergence is observed between the molecular weights thus deduced and that obtained by the more usual methods. J. F. S.

Solubility Differences on Crystal Surfaces. HANS KUESSNER (*Zeitsch. physikal. Chem.*, 1913, **84**, 313—320).—A theoretical paper in which the solubility and surface tension on crystal faces are considered. The conditions which must be fulfilled for equilibrium with a crystal possessing both cubic and octahedral faces are mathematically deduced. J. F. S.

Liquid Crystals of Ammonium Oleate. OTTO LEHMANN (*Zeitsch. Kryst. Min.*, 1913, **52**, 592—601).—A reply to Mlodziejovski (this vol., ii, 306). L. J. S.

New Theory of Allotropy. ANDREAS SMITS (*Zeitsch. physikal. Chem.*, 1913, **84**, 250—256).—Polemical, an answer to Tammann's criticism (this vol., ii, 193, 679) of the author's previous papers on the theory of allotropy (A., 1910, ii, 195, 400; this vol., ii, 393). J. F. S.

A New Theory of Allotropy. II. GUSTAV TAMMANN (*Zeitsch. physikal. Chem.*, 1913, **84**, 753—754).—Polemical. A reply to Smit's answer (preceding abstract) to the author's previous criticism (this vol., ii, 679). J. F. S.

Ostwald's Law of Transition by Steps in the Light of the Theory of Allotropy. ANDREAS SMITS (*Zeitsch. physikal. Chem.*, 1913, **84**, 385—409. Compare Ostwald, A., 1897, ii, 308).—The author shows that the theory of allotropy (A., 1910, ii, 400) leads to the following conclusions: (1) On suddenly cooling the vapour of a stable modification of a substance, separation takes place of a liquid or of that solid form which corresponds most nearly in its composition with the vapour. (2) Sudden precipitation of an allotropic substance from a solution gives rise to that form which corresponds with the equilibrium conditions of the solution. If this equilibrium lies strongly to the side of the pseudo-component which prevails in the metastable modification, then the precipitated solid substance will be transformed into the metastable modification. A new hypothesis is put forward to cover the phenomena which occur during slow operations, namely, that every phase is operative in part in the formation of a new phase. The theory of allotropy coupled with the new hypothesis leads to the following conclusions: (1) When the composition of the different modifications of a substance are widely dissimilar, then that modification which has a composition most nearly like that of the liquid phase will separate from the supercooled system. The same applies to the separation of new phases from the vapour phase. (2) In those cases where the various modifications have similar compositions irregularities are likely to occur. (3) The spontaneous crystallisation of the stable or metastable form of a substance from a supersaturated solution depends entirely on the internal equilibrium of the solution. J. F. S.

Relationship of Unstable Forms to Stable Forms. HERMANN LAUTZ (*Zeitsch. physikal. Chem.*, 1913, **84**, 611—641).—The relationships between the stable and unstable forms of a number of substances are studied. Resorcinol is shown to exist in two stable and two unstable forms. At 70·8° the stable form II passes into the stable form I. These have specific volumes at 20°: I, 0·774; II, 0·787. The linear crystallisation velocity of the two stable forms is determined and shown to be about the same as

that of the unstable form III: 0·8 mm.—1·0 mm. per minute. The two crystalline forms and the amorphous form are examined, and the linear crystallisation velocity is determined for the pure substances and for mixtures of these substances and phthalide. Similar velocity determinations are carried out for the two forms of phthalide with addition of triphenylguanidine. Experiments are described on the transition of the stable form of tristearin into the unstable form, as well as on the crystallisation velocity. The relationships between the unstable forms of the following binary mixtures are studied: Acetamide–triphenylguanidine, acetamide–phthalide, triphenylguanidine–triphenylmethane, and triphenylguanidine–phthalide. J. F. S.

Method for the Determination of the Size of Colloidal Particles. A. V. Dumanski (*Kolloid. Zeitsch.*, 1913, **13**, 222—223).—A correction. The formula of Einstein, which was employed by the author in computing the density of colloidal particles (this vol., ii, 194) has now been replaced by Einstein's more exact formula, and corrected numbers representing the density of the colloidal particles of arsenious sulphide are recorded. H. M. D.

Precipitation of Colloids. III. Karl Spiro (*Biochem. Zeitsch.*, 1913, **56**, 11—16).—The $H^{\cdot}$ concentration of mixtures of solutions of various salts with egg-white solutions was determined colorimetrically and electrometrically. The $H^{\cdot}$ of such mixtures was calculated on the assumptions that the product (H) . (OH) = constant = K_w, and that in mixtures of solutions containing only completely dissociated electrolytes, the difference between the sum of the total H and total (OH) ions does not change. The numbers experimentally found differed from the calculated numbers. In the majority of cases, the numbers found for p_H approximated more to the p_H of the protein solution. In the case of acetates and fluorides, the p_H numbers found approximated more to those of the salts. S. B. S.

A Neutral Oil Emulsion as a Model of a Suspension Colloid. Ridsdale Ellis (*Trans. Faraday Soc.*, 1913, **9**, 14—25).—The effect of acids and alkalis on the interface potential of an oil emulsion (A., 1912, ii, 13) has been determined. A strong maximum is found in neutral or faintly alkaline solutions. These emulsions have the advantage over other colloids of not undergoing coagulation. The effect on stability has been determined approximately by experiments with a simplified form of nephelometer. Maximum stability is found in a $N/1000$-alkali solution. The surface tension of the oil is very little affected by acids or alkalis. The concentrations of salts with ter-, bi-, and uni-valent cations required to neutralise the charge on the globules are in geometrical ratio. The results are in accordance with the hypothesis of an electrical double layer around the particles. With colloidal ferric hydroxide, the oil globules first become coated with a solid or semi-solid layer, which prevents coalescence of the globules, and

then coagulation occurs by the adhesion of the hydroxide precipitate. These phenomena have been observed microscopically.

C. H. D.

New Experiments on Colloids. T. A. COWARD (*Trans. Faraday Soc.*, 1913, **9**, 142—154).—Experiments with a solution of casein, pepsin and hydrochloric acid show that the enzyme is greatly checked, without being destroyed, by dilution. Further experiments with hydrosols of gold, gamboge, mastic and arsenious sulphide show that the number of submicrons per unit volume may even be reduced when the concentration of the hydrosol is increased. Both negative and positive sols show at one stage of dilution a departure from the usual course of increasing submicrons with increasing dilution. This stage is assumed to be that of electrical neutrality.

Cataphoretic measurements show an increase of submicrons with increased acidity of the dispersion medium; at the same time the velocity of the submicrons increases to a maximum. The charge is not reversed in sign at the acid coagulation point. C. H. D.

The Condition Diagram of Water. GUSTAV TAMMANN (*Zeitsch. physikal. Chem.*, 1913, **84**, 257—292).—The author constructs a diagram of condition for water from the results of his previous experiments (A., 1910, ii, 495), which are compared with those of Bridgman (this vol., ii, 39). The transformations of the various forms of ice into one another are discussed, and the general relationships under pressures of 2000—2500 kilos. From a study of the ζ surface, it is shown that four forms of ice of group I, one form of group II, and two forms of group III exist. J. F. S.

Relationship of the Volume Surface and Polymorphism of Water. GUSTAV TAMMANN (*Zeitsch. physikal. Chem.*, 1913, **84**, 293—313. Compare preceding abstract).—The determinations of Amagat on the volume surface of water appeared to show that above pressures of 3000 kilos., water would behave as a normal liquid. The researches of Bridgman have shown, however, that as the pressure is increased to 20,000 kilos., the abnormalities increase, and that consequently the view deduced from Amagat's work is incorrect. The present paper is a mathematical examination into the connexion between the abnormalities of the volume surface and the polymorphism of water. It is shown that evidence is obtainable of six molecular groupings on the volume surface, and that five modifications of ice are known. The sixth molecular grouping can only crystallise under very high pressure and at relatively high temperature. J. F. S.

The Change $S_{rh} \longrightarrow S_{mon}$. HUGO R. KRUYT (*Zeitsch. physikal. Chem.*, 1913, **84**, 498—500).—Polemical. An answer to Nernst's criticism (this vol., ii, 668) of the author's paper (this vol., ii, 132).

J. F. S.

Equilibria in the System $MgCl_2$-NH_3-H_2O. D. E. DIONISIEV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 905—912).—Loven's investigations (A., 1896, ii, 413) showed that, in systems containing a magnesium salt, ammonia, and water, no double or complex magnesium salt is formed, and that the concentrations of the reacting molecules are subject to the law of mass action. When ammonia acts on a magnesium salt, the magnesium hydroxide formed is not wholly precipitated, but remains partly in solution, the dissociated portion being in equilibrium with the non-dissociated. Loven's data refer to the region of increasing precipitate, and the author has now investigated the equilibria also in the region of diminishing precipitate.

The results show that, in the region of increasing precipitate, gradual increase in the concentration of the ammonia is accompanied by gradual increase of the ammonia-content of the liquid phase, whilst the quantity of magnesium constantly diminishes. In the region of diminishing precipitate, similar results are obtained with the exception that the concentration of the magnesium in the liquid phase shows continuous increase; when, however, the ammonia reaches a certain concentration, the magnesium- and ammonia-contents of the liquid phase undergo, firstly, a sudden increase, and then a decrease. This behaviour seems to be due to the separation of a product of variable composition (compare Kurilov, A., 1906, ii, 349). T. H. P.

Equilibria in Systems Composed of Copper Nitrate, Ammonia and Water. NIKOLAUS V. STASEVITSCH (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 912—930).—In the region of increasing precipitate, the composition of the precipitate formed by this system varies with the concentration from $2{\cdot}79Cu(OH)_2,Cu(NO_3)_2$ to $2{\cdot}97Cu(OH)_2,Cu(NO_3)_2$. The divergence of these compositions from $3Cu(OH)_2,Cu(NO_3)_2$ or $Cu(OH)_2,Cu(OH)NO_3$ may be due to experimental error, so that the composition may correspond with that of the zinc compounds obtained under similar conditions (A., 1911, ii, 476). This solid phase must be classed with products of combination of the first group (compare Kurilov, A., 1911, ii, 873). As regards the liquid phase, the concentration of the NH_4-ions here increases parallel with that of the ammonia added, the latter being almost completely converted into ammonium nitrate; the copper nitrate, being a salt of a weak base, undergoes hydrolysis, and leads to the formation of the product of combination mentioned above.

In the region of diminishing precipitate, the composition of the solid phase is characterised by the following values for the coefficient of the cupric hydroxide: 2·88, 2·89, 9·38, 114·63, 219·82, 90·33, 49·55, 31·20, 44·42, 41·24. The liquid phase is characterised by a rapid rise in the free ammonia, as was found with salts of zinc (*loc. cit.*), but the same is not the case with the nitric acid and the ammonia.

The phenomena in the region of discontinuity were found to depend on the concentration, temperature, and time. In the solid

phase blackening occurs, just as was observed by van Bemmelen ("Die Absorption," 180) in his experiments with cupric hydroxide obtained from copper sulphate and alkali hydroxide.

Investigations were also made of the electrical resistance and electromotive force of the systems, which were likewise submitted to ultra-microscopical examination. T. H. P.

The Nature of the Process which Occurs in the Partition of a Substance between Two Solvents. GEORG VON GEORGIEVICS (*Zeitsch. physikal. Chem.*, 1913, **84**, 353—364).—The partition coefficient law and the Boedecker modification of it are theoretically considered. It is shown that whilst the x value less than unity in the Boedecker formula can be explained by a dissociation of associated molecules, it is impossible to find an explanation for those cases in which x is greater than unity. The author shows that if the partition of a substance between two solvents is strictly dependent on the molecular size of the dissolved substance, then the x value of the partition formula must run parallel with the association factor for the freezing-point determinations. This is shown in the case of formic acid and butyric acid in water and benzene not to be in accordance with fact. Consequently the conclusion is drawn that the partition law cannot be applied to all solutions any more than it can to the partition of a substance between a liquid and a solid. It is shown that there is no real difference between the two processes, and consequently some cases of abnormal partition must be explainable on the assumption that an adsorption in addition to a solution has taken place. The similarity between adsorption by solid substances and cases of abnormal partition is pointed out, and possible results which may accrue should a liquid absorption in these cases be investigated.

J. F. S.

The Combustion of Gaseous Mixtures and the Ignition Temperatures. J. TAFFANEL and LE FLOCH (*Compt. rend.*, 1913, **157**, 469—471. Compare this vol., ii, 574).—A study of the ignition temperatures of several gases, namely, methane, hydrogen, carbon monoxide, acetylene, ethylene, pentane, and finely divided oil, in varying proportions with air. The mixture is suddenly introduced into a vessel the walls of which are at a definite temperature, and the time of ignition recorded by a manometer. The effect of varying the size of the vessel is also given. The ignition temperature is a relative value depending on the conditions of ignition. The retardation of ignition (compare *loc. cit.*) is a general property, and not particular to methane. W. G.

Rôle of the Solvent in Chemical Kinetics. II. HANS VON HALBAN (*Zeitsch. physikal. Chem.*, 1913, **84**, 129—159. Compare A., 1909, ii, 722).—The solubility of *p*-nitrobenzyl chloride has been determined in twenty-six solvents, and the following gram-molecular concentrations per litre found: methyl alcohol, 0·39; ethyl alcohol, 0·31; propyl alcohol, 0·25; amyl alcohol, 0·20; butyl alcohol, 1·12;

acetic acid, 0·97; acetone, 3·02; acetophenone, 2·54; paracetaldehyde, 1·23; ether, 0·85; acetonitrile, 2·87; nitromethane, 2·87; *o*-nitrotoluene, 2·40; nitrobenzene, 2·66; ethyl acetate, 2·19; ethyl benzoate, 1·98; ethyl nitrate, 2·31; *iso*amyl bromide, 0·66; bromobenzene, 2·50; chloroform, 2·70; carbon tetrachloride, 0·52; benzyl chloride, 1·99; α-bromonaphthalene, 2·03; *n*-hexane, 0·049; *iso*pentane, 0·028; and benzene, 2·14. The solubility of trimethylamine was determined in methyl alcohol, propyl alcohol, ethyl alcohol, amyl alcohol, benzyl alcohol, acetone, acetophenone, ether, acetonitrile, nitromethane, *o*-nitrotoluene, nitrobenzene, ethyl acetate, ethyl benzoate, chloroform, α-bromonaphthalene, hexane, and benzene. The solubility of triethylamine was determined in hexane and nitromethane. The vapour-pressure curves of mixtures of ethyl iodide and *n*-hexane, and of ethyl iodide and nitromethane, were determined, and both shown to exhibit maxima. The velocity of reaction between *p*-nitrobenzyl chloride and trimethylamine was determined in the same sixteen solvents in which the solubility of trimethylamine was determined. In every case the reaction is of the second order, and the influence of the solvent is generally of the same nature as that found by Menschutkin and Walden for the reaction between ethyl iodide and triethylamine (A., 1908, ii, 159). It is shown that the product of the solubilities of *p*-nitrobenzyl chloride and trimethylamine in different solvents varied but slightly with the solvent. Consequently the van't Hoff constants, made up of the product of the solubilities of the two reacting substances and their velocity constant, varied in the same way as the velocity constants. It is therefore not possible to explain the influence of the solvent on the velocity constant in these cases to a shifting of the equilibrium conditions. This is seen more markedly when the variations of the van't Hoff constant are considered alongside the variations of the velocity constant; the former can be represented by 400,000, whilst the latter are represented by 9300. The results are discussed, and it is shown that it is not possible to state generally that the influence of the solvent on the velocity constant is due to a shifting of the equilibrium conditions, but that a catalytic action of the solvent must be assumed to take place in many cases. J. F. S.

Kinetics of Reactions of Ester Formation. VIII. EGOR I. ORLOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 706—740. Compare this vol., ii, 681, 682, 683).—According to Kistiakovski (A., 1899, ii, 13), the reaction velocity for the formation of ethyl formate in aqueous ethyl alcohol is expressed by the equation, $dx/dt = k(A - x) - k_1x$. Calculations in accordance with the considerations advanced by the author show that the results are in good agreement with the general formula: $dx/dt = k(A - mx)$.

Further, in order to calculate the velocity constants of ester formation in methyl alcohol, it is unnecessary to make use of the complex empirical equations suggested by Goldschmidt and Thuesen (A., 1912, ii, 1154). When the esterification takes place in absence of water, the results obtained by these authors are in good agree-

ment with the formula $dx/dt = k(A - mx)$, whilst when water is present, the course of the esterification follows the more complete equation deduced by the author (*loc. cit.*).

An ionic theory of esterification is developed, according to which charges are communicated to the alcohol molecules from the ions of the catalyst and of the organic acid. This theory completely explains the processes of ester-formation, and is in agreement with the experimental data and with the law of mass action.

T. H. P.

The Decomposition of Chloroacetic Acid. HANS VON EULER and HENRY CASSEL (*Zeitsch. physikal. Chem.*, 1913, **84**, 371—379).—It is shown that the reaction:

$$Cl{\cdot}CH_2{\cdot}CO_2H + H_2O = HCl + OH{\cdot}CH_2{\cdot}CO_2H,$$

is influenced very strongly by ultra-violet light of short wave-length. A series of experiments on the velocity of this reaction have therefore been effected in the dark, and in the light of a quartz mercury lamp. It is shown that just as in the experiments carried out in the dark the amount of decomposition is not quite proportional to the time of exposure to the light, but that the reaction constant decreases with the time of exposure. This is due to the retarding influence of the acid formed in the reaction. In the dark experiments the reaction constant is practically independent of the concentration of the chloroacetic acid, whilst in the illuminated experiments the constant decreases with increase in the concentration. The reaction constant at 27·5° is $10^6k = 38{\cdot}0$, which implies that the light has increased the velocity of the reaction 50 times. Bromoacetic acid is shown to be much less sensitive to light than chloroacetic acid, the reaction constant being about three times as large in the latter case as in the former for a normal solution.

J. F. S.

Catalysis of Hydrazine by Platinum Black. ALEXANDER GUTBIER and K. NEUNDLINGER (*Zeitsch. physikal. Chem.*, 1913, **84**, 203—249).—The catalysis of hydrazine hydrate by platinum black and the influence of the presence of ammonia, barium hydroxide, and sodium hydroxide has been studied. It is shown that the results of Tanatar (A., 1902, ii, 386, 495) and Purgotti and Zanichelli (A., 1904, ii, 329) do not strictly represent the course of the decomposition, but that those of Tanatar under special conditions will be correct. Hydrazine is catalysed by platinum black according to the equation $3N_2H_4 \longrightarrow 4NH_3 + N_2$, and there is no evidence of the formation of hydrogen or nitrous oxide. The attempt to determine the order of the reaction led to indefinite results, from which the conclusion was drawn that a heterogeneous catalysis occurred. The platinum black, although prepared by the same process, showed widely differing catalytic activity. The constants calculated for the second and third order reactions decreased rapidly as the reaction proceeded, and this is attributed to the retarding action of the ammonia as it is formed, although the addition of ammonia previous to the reaction had not this effect.

In the presence of barium hydroxide the catalysis followed different lines, and the liberated gas contained hydrogen; if the relationship of barium hydroxide and hydrazine was equimolecular, 50 per cent. of the evolved gas was hydrogen, and these conditions represent the case from which Tanatar deduced the reaction $2N_2H_4 \longrightarrow 2NH_3 + N_2 + H_2$ for the catalysis of hydrazine. The maximum percentage of hydrogen in the evolved gas is 66·6%, and this is obtained when the concentration of the barium hydroxide is infinitely large. This corresponds with a decomposition $N_2H_4 = N_2 + 2H_2$. The decomposition of hydrazine in the presence of barium hydroxide is represented by the equations below, in which x is the number of molecules of barium hydroxide present when one molecule of hydrazine is employed: $3N_2H_4 \longrightarrow 4NH_3 + N_2$; $xN_2H_4 = xN_2 + 2xH_2$; $(3 + x)N_2H_4 = 4NH_3 + (1 + x)N_2 + 2xH_2$.

Barium hydroxide, in addition to changing the direction of the decomposition, also retards it. Sodium hydroxide has the same influence as barium hydroxide, except that double the quantity is required. The action of the two hydroxides is attributed to the driving back of the dissociation of hydrazine hydrate, which indicates that it is the undissociated hydrazine which breaks up into hydrogen and nitrogen. The mechanism of the decomposition is shown to be as follows: The hydrazine breaks up into hydrogen and nitrogen in the presence of platinum black; the nascent hydrogen then reduces two molecules of hydrazine to ammonia. Should, however, the dissociation of the hydrazine hydrate be prevented by the presence of strong bases, the reducing action of the nascent hydrogen is retarded, and consequently free hydrogen is liberated. The velocity of the decomposition of hydrazine is proportional to the quantity of the catalyst present, and is uninfluenced by glass. The hydrazine can only be decomposed to the extent of 93%. The order of reaction could not be determined, but is shown to depend on the condition of the platinum black.

J. F. S.

Action of Neutral Salts in the Catalysis of Esters. HUGH S. TAYLOR (*Medd. K. Vetenskapsakad. Nobelinst.* 2, No. 34, 1—20).—The influence of potassium chloride on the catalytic activity of hydrochloric acid has been examined in a series of experiments on the hydrolysis of methyl acetate, ethyl acetate, propyl acetate, ethyl propionate, ethylene diacetate, and triacetin.

The observations were made at 25°, the concentration of the acid being 0·1 molar, and that of the neutral salt 1 molar. The influence of the neutral salt is expressed in terms of Δ, where $\Delta = 100(K_2 - K_1 \cdot a_2/a_1)/K_1 \cdot a_2/a_1$, K_1 and K_2 being the velocity constants without and in presence of neutral salt respectively, a_1 and a_2 the corresponding degrees of ionisation of the acid.

Although the results seem to show a slight increase in salt effect with increasing complexity of the ester, it is probable that the variation from the mean value of $\Delta = 45$ is within the limits of experimental error. This leads to the conclusion that the influence of neutral salts is independent of the nature of the ester which

is hydrolysed, and that the correct explanation of such action will be such as does not involve the hydrolyte.

Experiments on the neutral salt action in solutions saturated with triacetin show that the effect is the same as in a homogeneous unsaturated system. H. M. D.

Action of Neutral Salts and the Concentration of the Catalyst. HUGH S. TAYLOR (*Medd. Vetenskapsakad. Nobelinst.*, 1913, **2**, No. 35, 1—12).—The influence of potassium chloride on the catalytic activity of hydrochloric acid has been examined in a series of experiments on the rate of hydrolysis of ethyl acetate in aqueous solution. The concentration of the acid was varied from 0·01 to 0·5 mol. per litre, and in each case the effect of the addition of potassium chloride in 1 molar concentration was observed. The results indicate that the neutral salt effect Δ (see previous paper) increases regularly with increasing dilution of the acid from about 41% to 55%. The only exception occurs at the highest concentration of acid, but it is considered that this anomaly may be due to experimental error.

When a comparison is made between these numbers and the corresponding values obtained by earlier observers for the influence of neutral salts on the rate of the inversion of the sucrose at different acid concentrations, it is found that the variation of the salt effect with the acid concentration is much greater with sucrose as hydrolyte than with ethyl acetate. This result is apparently not in agreement with the view that the ratio of the catalytic activities of the hydrogen ion and of the undissociated acid is only dependent on the affinity constant of the acid, and independent of the solvent medium and the nature of the substrate. H. M. D.

The Catalytic Activity of the Undissociated Molecule. HUGH S. TAYLOR (*Medd. K. Vetenskapsakad. Nobelinst.*, 1913, **2**, No. 37, 1—18).—Measurements have been made of the rate of hydrolysis of ethyl acetate in aqueous solution at 25° under the catalytic influence of trichloroacetic and dichloroacetic acids of varying concentration and in the presence and absence of the corresponding potassium salts. The data thus obtained, as well as those recorded in the two previous papers, are interpreted on the assumption that the catalytic action of the acid is due to the composite effect of the hydrogen ion and of the undissociated acid, as expressed by the formula $K = n_H \cdot K_H + n_M \cdot K_M$, in which K is the observed velocity constant, n_H and n_M the concentrations of the hydrogen ion and the undissociated acid, and K_H and K_M the corresponding catalytic activities. By substitution of the experimental data in this equation, values have been obtained for the ratio K_M/K_H in the case of the three different acids.

The author states that the two sets of experiments with varying acid concentration and with and without neutral salt yield values for the ratio which are of the same order of magnitude. For hydrochloric acid the ratio is 2, for trichloroacetic acid, 0·35, and for dichloroacetic acid, 0·08. In the case of trichloroacetic acid

the separate values of the ratio are in much better agreement than those obtained for hydrochloric and dichloroacetic acids. In particular, it may be noted that the divergence in the case of dichloroacetic acid is verv considerable, the tabulated values of the ratio being 0·16, 0·07, and 0·02.

The results are discussed in reference to the general theory of acid catalysis, and more particularly with regard to the presumed independence of the catalytic activity of the nature of the solvent and of the hydrolyte. H. M. D.

Catalysis by Cations. III. BROR HOLMBERG (*Zeitsch. physikal. Chem.*, 1913, **84**, 451—474. Compare A, 1912, ii, 443, 1048).—A continuation of the work described in Part II (*loc. cit.*). The hydrolysis of acetoxyacetic acid is studied in aqueous solution and in the presence of sodium hydroxide, barium hydroxide, and mixtures of these bases, also in the presence of hydrochloric and nitric acids. It is shown that the alkaline hydrolysis is a simple bimolecular reaction, the velocity constant of which is proportional to the seventh root of the concentration of the cation present. At 25° the catalysis constants are $C_{Na}=5·48$ and $C_{ba}=7·05$. When both sodium and barium ions are present together, the catalysis constant is given by the formula $C=(C^7_{Na}[Na^{\cdot}]+C^7_{ba}[ba^{\cdot}])^{1/7}$. In the acid hydrolysis the reaction is unimolecular, when so much of the catalyst is present that the concentration of the hydrogen ion is not reduced appreciably during the reaction. At 25° the relationship, between the velocity constant and the concentration of the hydrogen ion, is expressed by the formula $C=0·00044+0·108H^{\cdot}$. This formula is deduced on the assumption that the anion of acetoxyacetic acid is hydrolysed much more rapidly than the undissociated acid. The affinity constant of acetoxyacetic acid at 25° is calculated as $k=0·00122$. The paper concludes with a general theoretical discussion on cation catalysis, in which the author's views are stated. The views of Bredig, Acree, and Senter on this subject are stated and criticised. J. F. S.

The Effect of Ultra-violet Light on the Catalytic Activity of Colloidal Platinum. CHESTER J. FARMER and FREDERICK PARKER, jun. (*J. Amer. Chem. Soc.*, 1913, **35**, 1524—1527).—The authors find that ultra-violet light gradually destroys the catalytic activity of colloidal platinum. T. S. P.

The Structure of the Atom. Sir JOSEPH J. THOMSON (*Phil. Mag.*, 1913, [vi], **26**, 792—799).—The author describes an atom so constituted that the transformation of radiant energy into kinetic energy takes place according to Planck's law. It is shown that in such an atom the forces acting on a corpuscle in the atom are: (1) a radial repulsive force, varying inversely as the cube of the distance from the centre, diffused throughout the whole of the atom, and (2) a radial attractive force, varying inversely as the square of the distance from the centre, confined to a limited number

of radial tubes in the atom. It is shown that the photoelectric law follows as a consequence of these forces. The conversion of potential energy into radiant energy by the atom is considered mathematically. J. F. S.

Constitution of Atoms and Molecules. II. N. BOHR (*Phil. Mag.*, 1913, [vi], **26**, 476—502. Compare this vol., ii, 689).—This is an attempt to show that the application of Planck's theory of radiation to Rutherford's atom-model, through the hypothesis of the universal constancy of the angular momentum of the bound electrons, leads to agreement with experimental results. The evidence supports the view that the actual number of electrons in a neutral atom is equal to the number which indicates the position of the element in the series of elements arranged in order of increasing atomic weight—oxygen, the eighth element, for example, having eight electrons. The angular momentum of every electron round the centre of its orbit is assumed to be $h/2\pi$, where h is Planck's constant, and this, when the charge on the positive nucleus and the number of electrons in different rings is known, determines the configuration of the system, that is, the frequency of revolution and diameter of the rings. There will, however, be in general more than one stable configuration satisfying the conditions.

After a discussion on the configuration and stability of possible systems, the constitution of atoms containing very few electrons—hydrogen, one; helium, two; lithium, three; glucinum, four—is considered. The formula deduced for the frequencies of the hydrogen spectrum $\nu = K(1/\tau_2^2 - 1/\tau_1^2)$, where τ_1 and τ_2 are integers and $K = 2\pi^2 e^4 m/h^3$, gives for the constant K the value $3{\cdot}26 \times 10^{15}$, in agreement with the constant $3{\cdot}29 \times 10^{15}$ in the Balmer spectrum, and the calculated value for the diameter of the orbit $a\,0{\cdot}55 \times 10^{-8}$ is of the order of magnitude expected from the diameter of the hydrogen atom. The calculated potential required to ionise the atom is 13 volts, agreeing with the value found with positive rays, 11 volts.

For helium the frequency formula is the same, except that the integers τ_1 and τ_2 are replaced by $\tau_1/2$ and $\tau_2/2$. This gives the two spectrum series, hitherto associated with hydrogen, observed by Pickering for ζ Puppis, and by Fowler in vacuum tubes containing helium and hydrogen. Both electrons in the neutral helium atom are more firmly bound than the one in the hydrogen atom, and the calculated value for the ionisation potential is 27 volts. A helium nucleus with three electrons is unstable, indicating that the helium atom can never acquire a negative charge.

For lithium the spectrum corresponding with the removal of all three electrons should only be observed in extraordinary cases, owing to the great energy required, but in certain stars, showing the Pickering spectrum with special brightness, lines are observed corresponding with the formula. In this formula $\tau_1/3$ and $\tau_2/3$ replace τ_1 and τ_2 of the hydrogen spectrum, and the lines observed

correspond with $\tau_2=6$ and $\tau_1=10$, 13, and 14. With $\tau_2=1$, 2, or 3 only ultraviolet series are obtained, and for $\tau_2=4$, one line in the visible region (with $\tau_1=5$) of wave-length 4503, corresponding with a line 4504 of unknown origin, but there are no unidentified lines known with $\tau_2=5$. The most probable configuration for the lithium atom gives an outermost electron, bound even more lightly than for the hydrogen atom (ionising potential 1·4 volts), and two symmetrical inner electrons more strongly bound than in the helium atom. For glucinum two rings, each containing two electrons, the outer pair more lightly bound than for the helium atom, is deduced.

With various simplifying assumptions more complicated atomic structures are considered. For all numbers of electrons above 10 (neon) up to large numbers it is assumed that a ring of eight electrons occurs. A ring of sixteen electrons will not be stable until the number is large.

The characteristic X-radiation of an atom is assumed to be due to settling down of the system if electrons in the inner rings are removed. as by bombardment with cathode-rays, in contrast with the light-frequencies in which the outer rings are concerned. The theory leads to a formula for the velocity of the cathode-ray required to excite the characteristic X-radiation in an element, in agreement with Whiddington's experiments. Finally, radio-active phenomena are briefly discussed. F. S.

Some New Multiple Relations of the Atomic Weights of Elementary Substances; and the Classification and Transformations of Neon and Helium. HENRY WILDE (*Phil. Mag.*, 1913, [vi], **26**, 732—740 *).—The author divides the elements into seven groups, the atomic weights of which he states are multiples of one, two, three, four, five, six, and seven times that of hydrogen. Silicon he places in the group $n7H$, and he gives it the atomic weight 35, which he is of the opinion is supported by Dulong and Petit's law. The atomic weight of helium he places as 2; many other atomic weights are similarly changed. The recent experiments on the production of helium and neon from glass are explained by the author on the assumption that these elements are the primates of barium, lead and calcium, and silicon respectively. J. F. S.

Curious Atomic Weight Relations: Quaternian Series. FREDERICK H. LORING (*Chem. News*, 1913, **108**, 188—189).—In a previous paper (*ibid.*, 95) it has been pointed out that certain series of four elements exhibit secondary atomic-weight differences which form a geometrical progression. Such a series is represented by argon, iron, bromine, and silver. It is now suggested that helium, aluminium, manganese, and rubidium form a similar series, and that corresponding members of these two series are more or less closely related. Other series of the same type are formed by neon, nickel, tellurium, and an element of atomic weight 211·4, and

* and *Mem. Manchester Phil. Soc.*, 1913, **57**, No. XII., 1—11.

by an element of atomic weight 0·27, boron, magnesium, and potassium. H. M. D.

Valence and Tautomerism. WILLIAM C. BRAY and GERALD E. K. BRANCH (*J. Amer. Chem. Soc.*, 1913, **35**, 1440—1447).—Many chemists insist that the valence numbers of nitrogen in ammonia and ammonium chloride are 3 and 5 respectively, thus emphasising the total number of valence bonds, as illustrated by the usual structural formulæ. Others insist that the valence number of nitrogen is -3 in both cases, the valence number of hydrogen in its compounds being $+1$, and that of chlorine in chlorides -1. Two separate ideas are here involved, however, that of polarity and that of the total number of bonds. It seems advisable to retain the term valence for the two ideas, and the authors suggest the use of the distinguishing terms *polar* number and *total* valence number, whenever necessary. The valence of nitrogen in ammonium chloride can then be completely described as $(-3, 5)$, where, for convenience, the polar number is placed first.

Comparison of the properties of inorganic and organic substances leads to the conclusion that the nature of the union between two atoms may be either polar or non-polar in character, according as it is assumed that an electron passes completely or does not pass from one atom to the other. The non-polar character of certain organic compounds is well shown, for example, by comparison of the compounds methane and carbon tetrachloride. Their behaviour suggests that the valence of carbon is $(0, 4)$, that is, non-polar in both cases, since the assumption that they contain carbon with the valencies $(-4, 4)$ and $(+4, 4)$ respectively, would demand greater differences between the compounds than actually exist.

In the latter part of the paper tautomeric equilibria are discussed and classified on the basis of the valence changes involved. T. S. P.

Valence and Tautomerism. GILBERT N. LEWIS (*J. Amer. Chem. Soc.*, 1913, **35**, 1448—1455).—A discussion of the views put forward by Bray and Branch (compare the preceding abstract). T. S. P.

A Head to Prevent Spirting during Steam Distillations. JAMES J. POLAK (*Chem. Weekblad*, 1913, **10**, 870).—A description of a head for steam distillation. The steam from the boiler passes into the liquid in the flask through a tube sealed into a glass globe resembling an inverted flask with the usual neck. The steam escapes through this neck into the globe, and then passes to the condenser through a tube sealed into the top of the globe, the portion of this tube within the globe being bent out of the vertical to eliminate danger of spirting. A. J. W.

Inorganic Chemistry.

Recovery of Iodine from Residues. HAROLD W. GILL (*Analyst*, 1913, **38**, 409).—The following method, which depends on the solubility of sodium iodide in absolute alcohol, may be applied to the recovery of iodine from the waste solutions obtained in iodometric analysis, provided that the iodine has been dissolved originally in sodium iodide solution instead of potassium iodide solution: The residues are evaporated, heated in an air-oven until completely dry, and the coarse powder obtained is then extracted in a Soxhlet apparatus with absolute alcohol. The crystals of sodium iodide separated from the alcoholic solution may be recrystallised from alcohol, and in any case require to be dried first in an air-oven and afterwards under reduced pressure to expel traces of alcohol.

W. P. S.

The Glow of Sulphur. WALTER H. WATSON (*Chem. News*, 1913, **108**, 187—188).—Experiments are described relating to the phosphorescent glow which is exhibited by sulphur under certain circumstances. The glow is readily obtained when a current of air is passed over sulphur heated to a temperature below its ignition point, and then through a tube which is maintained at an appreciably lower temperature. Under these conditions the air becomes charged with sulphur vapour, which separates out in the form of a cloud of very small particles when the temperature falls. The oxidation of this finely-divided sulphur is the cause of the phosphorescence. There is no evidence of the formation of any other oxide than sulphur dioxide at any stage of the process.

H. M. D.

Heterogeneous Equilibria in the System Sulphur Dioxide Halogen. TETTA POLAK-VAN DER GOOT (*Zeitsch. physikal. Chem.*, 1913, **84**, 419—450).—The fusion curves of the systems chlorine–sulphur dioxide, sulphur dioxide–sulphuryl chloride, chlorine–sulphuryl chloride, and the ternary system chlorine–sulphur dioxide–sulphuryl chloride have been determined. It is shown that the unexplained thermal effects observed by Smits and de Mooy (A., 1910, ii, 1049) were due to the presence of sulphuryl chloride which had been formed in the dark and in the absence of catalysts. In the chlorine–sulphur dioxide mixtures, which were rich in chlorine, mixed crystals were formed. The equilibrium

$$SO_2 + Cl_2 \rightleftharpoons SO_2Cl_2$$

was studied in the presence of various catalysts, of which camphor is shown to be the best, for in the liquid condition the two substances combine entirely to form sulphuryl chloride. The light catalysts could not be brought to an equilibrium. The solidification curve of sulphur dioxide and bromine was determined, and shown to be similar to that of sulphur dioxide–chlorine. Attempts were made to prepare sulphuryl bromide, but they were unsuccessful.

J. F. S.

The Action of Sulphur Trioxide on Salts. WILHELM TRAUBE (*Ber.*, 1913, **46**, 2513—2524).—The author has devised a special apparatus by means of which anhydrous salts may be submitted to the action of sulphur trioxide, and then the products be completely freed from the excess of sulphur trioxide before being allowed to come into contact with the air. The amount of absorption occurring was determined by direct weighing in each case, and the products were analysed.

One molecule of sodium chloride absorbs two molecules of sulphur trioxide, with the formation of a hard, crystalline mass, which is considered to be *sodium chloropyrosulphonate*, $ONa\cdot SO_2\cdot O\cdot SO_2Cl$, sodium chlorosulphonate being probably an intermediate product in the reaction. It fumes in the air, and is decomposed by water, more slowly by alcohol. When added to a chloroform solution of diamylamine, diamylamine sulphamate is formed, which agrees with the formulation of the salt as a chloropyrosulphonate. No evidence of the existence of the product $NaCl(SO_3)_4$ (Schultz-Sellack, A., 1871, 193) could be obtained.

Ammonium chloride first liquefies under the action of sulphur trioxide, and then gives a crystalline product consisting of *ammonium chloropyrosulphonate*, $NH_4\cdot O\cdot SO_2\cdot O\cdot SO_2Cl$, which has properties similar to that of the sodium salt. It cannot be the hydrochloride of a sulphamic acid, since the latter is not found in solution when the salt is decomposed with alkalis.

Sodium nitrite swells up considerably when submitted to the action of sulphur trioxide, and then gives a colourless, crystalline mass, which is decomposed by water with vigorous evolution of oxides of nitrogen. Three molecules of sulphur trioxide are absorbed for each molecule of nitrite, the compound formed being probably *sodium nitrosotrisulphonate*, $NO_2(SO_3)_3Na$.

Persulphates absorb sulphur trioxide, at the same time losing some of their active oxygen, with the formation of what are probably *perpyrosulphates*, in accordance with the equation: $K_2S_2O_8 + 2SO_3 = KS_2O_6\cdot O_2\cdot S_2O_6K$. These compounds fume in the air, the fumes not consisting, however, of sulphur trioxide, and gradually deliquesce. No oxygen is evolved during the deliquescence, and the solution formed contains considerable quantities of hydrogen peroxide and persulphuric acid in varying proportions. When put into water the salts dissolve with violent hissing, and ozonised oxygen is evolved; the solution formed contains only traces of hydrogen peroxide and persulphuric acid. T. S. P.

Fluorosulphonic Acids and Its Salts. WILHELM TRAUBE (*Ber.*, 1913, **46**, 2525—2530).—In contradistinction to the salts described in the previous abstract, sodium fluoride reacts with sulphur trioxide, giving a product which does not immediately react with water with the formation of sulphuric acid. One molecule of sulphur trioxide is absorbed by one molecule of the salt, giving *sodium fluorosulphonate*, $F\cdot SO_3Na$, which can be readily dissolved from unaltered sodium fluoride by extraction with alcohol. Ammonium fluoride reacts more readily than sodium

fluoride, and treatment of the reaction product with ammoniacal methyl alcohol gives a solution from which the well-crystallised *ammonium fluorosulphonate*, $F \cdot SO_3NH_4$, m. p. 245°, is readily obtained by evaporation. Other fluorides react similarly to the sodium and ammonium salts.

Simpler methods of preparing these salts were devised when it was found that not only they, but also fluorosulphonic acid (compare Thorpe and Kirman, T., 1892, **63**, 921), are fairly stable in aqueous solution. If ammonium fluoride is dissolved in fuming sulphuric acid and the solution heated, fluorosulphonic acid distils over; if the solution is treated with ammoniacal methyl alcohol and then separated from insoluble matter, which is chiefly ammonium sulphate, a solution of ammonium fluorosulphonate is formed, from which the solid salt is readily obtained.

Fluorosulphonates are formed not only when a dry mixture of fluorides and pyrosulphates is heated, but also when the two are mixed in the presence of a little water. The ammonium salt is readily obtained in this way. They can also be obtained by the direct action of alkali on an aqueous solution of fluorosulphonic acid, proving that the latter is not immediately decomposed by water.

Both sodium and ammonium fluorosulphonate react neutral to litmus. The aqueous solution of the latter is not completely decomposed even after keeping for days, and the salt can even be recrystallised from hot water. The salts are readily decomposed by warming with hydrochloric acid, or with alkalis. When distilled with 99% sulphuric acid, a good yield of fluorosulphonic acid is obtained.

When the sodium salt is heated in an atmosphere of carbon dioxide a gas is obtained which is not absorbed by potassium hydroxide in a short time, and which is probably sulphuryl fluoride (compare Moissan and Lebeau, A., 1901, ii, 233),

$$2F \cdot SO_3Na = Na_2SO_4 + SO_2F_2.$$

The compounds obtained by Weinland and Alfa (A., 1899, ii, 594) are not identical with the above salts. T. S. P.

The Atomic Weight of Selenium. JOSEF JANNEK and JULIUS MEYER (*Zeitsch. anorg. Chem.*, 1913, **83**, 51—96; *Ber.*, 1913, **46**, 2876—2882).—The decomposition of selenious acid into selenium dioxide and water begins below 50°, but even at this temperature selenium dioxide has an appreciable vapour-pressure. The molecular heat of hydration of selenium dioxide is 3192 cal. The vapour-pressure of selenium, determined by Ruff and Graf's dynamic method (A., 1907, ii, 947), is found to be extremely small, so that at 170—220° volatilisation is inappreciable. Crystalline selenium is quite insoluble in water.

As it is impossible to prepare anhydrous selenium dioxide by sublimation of the acid, the oxidation of selenium (purified by reduction from selenious acid by sulphurous acid, hydrazine sulphate, or hydroxylamine hydrochloride) with nitrogen peroxide has been employed. Nitric and hydrochloric acids and water are

purified by distillation from silica vessels. Hydrazine hydrate is distilled from a platinum flask, and kept in a silver vessel in a desiccator.

Oxidation of selenium with nitric acid gives selenic acid. To obtain selenium dioxide from this, it is necessary to add some hydrochloric acid during oxidation or before sublimation; otherwise the product is coloured. In any case it retains water.

Commercial nitrogen peroxide is purified by passing over hot copper oxide, condensing, passing air through the liquid, and distilling from silver nitrate to remove chlorine. A current of dry oxygen, charged with nitrogen peroxide, is then passed into a weighed silica vessel containing selenium, the temperature of which is at first 215°, and is gradually raised above the melting point of selenium. After oxidation is complete, the nitrogen peroxide is removed by dry air, and the dioxide sublimed a second time and weighed. Attempts to reduce the product to selenium by means of dry gases are unsuccessful, but hydrazine hydrate reduces it quantitatively, the original selenium being very exactly recovered.

The value, corrected to vacuum, found for the atomic weight of selenium is 79·141.

For the colorimetric estimation of selenium, sodium hyposulphite gives a sensitiveness of 0·005% SeO_2 in water, or 0·002% in concentrated sulphuric acid, whilst with potassium iodide and starch even 0·0000005 gram SeO_2 in 1 c.c. of solution may be detected, or five times that quantity in concentrated sulphuric acid.

Concentrated hydrazine hydrate and selenious acid yield a red solution containing hydrazonium selenite and polyselenides, which on dilution forms very stable colloidal selenium. C. H. D.

Preparation of Tellurous Acid and Copper Ammonium Tellurite. G. O. OBERHELMAN and PHILIP E. BROWNING (*Amer. J. Sci.*, 1913, [iv], **36**, 399—400).—Tellurous acid may be obtained from the residues from the electrolytic refining of copper as follows: The residues are treated with a solution of ammonium hydroxide, and the tellurous acid precipitated from the solution so obtained by means of acetic acid (compare Browning and Flint, A., 1909, ii, 934). By dissolving the tellurous acid thus obtained in sodium hydroxide and precipitating again by acetic acid, copper and many other metals, the hydroxides of which are insoluble in sodium hydroxide, are removed.

If the precipitation of the tellurous acid by acetic acid is brought about without warming the solution, and the product is dried without heating, the tellurous acid obtained is readily soluble in the alkali hydroxides. If, however, the precipitation takes place in hot solution and the precipitate is dried by the application of heat, the product tends to be quite insoluble in the alkali hydroxides.

After the first treatment of the residues with ammonia in this extraction process it was observed that a purple, crystalline salt separated from the alkaline solution on keeping. A similar salt could be obtained by allowing an ammoniacal solution of tellurous

acid containing some copper salt to evaporate over sulphuric acid, and in the presence of soda lime; also, by adding slowly, with constant stirring, acetic acid to an ammoniacal solution of tellurous oxide and copper chloride. This salt, on analysis, gave TeO_2,83·84, CuO,4·63, NH_3,5·22, H_2O,6·10, and is a *copper ammonium tellurite.*

Similar salts could not be obtained with nickel, cobalt, zinc, cadmium, or silver in the place of copper. T. S. P.

Influence of Various Conditions on the Oxidation of Nitrogen in the Voltaic Arc. ALEXEI V. SAPOSHNIKOV, A. GUDIMA, and V. KUTOVSKI (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1076—1091).—Experiments made with an arc passing between carbon electrodes show that, as the air-supply, V (cub. metres per hour), is increased, the ratio of V to the power consumed, KW, also increases. The yield of nitric acid per kilowatt-hour at first increases to a maximum of 65·3 grams for $V : KW$ = about 1, then diminishes somewhat, and finally increases again to 78 grams per kilowatt-hour for a value 1·90 of the ratio $V : KW$. With both dry air and air saturated with moisture, the percentage of nitric oxide in the issuing gases increases to a maximum, and then decreases as the air-supply is continuously increased, but the wet air gives the higher yields in all cases, the difference in yield diminishing as the air-supply increases. The action of the moisture is probably expressed by the equations: $N_2 + 2H_2O = 2NO + 2H_2$ and $2H_2 + O_2 = 2H_2O$.

As material for the electrodes, carbon is greatly to be preferred from an industrial point of view. It gives a very constant arc, requires no cooling arrangement, and allows of the ready introduction into the arc of extraneous substances; it burns away rapidly, but this may be avoided by coating the lateral surfaces electrolytically with nickel. Of metallic electrodes, those of copper give the best results, whilst the use of platinum is not to be recommended. T. H. P.

Combustion of Air in the Voltaic Arc. ALEX. I. GORBOV and V. F. MITKEVITSCH (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1109—1136).—The principal conclusions arrived at by the authors as a result of theoretical considerations and of experimental data obtained with a small Birkeland-Eide furnace and with one of their own design, are as follows:

The relation between c, the percentage of nitric oxide formed on combustion of air under the influence of the voltaic arc, δ, the volume of air introduced into the furnace per hour per kilowatt, and G, the number of grams of nitric acid into which the nitric oxide may be transformed, is expressed by the equation

$$8G/225 = c\delta \quad \text{(I)},$$

which is similar in form and in the significance of its terms, to the Clapeyron gas equation, $RT = pv$. From this it follows that (1) if with a given air-supply the conditions of combustion are changed so as to maintain a certain definite percentage of nitric oxide, the number of grams of nitric acid per kilowatt-hour will be the greater

the less the number of kilowatts supplied to the arc, and (2) one and the same quantity of nitric acid per kilowatt-hour may be obtained with various concentrations of nitric oxide, if with constant arc-power and variable conditions of burning the percentage of nitric oxide changes in inverse proportion to the air-supply.

The general relationship between the air-supply and the percentage of nitric oxide in the issuing gas may be derived a priori on the assumption that the divergence of technical apparatus from the ideal is expressible as a certain air-supply to be applied as a correction to that actually used. The conclusion thence drawn is that, with the limits in concentration of nitric oxide as yet attainable in practice, this relationship is expressed by the hyperbolic formula $c=b/(\delta+a)$ (II). Writing b' for b/a, this gives $G=225a(b'-c)/8$ (III) and $G=225b\delta/8(\delta+a)$ (IV). These equations are regarded as general, and are probably applicable to the data obtained with any electric furnace.

Comparison of equation (III) with the fact that a furnace may work with a constant yield of nitric acid, but with a variable percentage of nitric oxide, leads to the conclusion that, for each furnace, there is possible not a single equation of type (III), but a series of them corresponding with varying utilisation of the energy. In agreement with the observations of other investigators, it is found that the values of a'' and b'', a''' and b''', etc., for this series of equations exhibit a constant ratio, that is,

$$b''/a''=b'''/a'''= \ . \ . \ . =\text{const.}=b'.$$

In the diagram representing the values of G as ordinates and the corresponding ones of c as abscissæ, each furnace is represented by a group of straight lines beginning in the point b' and spreading upwards from right to left in the shape of a fan. The constancy of b' does not follow immediately from the above equations, but is found to be in agreement with the fundamental hypothesis expressed by $c=b/(\delta+a)$.

A further conclusion drawn from the experimental data is that the concentration of nitric oxide on breaking of the arc is independent of the power of the arc, and almost independent of the detailed construction of the furnace, although characterised by its type; such a conclusion is, however, based on a comparatively small number of results.

The magnitudes of b and b' are regarded as characterised principally by the density of the energy in the region where the nitric oxide is formed, and the technical plant now in use leaves considerable room for increasing them; the magnitude of a should be as small as possible. T. H. P.

The Action of Finely Divided Nickel on Nitric Oxide. R. S. Felgate (*Chem. News*, 1913, **108**, 178).—Nitric oxide can be catalytically decomposed by finely-divided nickel suspended in hot water, the products of decomposition being nitrogen and nickel oxide. The nickel should be prepared by the reduction of the dry precipitated hydroxide in an atmosphere of hydrogen.

Colloidal nickel prepared by Bredig's method does not act in a

similar manner. The action appears to depend on the state of aggregation and method of preparation of the nickel catalyst, but further investigation of this point is necessary. T. S. P.

Hydrazine and Its Inorganic Derivatives. I. Hydrazine Nitrites and Their Decomposition Products. FRITZ SOMMER (*Zeitsch. anorg. Chem.*, 1913, **83**, 119—137).—*Hydrazine nitrite*, $N_2H_5NO_2$, may be prepared by mixing solutions of barium nitrite and neutral hydrazine sulphate, stirring to convert the thick, gelatinous barium sulphate into the crystalline form, and filtering by means of a vacuum. The stable solution is then evaporated in a vacuum over phosphoric oxide. The oil thus obtained does not crystallise spontaneously, but does so on inoculating with a small quantity of solid obtained by extracting a portion with methyl alcohol, partly precipitating with ether, and cooling in ether and solid carbon dioxide. The solid salt is almost white, but becomes yellow on fusion. It is hygroscopic, and dissolves readily in alcohol, but not in ether, and may be obtained from a mixture of these in large, probably monoclinic prisms. It explodes violently with a blow, less vigorously if rapidly heated.

For analysis, hydrazine is estimated with iodine by Stollé's method (A., 1903, ii, 100). The same solution, after the addition of solid potassium iodide, is mixed with a known quantity of dilute sulphuric acid in an atmosphere of carbon dioxide. The iodine liberated according to the equation

$$2HNO_2 + 2HI = 2NO + 2H_2O + I_2$$

is then titrated with thiosulphate.

The salt decomposes according to the equation

$$N_2H_5NO_2 = NH_3 + N_2O + H_2O,$$

and this decomposition is very greatly accelerated by nitrous acid. The preparation of hydrazine dinitrite in aqueous solution is thus impossible, as the weakly basic character of hydrazine would cause the salt to be so far hydrolysed that much nitrous acid would be present in the solution. If hydrazine disulphate and barium nitrite react together, the products are ammonium nitrite and nitrous oxide. The decomposition of hydrazine nitrite is thus due to the action of nitrous acid on the undissociated compound, and is autocatalytic. The secondary reaction, the formation of hydrazoic acid from hydrazine and nitrous acid, is due to the action of nitrous acid on the N_2H_5 ion.

Under similar conditions hydrazine nitrite is less stable than ammonium nitrite, but aqueous solutions of the former are the more stable, as the traces of ammonia first formed check the hydrolysis.

The failure to obtain the compound from barium nitrite and ordinary hydrazine sulphate (Dey and Sen, A., 1911, ii, 822) is due to the fact that the latter substance is mainly the disulphate, which behaves as an acid salt. The normal sulphate, prepared by digesting the ordinary salt with barium carbonate, forms perfectly stable, hexagonal crystals, $(N_2H_5)_2SO_4,H_2O$, which dissociate into the anhydrous salt and water at 47·3°. The anhydride has m. p. 117°.

The method of Dey and Sen for the detection of nitric in presence of nitrous acid (A., 1912, ii, 296) is not exact. The diphenylamine test should not be applied until the excess of hydrazine has been destroyed, as otherwise the blue colouring matter may be reduced by the hydrazine. C. H. D.

Preparation of Phosphonium and Ammonium Iodides and the Action of Heat on those Substances. ALFRED HOLT and JAMES E. MYERS (*Zeitsch. anorg. Chem.*, 1913, **82**, 278—282. Compare P., 1913, **29**, 61).—Phosphonium iodide may be prepared by distilling purified iodine with fused calcium nitrate, and allowing it to react with a solution of phosphorus in carbon disulphide, thoroughly dried by anhydrous sodium sulphate, the reaction taking place in an atmosphere of nitrogen. The best results are obtained by using a minimum quantity of solvent and adding the iodine in the solid form. The iodide thus obtained may be sublimed without decomposition. It retains some of the water used in its preparation, and may be dried by subliming through a column of phosphoric oxide in an apparatus which is described.

Hydrogen phosphide, purified by conversion into and decomposition of its compound with cuprous chloride, is freed from hydrogen chloride, dried by phosphoric oxide, and allowed to react with hydrogen iodide, prepared from potassium iodide and metaphosphoric acid, and purified by means of red phosphorus and phosphoric oxide, followed by liquefaction and fractionation.

A third method consists in combining iodine vapour with yellow phosphorus and adding the required quantity of water.

The yellow tint of phosphonium iodide which has been distilled is not due to iodine, but to a phosphorus iodide, which yields phosphoric acid with water. Phosphonium iodide may be distilled without discoloration in a moist inert gas or in steam.

Ammonium iodide does not form nitrogen iodide under similar conditions. C. H. D.

Modifications of Arsenic. I. Grey and Brown Arsenic. VOLKMAR KOHLSCHÜTTER, E. FRANK, and CURT EHLERS (*Annalen*, 1913, **400**, 268—301).—The differences in the natural forms of solid substances of the same composition may be due to differences in crystalline structure, to chemical isomerism, or to various physical and chemical factors which impress on the substance a definite form during the process of its formation; for example, of the modifications of carbon, the diamond and graphite are each sharply defined, but the appearance of amorphous carbon is influenced by the various factors operating during its process of formation. The present research has brought to light the importance of certain factors in determining the form of a substance during its process of formation; one factor of especial importance is the original state of distribution of the molecules of the material which is undergoing change. Many substances, which are generally regarded as monotropic modifications, are certainly only one and the same substance in different states of distribution.

Well-known forms of arsenic are (1) "metallic," hexagonal arsenic, D 5·73; (ii) yellow arsenic, D^{18} 2·03, crystallising in the regular system; (iii) grey or black arsenic, D 4·60—4·72, obtained in arsenic mirrors; (iv) brown arsenic, D 3·7—4·7, obtained by the reduction of arsenic compounds in aqueous solution or by the action of oxygen or arsenious bromide on yellow arsenic dissolved in carbon disulphide. Erdmann (A., 1908, ii, 584) regards the differences in these four modifications as being due to differences in molecular complexity, and represents metallic arsenic, the densest modification, as consisting of monatomic molecules.

The authors are of opinion that yellow arsenic (specific volume 0·5), in comparison with metallic arsenic (sp. vol. 0·175), is the same quantity of matter distributed throughout a very much larger space, and the conversion of yellow into metallic arsenic is a process of condensation, analogous to that which obtains in the formation of silver from silver oxide (Kohlschütter and Eydmann, this vol., ii, 589). Such a process offers the best of opportunities for a substance to be obtained in different modifications. The conversion of yellow into metallic arsenic has been studied from this point of view, attention being particularly directed to the production of the intermediate forms, grey and brown arsenic.

Grey arsenic is obtained by the action of light on yellow arsenic prepared either from carbon disulphide solution or by the sublimation of metallic arsenic. The formation of the grey arsenic is the more rapid the finer is the state of division of the yellow arsenic; it collects on the walls of the vessel as a grey or black mirror, only a little being obtained in the form of a dust. It has D^{18} 4·69—4·707, and is amorphous. Reasons are given for the authors' belief that grey arsenic is only metallic arsenic in a finer state of distribution; that is, the same matter occupying a larger space.

Brown arsenic is obtained in various ways by the reduction of arsenic compounds. It changes directly to metallic arsenic by heating. The purest brown arsenic obtained by the authors has D 4·52, and there is no doubt that the densities of grey and of brown arsenic, free from all impurities, are nearly the same, so that the density is not a sufficient criterion to distinguish these substances as different modifications. The authors' experiments indicate that grey and brown arsenic are simply the same modification of metallic arsenic in different states of distribution, that of brown arsenic being the more diffuse. Brown arsenic is only obtained under the influence of a foreign substance which acts in a certain sense as a dispersing medium, the nature and concentration of which determines the state of distribution. C. S.

The Oxidisability of Charcoal at Moderate Temperatures. KARL A. HOFMANN, K. SCHUMPELT, and K. RITTER (*Ber.*, 1913, **46**, 2854—2864).—It has previously been shown (this vol., ii, 609) that amorphous carbon is oxidised by chlorate solutions at water-bath temperature in the presence of osmium tetroxide, to carbon dioxide, mellogen, and mellitic acid. Further experiments have shown that the oxidisability of carbon at medium temperatures is much greater

than hitherto supposed, and details are given of the action of chlorate solutions on various charcoals.

In dilute aqueous solution calcium hypochlorite acts so vigorously on various charcoals, with foaming evolution of carbon dioxide, that the energy of oxidation of the system is available in a few seconds, and the heat produced can be used, under proper conditions, for steam raising, etc. The results of calorimetric measurements with different charcoals are given.

The carbon dioxide evolved is always accompanied by carbon monoxide (compare Rhead and Wheeler, T., 1912, **101**, 846) in amounts up to 9%. The occurrence of this gas is explained by the formation of high-molecular carbonyl compounds as intermediate products, the presence of such compounds being indicated by the deep brownish-black to red, fluorescent solutions obtained during the reactions; further oxidation gives carbon monoxide and dioxide. In contradistinction to the black, amorphous varieties of carbon, powdered diamond, on treatment with hypochlorite solution, gives a *white* suspensoid, which is to be further investigated; the diamond is attacked only to a slight extent.

When black, amorphous carbon of various kinds is exposed to the air at 120—150° in the presence of alkalis, it gives, at first, dark brown to red colloids, which are then oxidised to formate and oxalate, and finally to carbonate.

Neglecting the different initial velocities of reaction, the different kinds of amorphous carbon react so similarly towards oxidising agents that no essential difference in chemical structure can be assigned to them. T. S. P.

The Action of Hydroxyl Ions on Silicates. PAUL ROHLAND (*Zeitsch. anorg. Chem.*, 1913, **83**, 138—142).—The coagulation of emulsions of kaolin or clay by salts depends on the concentration of hydroxyl ions. The coagulating effect increases with the hydroxyl concentration to a maximum. Cement and other silicates are similarly affected. Other physical factors are involved.

C. H. D.

The Action of Sulphur Monochloride on Certain Minerals. HIRAM STANHOPE LUKENS (*J. Amer. Chem. Soc.*, 1913, **35**, 1464—1469).—The author has investigated the action of sulphur monochloride, at different temperatures up to about 800°, on the following minerals: felspar, garnet, zircon, sphene, tourmaline, hornblende, pyroxene, spinel, rhodonite, and pyromorphite. Only those which contained a considerable quantity of elements the chlorides of which are volatile in sulphur monochloride were acted on to any marked extent. Garnet and sphene may be almost completely decomposed in this way, and iron completely removed from zircon. Pyromorphite is completely decomposed at 450—550°, the residue then being soluble in dilute hydrochloric acid, with the exception of any silica which may be present. T. S. P.

Potassium Ammonomagnesate, $Mg(NHK)_2,2NH_3$. EDWARD C. FRANKLIN (*J. Amer. Chem. Soc.*, 1913, **35**, 1455—1464).—*Potassium ammonomagnesate*, $Mg(NHK)_2,2NH_3$, a new salt belonging to the author's ammonia system of acids, bases, and salts (compare A., 1912, ii, 451), has been prepared by the action of potassium amide in liquid ammonia solution on magnesium iodide, magnesium nitrate, magnesium acetamide, and magnesium respectively, the reactions taking place according to the equations:

$$MgI_2,(NO_3)_2,(MeCONH)_2 + 4KNH_2 = Mg(NHK)_2,2NH_3 + 2KI,(NO_3),(MeCONH)$$

and $Mg + 2KNH_2 + 2NH_3 = Mg(NHK)_2,2NH_3 + H_2$. The preparation was carried out by the methods previously described for similar compounds.

Potassium ammonomagnesate is a fine, crystalline powder, which is only slightly soluble in liquid ammonia, and is rapidly hydrolysed by liquid water or water vapour. It is not explosive, and may be heated to 100° without loss of ammonia.

For the purpose of the preparation it was necessary to obtain anhydrous magnesium iodide, nitrate, and acetamide. The first two were obtained by the action of magnesium on liquid ammonia solutions of ammonium iodide and nitrate respectively, hydrogen being evolved with the formation of the compounds *magnesium hexammine iodide*, $MgI_2,6NH_3$, and *magnesium hexammine nitrate*, $Mg(NO_3)_2,6NH_3$. Magnesium acetamide has been described by Franklin and Stafford (A., 1902, i, 748). T. S. P.

Potassium Hydroxopentafluorostannate [Stannihydroxopentafluoride]. SAMUEL H. C. BRIGGS (*Zeitsch. anorg. Chem.*, 1913, **82**, 441—444).—The salt K_2SnF_6,H_2O, prepared from stannic chloride and potassium fluoride, and crystallising in octahedra, has been described by Marignac, who also assigned the same formula to a salt crystallising in lamellæ, and obtained from the former by the addition of potassium hydroxide. This salt is now shown to be

$$K_2(SnF_5OH),H_2O.$$

Potassium carbonate is preferable to the hydroxide. The salt forms highly glistening leaflets, and is more soluble than the hexafluoro-compound. An anhydride, probably $K_4(SnF_5{\cdot}O{\cdot}SnF_5)$, is formed at 160—170°. C. H. D.

Crystallisation of Sodium Chloride, Bromide, and Iodide from Fusion and Aqueous Solution. E. SCHOBERT (*Jahrb. Min.*, 1913, ii, *Ref.* 186—187; from *Diss.*, Leipzig, 1912).—The three binary systems of sodium haloids were investigated. The melting points of the simple salts are: the chloride, 800° (Walther and White); bromide, 748°; iodide, 670°.

NaCl–NaBr.—When fused together, these form a continuous series of mixed crystals, with a minimum at 731° and NaBr 72 mol. %. From solution the chloride crystallises below 0·15° as the dihydrate $NaCl,2H_2O$ in six-sided plates; and the bromide forms the monoclinic dihydrate $NaBr,2H_2O$ below 50·7°. The hydrated and the anhydrous salts each form mixed crystals; at

60° the series Na(Cl,Br) is continuous, but at -10° there is a break in the mixed crystals of the dihydrates. At 15° anhydrous or hydrated crystals appear according to the ratio of chloride to bromide in the solution.

NaBr–NaI.—Fusions give a continuous series of mixed crystals, with a minimum at 636° and NaI 67 mol. %. These mixed crystals are unstable, becoming cloudy at the ordinary temperature. The hydrates, $NaBr,2H_2O$ and $NaI,2H_2O$, are both monoclinic, although of different habit, and they do not form mixed crystals.

NaCl–NaI.—These give a eutectic at 570° with NaI 62·5 mol. %. The chloride separates with a maximum isomorphous intermixing of NaI 2—3 mol. %; and the iodide with NaCl 24 mol. %. From solution at 60° pure sodium chloride cubes separate even in the presence of much iodide; and at lower temperatures there is no appreciable isomorphous mixing. L. J. S.

Colloidal Metal Chlorides and Sulphates. László Karczag (*Biochem. Zeitsch.*, 1913, **56**, 117—121).—When sodium salicylate is treated with thionyl chloride, the sodium chloride resulting from the reaction, $OH\cdot C_6H_4\cdot CO_2Na + SOCl_2 = OH\cdot C_6H_4\cdot COCl + NaCl + SO_2$, separates in a colloidal form. The sodium salt of benzoic and other acids on similar treatment also yield sodium chloride in a colloidal form, and chlorides of other metals can also be obtained by using salts of metals other than sodium. The appearance and properties of these colloids can be varied by varying the conditions, such as using indifferent solvents like benzene or light petroleum. These colloids can also be dissolved in certain indifferent solvents, from solutions in which they can be precipitated by other liquids. By using sulphuryl chloride instead of thionyl chloride, metallic sulphates can be obtained in colloidal form. S. B. S.

Theory of the Causticising of Alkali Carbonate Solutions. P. P. Fedotéev (*Zeitsch. anorg. Chem.*, 1913, **82**, 341—352).—The reaction $Na_2CO_3 + Ca(OH)_2 \rightleftharpoons 2NaOH + CaCO_3$, has been studied, using the experimental data of Wegscheider and Walter (A., 1907, ii, 259, 686), with some data from other authors. An equilibrium diagram is constructed for 80°, the solid phases being $Ca(OH)_2$, $CaCO_3$ and $CaCO_3,Na_2CO_3,2H_2O$ (pirssonite). The end of the mass-action curve lies at 80° on the line of total sodium concentration corresponding with 5·3 equivalents Na. The concentration of the solution at this point is $\Sigma OH = 4{\cdot}3$ and $\Sigma CO_3 = 0{\cdot}5$ mols. per litre. A shaded area in the diagram, within which causticising is technically performed, is so situated that a double salt is not deposited, even when the temperature falls greatly during settling and cooling. C. H. D.

Bromides. V. Icilio Guareschi (*Atti. R. Accad. Sci. Torino*, 1913, **48**, 929—947. Compare this vol., ii, 692).—The present paper deals with the four bromides: $CaBr_2,6H_2O$, $SrBr_2,6H_2O$, $BaBr_2,2H_2O$, and $CoBr_2,6H_2O$. By keeping them under various conditions (at various temperatures, in the presence or absence of

dehydrating agents, and with or without the use of a current of dry air) until of constant weight, a number of hydrates can be obtained.

In the case of calcium bromide, hydrates exist containing $6H_2O$, $5H_2O$, $4H_2O$, $3H_2O$, $1\frac{1}{2}H_2O$, $1H_2O$, and $\frac{1}{2}H_2O$. Strontium bromide forms two hydrates: $SrBr_2,6H_2O$ and $SrBr_2,H_2O$. Barium bromide exists in the two hydrated forms: $BaBr_2,2H_2O$ and $BaBr_2,H_2O$.

Cobaltous bromide exists in the following forms (compare Hartley, this Journal, 1874, **27**, 501): $CoBr_2,6H_2O$ (red prisms, m. p. 47—48°); $CoBr_2,5\frac{1}{2}H_2O$ (?) (rose-coloured); $CoBr_2,5H_2O$ (pink); $CoBr_2,4H_2O$ (reddish-violet, m. p. 70—71°); $CoBr_2,2H_2O$ (reddish-violet); $CoBr_2,H_2O$ (blue); $CoBr_2,\frac{1}{2}H_2O$ (?); $CoBr_2$ (anhydrous, green). R. V. S.

Supposed Occurrence of a Peroxide in Calcium Hydroxide Exposed to the Action of Air. HUGO DITZ (*J. pr. Chem.*, 1913, [ii], **88**, 443—456. Compare this vol., ii, 320).—The author adversely criticises Vaubel's work (A., 1912, ii, 1180; this vol., ii, 706) on the occurrence of a peroxide in calcium hydroxide after exposure to air, and maintains that the benzidine, *m*-phenylenediamine and starch-iodide reactions, used by Vaubel for the detection of the peroxide, are not suitable for this purpose. The starch-iodide reaction cannot be used in the presence of iron, the small amount of iron present in calcium hydroxide being sufficient to cause the rapid development of the blue colour.

The reaction with benzidine is probably due to the presence of manganese in the calcium hydroxide, whilst the *m*-phenylenediamine reaction cannot be used for the detection of peroxides in the presence of iron and manganese.

On the other hand, the titanic acid reaction is not influenced by the presence of calcium hydroxide as stated by Vaubel; a specimen of calcium hydroxide, which gave no reaction with this reagent, at once developed an intense yellow coloration on the addition of a trace of hydrogen peroxide. Even after 100 days' exposure to air, no trace of peroxide could be detected in the calcium hydroxide.

The author accordingly reaffirms his view that the starch-iodide and other reactions shown by calcium hydroxide are due to traces of manganese and iron, or to the formation of nitrite by the action of nitrous acid in the air (compare following abstract).

F. B.

Occurrence and Manner of Formation of Nitrite and Nitrate in Calcium Hydroxide and Other Compounds Exposed to the Action of Air. HUGO DITZ and FRANZ KANHÄUSER (*J. pr. Chem.*, 1913, [ii], **88**, 456—479).—The author has previously expressed the view (this vol., ii, 320) that the increase in the intensity of the starch-iodide reaction, shown by calcium hydroxide on exposure to air, is probably due to the gradual formation of nitrite by the absorption of the nitrous acid from the air, since, after exposure, nitrites can be detected by means of α-naphthylamine and sulphanilic acid. It is now found that

both nitrite nad nitrate are produced, and their amounts have been determined after varying times of exposure. A specimen of calcium hydroxide, after twelve days' exposure to the laboratory atmosphere, contained nitrite corresponding with 0·020% of nitrous acid, and this amount did not appreciably increase even after exposure for forty days.

The formation of nitrites and nitrates by exposing calcium carbonate and other basic substances to air has already been investigated by Baumann (A., 1889, 183), who has shown that the nitrous and nitric acids concerned in the formation of the nitrites and nitrates are not produced by the oxidation of atmospheric nitrogen or ammonia in the presence of the basic substances, but are already pre-existent in the atmosphere, and probably owe their origin to the direct union of nitrogen and oxygen during the combustion of coal gas and other combustibles used in the laboratory for heating and lighting purposes. The author describes a series of experiments carried out with calcium hydroxide in support of this view. F. B.

Artificial Formation of Dolomite. K. SPANGENBERG (*Zeitsch. Kryst. Min.*, 1913, **52**, 529—567).—Working on the lines suggested by Linck (A., 1911, ii, 294), solutions of calcium and magnesium chlorides and ammonium sesquicarbonate were experimented on in an atmosphere of carbon dioxide at various temperatures and pressures. Under the various conditions, dolomite, calcite, magnesite, or vaterite were obtained. Dolomite, D 2·825, was best prepared by the action of magnesium chloride and sodium carbonate solutions on vaterite at 180—200° in 50 atmospheres of carbon dioxide. Dolomite and calcite may be separated by means of a solution of copper nitrate. L. J. S.

Solubility of Calcium Sulphite. JULES ROBART (*Bull. Assoc. chim. Sucr. Dist.*, 1913, **31**, 108—111).—In experiments carried out with the object of ascertaining the solubility of calcium sulphite in various solutions, 1 litre of the solution containing the reagents, etc., was in each case boiled for three minutes, filtered at a temperature of 100°, and, after cooling, the amount of lime in the filtrate was estimated. One litre of water dissolved a quantity of calcium sulphite equivalent to 78 mg. of calcium oxide; this quantity was diminished to 37 mg. in the case of a 12% sugar solution. The presence of calcium carbonate causes a slight increase in the solubility of the sulphite, but when alkali hydroxides, carbonates, and sulphites are present, practically no calcium salts dissolve. With respect to sulphited sugar liquors, it is recommended that these should be filtered while hot, as the solubility of calcium sulphite increases when the temperature is lowered. W. P. S.

The Binary System $CaSiO_3$-CaF_2. FRANZ TURSKY (*Zeitsch. anorg. Chem.*, 1913, **82**, 315—322. Compare Karandéeff, A., 1910, ii, 954).—When the quantity of calcium fluoride is small, the

fluorine is completely volatilised on melting, larger quantities are partly retained as fluoride, but solid solutions are not formed in any case. Pseudowollastonite is obtained at high temperatures, but when the proportion of calcium fluoride is sufficient, wollastonite is obtained. In nature, the latter mineral can only have been formed in presence of mineralisers, such as fluorides. C. H. D.

Filtration of Barium Sulphate. J. L. OSBORNE (*J. Physical. Chem.*, 1913, **17**, 629—631).—Experiments are described which confirm the observation that barium sulphate can be filtered quite readily under suction if a concentrated solution of ammonium acetate is added to the precipitate and the mixture well stirred before filtration. The experiments show further that the coagulating effect of the ammonium acetate is dependent on the solubility of barium sulphate in concentrated ammonium acetate solution. In presence of ammonium chloride or hydrochloric acid, the effect of the ammonium acetate is less evident, and this is attributed to the lowering of the solubility of barium sulphate in presence of these substances. H. M. D.

Experiments at High Temperatures. I. Fusion and Volatilisation of Refractory Oxides in the Electric Vacuum Furnace. OTTO RUFF, HERMANN SEIFERHELD, and JOSEPH SUDA (*Zeitsch. anorg. Chem.*, 1913, **82**, 373—400. Compare A., 1910, ii, 575).—The melting point of most refractory oxides in a carbon furnace depends in a high degree on the character of the surrounding atmosphere. The only oxide which has a sufficiently well-defined melting point under the conditions employed to serve for calibration purposes is alumina ($2010 \pm 10°$).

Glucinum oxide, GlO, has m. p. 2525° under reduced pressure, but volatilises below that temperature. Magnesia melts above 2500°, but reacts vigorously with carbon, so that the true temperature has not been determined. Lime also reacts with carbon and nitrogen. Under reduced pressure it is not melted at 2450°, but volatilises rapidly from 2000° onwards. Zirconia is readily reduced, but the lower oxide formed has m. p. 2585°, almost independent of the pressure or of the rate of heating. Its vapour pressure is very low, even at the melting point. Stannic oxide melts in a zirconia crucible at 1625°, and is at once violently reduced.

The oxides of yttrium, cerium, thorium, and lanthanum are rapidly converted into carbides. Titanium dioxide is completely converted in a short time into the oxide Ti_7O_{12}. Columbium, tantalum, and chromium oxides are reduced to lower oxides. C. H. D.

Glucinum Compounds. WILHELM BILTZ (*Zeitsch. anorg. Chem.*, 1913, **82**, 438—440. Compare Mieleitner and Steinmetz, this vol., ii, 707).—Crude glucinum sulphide, prepared from the metal and sulphur vapour, is strongly phosphorescent.

Glucinum and scandium acetylacetonates have the simple

molecular weight in carbon disulphide solution, and are unchanged in the presence of ammonia, thus resembling aluminium rather than the rare earths.

Potassium glucinum fluoride, K_2GlF_4, crystallises from solutions having the composition $KGlF_3$. C. H. D.

The Corrosion of Lead in Lime Mortar, and the Supposed Peroxide Occurring in Calcium Hydroxide which has been Exposed to the Air. HUGO DITZ (*Zeitsch. angew. Chem.*, 1913, **26**, 596—598).—Polemical against Vaubel (A., 1912, ii, 1172; this vol., ii, 706, 777), the author maintaining that all Vaubel's results can be explained by the presence of iron or of nitrite in the calcium hydroxide, the nitrite having been formed by the action of the air (compare this vol., ii, 320, 958). T. S. P.

The Solubility of Lead Sulphate and Lead Chromate. GEORG VON HEVESY and FRITZ PANETH (*Zeitsch. anorg. Chem.*, 1913, **82**, 323—328).—Radium-*D*, being chemically inseparable from lead, may be used as an indicator in experiments with lead salts. The concentration of radium-*D* in the lead remains constant after mixture has once taken place, however small the quantity of the lead may be. A quantity of 10^{-10} grams of radium-*D* may be measured by means of an electroscope, using the β-radiation of radium-*E*, whilst by waiting until an equilibrium quantity of radium-*F* has formed, and using the α-radiation, the sensitiveness is increased to 10^{-12}.

The solubility of lead chromate is found by the former method to be $1{\cdot}2 \times 10^{-5}$ grams per litre at 25°. Kohlrausch's approximate estimate from the conductivity is 10^{-4}. This is the least soluble salt of lead. Lead sulphide gives the value 3×10^{-4} grams per litre in water, or $1{\cdot}5 \times 10^{-4}$ in presence of an excess of hydrogen sulphide, the higher value in the former case being due to partial hydrolysis.

The method of radioactive indicators has the advantage over methods involving the weighing of small quantities that there is no danger of the inclusion of impurities in the result. C. H. D.

Atomic Weight of Copper. WILLIAM ŒCHSNER DE CONINCK and F. DUCELLIEZ (*Rev. gen. Chim. pure Appl.*, 1913, **16**, 122—123).—A determination of the atomic weight of copper. The metal was purified by the method described by Vigouroux (*Société des Sciences physiques et Naturelles de Bordeaux*, 1905–1906, 34), and the estimation carried out by conversion into the oxide; the mean of five experiments gave the atomic weight of copper as 63·549. F. M. G. M.

The Action of Sulphides of the Allyl Group on Lead Amalgam and Mercury. MANINDRA NATH BANNERJEE (*Zeitsch. anorg. Chem.*, 1913, **83**, 113—118).—Mercury is not completely purified from lead by distillation in a vacuum. The lead is completely removed from lead amalgam by rubbing repeatedly with

garlic juice, lead sulphide being formed, and this method is found to purify crude mercury completely. Some mercuric sulphide is also formed. The action of the garlic juice is due to the presence of sulphides of the allyl group. C. H. D.

Solubility of Mercury Haloids in Haloid Salt Solutions. WALTER HERZ and W. PAUL (*Zeitsch. anorg. Chem.*, 1913, **82**, 431—437).—Determinations of the composition of a large number of saturated solutions of halogen salts of mercury and the alkali metals show a tendency to form complex salts, in which the molecular ratios are very simple. C. H. D.

Preparation of Mercury Derivatives of Aminosulphonic Acids which are Soluble in Water and Stable to Alkalis. KARL HOFMANN (D.R.-P., 261460).—The insolubility of the previously described mercury derivatives of aminosulphonic acids (Divers, T., 1896, **69**, 1634) detracts from their therapeutic value.

The *salt*, KO_3NSHg,H_2O, is prepared by treating an alkaline solution of aminosulphonic acid with mercuric oxide or chloride; the analogous *sodium* salt is crystalline, whilst the rubidium and lithium salts are also mentioned. F. M. G. M.

The Atomic Weight of Yttrium. II. RICHARD J. MEYER and M. WEINHEBER (*Ber.*, 1913, **46**, 2672—2675).—In a former communication (Meyer and Wuorinen, this vol., ii, 323) the atomic weight of yttrium was calculated from the ratio $Y_2O_3 : Y_2(SO_4)_3$, using 32 as the atomic weight of sulphur. Recalculation with correct atomic weights gives the atomic weight of yttrium as 88·71 and 88·73 respectively.

Fresh experiments on material which had been submitted to exhaustive fractionation by the iodate method gave the values 88·76, 88·80, and 88·73.

The authors have now determined the atomic weight from the ratio $Y_2(SO_4)_3 : Y_2O_3$, the yttrium sulphate, dehydrated at 400°, being transformed into the oxide by heating at a high temperature. The mean of six experiments gave 88·75 as the atomic weight of yttrium, the values obtained varying between 88·71 and 88·76.

As a mean of all experiments the atomic weight is taken to be 88·7. T. S. P.

Scandium in American Wolframite. HIRAM S. LUKENS (*J. Amer. Chem. Soc.*, 1913, **35**, 1470—1472).—The author has recovered pure scandium oxide from wolframite residues from the Zinnwald, using the method previously described by Meyer (A., 1909, ii, 45; 1910, ii, 853). The sulphate was prepared from the oxide and then re-converted into the oxide for the purpose of atomic-weight determinations. In two experiments the atomic weight of scandium was found to be 44·59 and 44·77 respectively.

The oxide was shown to be pure by spectral and radioactivity tests. T. S. P.

The Theory of the Preparation of Aluminium. RICHARD LORENZ, ASMUS JABS, and W. EITEL (*Zeitsch. anorg. Chem.*, 1913, **83**, 39—50, 328. Compare Pascal and Jouniaux, this vol., ii, 508; Puschin and Baskov, *ibid.*, 318; Fedotéev and Iljinsky, *ibid.*, 324).—The freezing-point curve of mixtures of cryolite and alumina is found to have a eutectic point at 33 mol. % Al_2O_3 and 937°. Solid solutions are formed up to 20 mol. % Al_2O_3, but not on the alumina side of the eutectic. Irregularities in the cooling curves are frequent, owing to the tendency to undercooling and the low thermal conductivity. Zonal structure is observed in the solid solutions under the microscope. On approaching the eutectic composition, marked segregation takes place, and needles of corundrum appear together with the crystallites of the solid solution. A definite eutectic structure is not obtained, but aggregate polarisation is observed in the ground mass.

The results obtained with cryolite and sodium fluoride differ somewhat from those of Fedotéev and Iljinsky, the eutectic point being found at 23 mol. % cryolite and 77 mol. % sodium fluoride at 886°. Solid solutions are formed on the sodium fluoride side.

C. H. D.

The Density of Aluminium. FRANCIS J. BRISLEE (*Trans. Faraday Soc.*, 1913, **9**, 162—173. Compare A., 1912, ii, 847).—Aluminium containing 0·36% of impurities has in the cast state D^4_{18} 2·703. Worked specimens of aluminium increase in density on annealing. With sheet metal containing 0·67% of impurities, the following values of D^{18}_4 have been obtained: hard, 2·7076 ± 0·0002; annealed for two hours, 2·7086 ± 0·0002; annealed for twenty-two hours, 2·7085 ± 0·0001.

C. H. D.

Some Colloidal Solutions Derived from Hydrated Alumina. WILLIAM B. BENTLEY and R. PHILLIPS ROSE (*J. Amer. Chem. Soc.*, 1913, **35**, 1490—1499).—When freshly precipitated and well-washed aluminium hydroxide is dissolved to saturation in a hot 8% solution of acetic acid, a colloidal solution is obtained which is coagulated by the addition of hydrochloric acid; nitric acid will similarly produce coagulation, and also potassium sulphate, but not sulphuric acid. The acetic acid may be replaced by formic, propionic, or butyric acid, but the last two are much less effective.

The various experiments carried out by the authors lead them to the conclusion that the colloidal solution is one of a basic aluminium acetate and not of aluminium hydroxide.

T. S. P.

The Constitution of Aluminates. WILLIAM BLUM (*J. Amer. Chem. Soc.*, 1913, **35**, 1499—1505).—The author has determined the changes in hydrion concentration taking place in a solution of aluminium chloride during the precipitation and re-solution of aluminium hydroxide by alkalis, by means of a hydrogen electrode (compare Hildebrand, this vol., ii, 721, 727). From the curves showing the relation between the *E.M.F.* and the number of c.c. of alkali added, the points at which precipitation of the aluminium

hydroxide begins and at which its re-solution is complete, can be determined, and the results indicate that one molecule of freshly-precipitated aluminium hydroxide dissolves in exactly one molecule of sodium or potassium hydroxide, that is, that an aluminate is formed of the composition $NaAlO_2$ or $KAlO_2$. This result disproves the conclusion of Mahin, Ingraham, and Stewart (this vol., ii, 139) that the solubility of aluminium hydroxide in bases is due principally to its colloidal properties, and not to the formation of salts.

T. S. P.

The Preparation of Aluminium Nitride from its Elements. JOHANNES WOLF (*Zeitsch. anorg. Chem.*, 1913, **83**, 159—162).—Preparation from fine aluminium by Fichter's method (A., 1907, ii, 691) having failed to give more than a small absorption of nitrogen, it was found that at a higher temperature, about 820°, a vigorous reaction set in, the product then containing 31·74% N, a quantity which was not further increased by powdering and heating for a short time in nitrogen, but after long heating rose to 32·58% (compare Fichter and Spengel, this vol., ii, 711). C. H. D.

Influence of Foreign Substances on the Crystal-form of Alum. PETR A. ZEMJATSCHENSKY (*Zeitsch. Kryst. Min.*, 1913, **52**, 604—606; from *Mém. Acad. Sci. St. Pétersbourg*, [viii], **30**, 1—19).—From solutions containing hydrochloric acid of varying concentration and at different temperatures crystals of alum sometimes present the form of the pentagonal dodecahedron (210). Under certain conditions the compounds

$$3(K_2Al_2S_4O_{16},24H_2O),K_2SO_4,8KCl,3Al_2Cl_6$$

and $2K_2SO_4,H_2SO_4,6H_2O$ also separate. L. J. S.

The Action of Hydroxyl Ions on Aluminium and Clayey Soils by Marling. PAUL ROHLAND (*Landw. Jahrb.*, 1913, **44**, 437—440).—A continuation of previous work on the action of hydroxyl ions on clay soils, the changes being studied by the adsorption of compounds such as malachite-green or aniline-blue (compare this vol., ii, 27, 302, 356, 412). F. M. G. M.

Decomposition of Felspar and its Use in the Fixation of Atmospheric Nitrogen. WILLIAM H. ROSS (*J. Ind. Eng. Chem.*, 1913, **5**, 725—729).—Many processes have been patented relating to the decomposition of felspar with the object of rendering the potassium contained in it available as a plant food. Most of the methods depend on heating the substance to a high temperature, either alone or mixed with calcium oxide, calcium sulphate, etc. The author has carried out an investigation in order to ascertain the efficiency of ignited felspar in fixing nitrogen through the agency of the combined alumina or silica present, and finds that when a mixture of felspar, calcium oxide, and carbon is heated at 1400° for a few hours in an atmosphere of nitrogen, the felspar may absorb 7·44% of its weight of nitrogen; this quantity is greater than that which would be required to combine with the alumina

present to form aluminium nitride, but no direct experiments have been made to determine in what form the nitrogen is combined. The mixture evolves ammonia when boiled with water or sodium hydroxide solution. During the ignition at the temperature mentioned the whole of the potassium present in the felspar is volatilised. W. P. S.

Binary Systems of Manganous Chloride with the Chlorides of Some Alkali Metals. CARLO SANDONNINI and G. SCARPA (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 163—168).—The paper deals with the thermal analysis of the systems $LiCl-MnCl_2$, $NaCl-MnCl_2$, and $KCl-MnCl_2$. The results show that in this case also lithium chloride resembles magnesium chloride rather than the chlorides of the alkali metals in its behaviour. Lithium chloride and manganous chloride form solid solutions in all proportions; the curve shows a minimum at about 48 mol. % of LiCl and 555°.

Sodium chloride and manganous chloride form (at 441° and 445° respectively) two compounds which decompose on fusion, and probably have the compositions $NaCl,2MnCl_2$ and $4NaCl,MnCl_2$.

Potassium chloride and manganous chloride form two compounds. One, $KCl,MnCl_2$, has m. p. 495°. The other, $4KCl,MnCl_2$, is formed at 445°, and decomposes on fusion. The eutectic mixture of $KCl,MnCl_2$ and KCl lies at 35 mol. % of KCl and 450°. That of the two compounds lies at 65 mols. % of KCl and about 428°. The compound $4KCl,MnCl_2$ corresponds with the chloromanganokalite recently found in the minerals of Vesuvius. R. V. S.

Studies on Oxidation. III. The Oxidative and Catalytic Activity of Manganese Compounds. REGINALD T. COLGATE (*J. Soc. Chem. Ind.*, 1913, **32**, 893—898).—The interactions of manganese salts, hydrogen peroxide, and potassium permanganate have been studied, as well as the oxidation of hydrogen by permanganate. The results are held to indicate that manganese salts resemble ferrous salts in so far as they promote oxidation at all, a similar explanation (see this vol., ii, 967) being given of their oxyphoric and catalytic power. Hydrogen peroxide, however, is not powerful enough to convert the manganese salt into a perhydrol. permanganate being necessary; the permanganate acts as a depolariser, and is itself eventually reduced to the dioxide.

A similar explanation of the catalytic activity of manganese dioxide is given. It is assumed that this compound, in its hydrated form, is converted into a perhydrol, which is itself either so unstable that it is at once resolved into oxygen and a manganous compound, or else it gives rise by hydrolysis to hydrogen trioxide, which immediately decomposes.

A peroxide character is assigned to potassium permanganate, and it is argued that it always acts as an oxidising and not as a reducing agent. It is, however, not the immediate agent of oxidation, but acts as a hydrogen depolariser, the OH-ion of the electrolyte being the effective oxidising agent when it is used. The suggestion previously put forward (this vol., ii, 498) that hydrogen

peroxide may be a product of the oxidation process is withdrawn, although it is probable that hydrogen peroxide may be a product of hydrolysis. T. S. P.

Melting Points of Refractory Elements. I. Elements with Atomic Weight 48–59. GEORGE K. BURGESS and R. G. WALTENBERG (*Zeitsch. anorg. Chem.*, 1913, **82**, 361—372; and *J. Washington Acad. Sci.*, 1913, **3**, 371—378).—The determinations are made by means of the micropyrometer (Burgess, *Physikal. Zeitsch.*, 1913, **14**, 158), using minute particles of the metals on a platinum or iridium strip in an atmosphere of purified hydrogen. It is shown that an appreciable error is not introduced by the formation of alloys. The melting points of nickel (1452°) and palladium (1549°) are used for calibration. The following results are obtained: Iron (electrolytic or reduced by hydrogen), 1533±1°; cobalt (Kahlbaum), 1477±2°; chromium, 1520°; manganese (97·5%), 1254°, the value for pure manganese being perhaps 20° higher; vanadium, 1720±30°; titanium, 1795±15°.

Photo-micrographs are also given, showing the stages of the melting process. C. H. D.

A Specimen of Ancient Iron from Ceylon. WALTER ROSENHAIN (*Trans. Faraday Soc.*, 1913, **9**, 132—135. Compare Hadfield, A., 1912, ii, 258).—A portion of a link from a chain, exposed to the air in Ceylon for two thousand years, was largely uncorroded. The iron had the structure of a somewhat porous wrought iron, and contained Si 0·138, S 0·054, P 0·223, Cu 0·076, and Ni 0·074%. In spite of the comparatively high sulphur content, the metal corroded very slowly, a result possibly connected with the simultaneous presence of copper and nickel. Manganese, chromium, molybdenum, and vanadium were absent. C. H. D.

Thermal Effects and Magnetic Changes of Ferromagnetic Substances at High Temperatures. KŌTARŌ HONDA (*Sci. Rep. Tōhoku Imp. Univ.*, 1913, [i], **2**, 69—94. Compare Honda and Tagaki, this vol., ii, 222).—The thermal method has now been made more sensitive, so that the thermal change accompanying the magnetic transformation may be recognised. The $\gamma \longrightarrow \alpha$ or $\beta \longrightarrow \alpha$ change in pure iron begins at about 800°, and the development of heat is still perceptible down to 700°. In nickel the thermal change extends from 375° down to about 250°. Cast cobalt gives a distinct development of heat, but after annealing this becomes less, and it almost disappears after repeated heating and cooling. The magnetic change also extends over a considerable range of temperature, which increases with increasing strength of field. The development of heat is independent of the strength of the magnetic field. At the eutectoid point the magnetic properties of steels change discontinuously.

The evidence favours the view that the supposed $\beta \longrightarrow \alpha$ change is not a phase change, but represents a change within a single phase. Similarly, nickel and cobalt are regarded as existing in one

modification only, which undergoes a magnetic change within an interval of temperature. The beginning of the magnetic change in steels on cooling is at 795—770°, and is independent of the carbon content. C. H. D.

An Electrolytic Theory of the Corrosion of Iron. BERTRAM LAMBERT (*Trans. Faraday Soc.*, 1913, **9**, 108—114. Compare T., 1910, 2426; 1912, 2056).—Oxygen acts in the corrosion of iron by destroying the hydrogen polarisation at the cathode. Iron which is sufficiently free from impurities to remain bright in water and air or in copper sulphate or nitrate reacts immediately in solutions of copper chloride. C. H. D.

The Oxidisability of Ferrosilicon. M. VON SCHWARTZ (*Zeitsch. anorg. Chem.*, 1913, **82**, 353—356).—The oxidation of ferrosilicon containing 50% Si is very slow in air at 850—1100°, the absorption of oxygen being incomplete after one hundred and twenty hours. In oxygen the reaction is more rapid, but is still far too slow for quantitative purposes. The material is used in fine powder. C. H. D.

Studies on Oxidation. II. The Nature of the Process in which Hydrogen Peroxide is Utilised. Iron Salts as Catalysts. C. S. MUMMERY (*J. Soc. Chem. Ind.*, 1913, **32**, 889—893. Compare this vol., ii, 498).—The author has studied the interaction of hydrogen peroxide with ferrous and ferric sulphates under different conditions, and also the oxidation of formic acid by hydrogen peroxide in the presence of iron salts. The results obtained are held to justify the conclusion that ferrous salts promote oxidation by means of hydrogen peroxide in virtue of the formation of a "perhydrol" of the type FeX(O·OH), which salt is formed reversibly, and is alternately produced from and reconverted into ferrous salt when an oxidisable substance is present together with hydrogen peroxide. Evidence for the formation of such a ferrous perhydrol is adduced from the fact that when hydrogen peroxide is added to ferrous sulphate in the presence of Trillat's agent (*pp'*-tetramethyldiaminodiphenylmethane) dissolved in citric acid, a brilliant blue colour is produced. The action does not take place, however, if the agent is added last, nor do ferric salts and hydrogen peroxide determine the appearance of the blue colour, but give rise to a brown colour instead of a blue.

The fact that ferric salts also promote oxidation may be accounted for by the formation of a ferric perhydrol, for example, $FeX_2(O{\cdot}OH)$. As, however, the ferric salts are less basic than ferrous salts, they give rise to a far smaller proportion of the perhydrol, and are consequently less active.

The catalytic decomposition of hydrogen peroxide by iron salts in the absence of an oxidisable substance is ascribed to the formation of higher perhydrols, which are regarded as derivatives of hydrogen trioxide.

The formation of the perhydrol converts the hydrogen peroxide

into an electrolyte, which can then act as an oxidiser, in accordance with the view expressed by E. F. and H. E. Armstrong (this vol., i, 1116) that "the catalyst may well be defined as the agent which brings about the inclusion of the interacting substances in the electrolytic circuit within which the change takes place so soon as the circuit is established, the electrolyte being the actual agent by which the change is affected." T. S. P.

The Thermal Dissociation of Cobaltammonias. WILHELM BILTZ (*Zeitsch. anorg. Chem.*, 1913, **83**, 177—192).—When the thermal dissociation of the cobalt-ammonias is studied by either the statical or the dynamical method, equilibrium is only reached very slowly. Hexa-amminocobaltichloride is stable even when heated for one hundred hours at 193°, but rapidly loses $1NH_3$ at 216°. With large quantities or shorter time very incomplete dissociation is obtained. Some of the changes proceed slowly for several days, and then more rapidly, the temperature remaining constant, and the reactions are irreversible. In many cases reduction to the cobaltous condition occurs. Cobaltic salts in presence of cobaltous salts may be estimated by adding an excess of alkaline arsenite in an atmosphere of nitrogen and titrating the excess of arsenite. In the case of the cobaltichloride, the compound $CoCl_2,\frac{1}{2}NH_3$ is formed, but the phosphate decomposes according to the equation:

$$6[Co(NH_3)_6]PO_4 = 3CoP_2O_7 + 34NH_3 + 3H_2O + N_2.$$

C. H. D.

Ammonia Compounds of the Nickel Haloids. WILHELM BILTZ and BRUNO FETKENHEUER (*Zeitsch. anorg. Chem.*, 1913, **83**, 163—176).—The isobars have been determined by passing ammonia over the substance in a combustion tube kept very exactly at a constant temperature until equilibrium is attained. The isotherms have been determined by heating the flask containing the substance in boiling aniline (179°) or thymol (230°), the flask being exhausted before heating, and the pressure read after heating for an hour. The weight of the substance then enables its composition to be calculated. The vapour-pressure curves have also been determined.

The hexa-ammines are best prepared in the wet way, compounds prepared by the action of ammonia gas on the anhydrous salts being very bulky. The curves show the compounds $NiCl_2,6NH_3$, $NiCl_2,2NH_3$, and $NiCl_2,NH_3$, this being bright yellow, easily distinguishable from anhydrous nickel chloride. The decomposition of the mono-ammine occurs at 373°. The bromide and iodide only form the hexa- and di-ammine.

The following heats of reaction have been found: $NiCl_2,6NH_3 \rightleftharpoons NiCl_2,2NH_3 + 4NH_3 = 16$ Cal.; $NiCl_2,2NH_3 \rightleftharpoons NiCl_2,NH_3 + NH_3 = 21{\cdot}6$ Cal.; $NiCl_2,NH_3 \rightleftharpoons NiCl_2 + NH_3 = 24{\cdot}2$ Cal.; $NiI_2,6NH_3 \rightleftharpoons NiI_2,2NH_3 + 4NH_3 = 18{\cdot}3$ Cal. A comparison of these heats of reaction with those determined calorimetrically gives a good agreement (compare Ephraim, this vol., ii, 129, 130). C. H. D.

Two Double Salts of Molybdic Acid. M. K. Eliaschevitsch (*Zeitsch. Kryst. Min.*, 1913, **52**, 630—632; from *Ann. Inst. Mines, St. Petersburg*, 1910, **2**, 345—351).—Descriptions are given, in Fedorov's nomenclature, of the monoclinic crystals of the potassium and ammonium cobalt salts $3K_2MoO_4,Co_2(MoO_4)_3,4MoO_3,10H_2O$ and $3Am_2MoO_4,Co_2(MoO_4)_3,4MoO_3,10H_2O$, prepared by N. S. Kurnakov.

L. J. S.

The Reduction of Tin Chlorides by Hydrogen, and a New Method of Reduction. Friedrich Meyer and Hans Kerstein (*Ber.*, 1913, **46**, 2882—2887).—When the vapour of tin tetrachloride, mixed with hydrogen, is passed through a horizontal quartz tube heated at 1000°, stannous chloride is produced. Stannous chloride and hydrogen, under the same conditions, give only small quantities (traces) of tin. Experiments in a special apparatus showed that the reduction of the stannic chloride commences at 200°, and that of stannous chloride at 350°.

For further experiments the authors used an apparatus arranged on the principle of a reflux condenser. The lower part of a quartz tube, sealed at the bottom, could be heated in an upright electric furnace; the upper part acted as a cooler. Into the top of the tube were fitted narrower tubes through which hydrogen and a mixture of hydrogen and stannic chloride vapour could be introduced; there was also an exit tube for waste gases. When stannous chloride was used, it was placed at the bottom of the quartz tube before the narrower tubes were introduced. With this apparatus, under appropriate conditions of temperature, etc., both stannic and stannous chlorides could be reduced to tin, or stannic chloride to stannous chloride, in a practically quantitative manner.

T. S. P.

Working Up of Platinum Residues. D. J. de Jong (*Chem. Weekblad*, 1913, **10**, 833—834).—To obtain platinum chloride free from potassium a concentrated hot alkaline solution of the residues is reduced with sodium formate, the platinum collected and ignited, dissolved in *aqua regia*, and the chloride recrystallised. A detailed account of the experimental conditions is given. A. J. W.

Platinoammine Compounds. Ludwig Ramberg (*Zeitsch. anorg. Chem.*, 1913, **83**, 33—38).—By adding sufficient ammonium chloride in the reaction between potassium platinochloride and ammonia, it is possible to prevent the replacement of chlorine by hydroxyl, and so obtain the pure chloro-compounds. The product obtained in such an experiment contains 85% of the compound $[Pt2NH_3]Cl_2$, the remainder being $[Pt4NH_3]PtCl_4$ and $[PtCl4NH_3]_2PtCl_4$. By dissolving in ammonia, filtering and evaporating, a white product, $PtCl_2,4NH_3,H_2O$, is obtained, which is converted into *trans*-platosoammine chloride by heating in a stream of air, first at 110° and then at 250—260°, until no more ammonia is expelled.

trans-Platosoammine iodide is best prepared from platinous iodide and ammonia, boiling until dissolved, and then blowing

steam through the solution to expel excess. A yield of 90—95% is thus obtained.

The *cis*- and *trans*-nitrites have also been obtained in a colourless form. C. H. D.

Mineralogical Chemistry.

Marcasite Nodules from Podolia, Russia. N. S. WATITSCH (*Zeitsch. Kryst. Min.*, 1913, **52**, 634; from *Annuaire Géol. Min. Russie*, 1910, **12**, 16—19).—Nodular concretions of marcasite occur in the chalk-marl at Lyadava, govt. Podolia. Analysis gave: Fe, 47·87; S, 51·96; P_2O_5, trace; D 4·76. They weather to limonite, containing: Fe_2O_3, 62·47; Al_2O_3, 1·43; P_2O_5, 1·32; insol., 23·91; loss at 100°, 14·50; loss on ignition, 9·75; total, 98·83. L. J. S.

Minerals of the Ore-deposits of Kerch and Taman, Crimea. SERGEI P. POPOV (*Zeitsch. Kryst. Min.*, 1913, **52**, 606—614; from *Travaux Mus. Géol. Pierre le Grand, Acad. Sci. St. Pétersbourg*, 1910, **4**, 99—198).—A detailed description is given of the various minerals, and several analyses are given of brown iron-ore (limonite), siderite, anapaite (A., 1903, ii, 303), vivianite and its alteration products (paravivianite, kertschenite and oxykertschenite, A., 1906, ii, 236), and wad. L. J. S.

Autunite of Lurisia. GABRIELE LINCIO (*Atti R. Accad. Sci. Torino*, 1913, **48**, 959—967).—The mineral has the composition:

P_2O_5.	UO_3.	CaO.	H_2O.	Gangue.	Total.
13·21	60·57	5·64	19·95	0·76	100·13

It crystallises in fluorescent tablets in the rhombic system, is feebly radioactive, and hence resembles the autunite of Autun. R. V. S.

Barytes from Kerch, Crimea. A. A. KASCHINSKI (*Zeitsch. Kryst. Min.*, 1913, **52**, 624; from *Ann. Inst. Mines, St. Petersburg*, 1910, **2**, 251).—A specimen of yellowish radiating barytes, fungoid in external form, from a limonite mine, gave:

BaO.	SO_3.	SiO_2.	Al_2O_3, Fe_2O_3, Mn_2O_3.	CaO.	MgO.	Na_2O.	Ign.	Total.
63·35	34·21	0·19	0·16	0·74	0·08	0·22*	0·76	99·71 †

* Including trace of K_2O. † Also traces of Cl and P.

L. J. S.

Chemical Investigation of Certain Minerals from Ceylon Gravel. III GEORGEI P. TSCHERNIK (*Bull. Acad. Sci St. Pétersbourg*, 1913, 721—732. Compare this vol., ii, 421, 518).—Gravel from the Ratnapura district contains dark grey, somewhat oblong pebbles,

one side of which retains traces of crystalline form, and has a black colour. This mineral gives a conchoidal fracture with velvet-black colour and semi-metallic lustre, its streak being grey. It is brittle, but shows no sign of cleavage, and its hardness is almost identical with that of orthoclase. At the edges of thin fragments a faint reddish-brown light is transmitted. Analysis gave the percentage composition:

CaO.	Y_2O_3.	Ce_2O_3.	UO_2.	ThO_2.	FeO.	MnO.	Ta_2O_5.	Cb_2O_5.	H_2O.	SnO_2, WO_3 and Na_2O.	Total.
1·89	17·85	3·72	6·06	1·52	3·41	0·21	49·58	14·96	0·12	Traces	99·41

Calculation from these numbers gives the formula:

$$12(Y_2O_3,Ta_2O_5) + 2(Ce_2O_3,Ta_2O_5) + 3[(FeO)_3,Ta_2O_5] + 4[UO_2,(Cb_2O_5)_2] + ThO_2,(Cb_2O_5)_2 + 3[(CaO)_2,Ta_2O_5].$$

The mineral has therefore the chemical constitution of a modified yttrotantalite, although its physical properties resemble more closely those of the allied fergusonites.

The properties of the mineral are discussed in their relations to those of other yttrotantalites. T. H. P.

Olivine and Melilite Crystals from Furnace Slags. KARL BUSZ and F. W. RÜSBERG (*Centr. Min.*, 1913, 625—634).—Crystals of a pure iron-olivine, Fe_2SiO_4 (fayalite), gave analysis I. A mangan-fayalite gave II, corresponding with $3Fe_2SiO_4,Mn_2SiO_4$. The sulphur shown in this analysis is due to the presence of fine, dusty enclosures of iron and manganese sulphides in the crystals. From analyses of another mangan-fayalite, rendered impure by enclosed spinel, the composition $5Fe_2SiO_4,Mn_2SiO_4$ is deduced. Analysis of the enclosed spinel corresponds with $3(Ca,Mg,Mn)O,2(Fe,Al)_2O_3$. Lime-olivines gave III and IV, corresponding with: $10Ca_2SiO_4,6(Fe,Mg)_2SiO_4,3Mn_2SiO_4$ and

$$3Ca_2SiO_4,2(Mg,Fe)_2SiO_4,Mn_2SiO_4$$

respectively, these both approximating to the double salt, Ca_2SiO_4,R''_2SiO_4:

	SiO_2.	Al_2O_3.	FeO.	MnO.	CaO.	MgO.	S.	Total.
I.	29·59	1·54	69·18	trace	—	—	trace	100·31
II.	27·79	0·39	51·90	17·44	0·88	—	1·45	99·85
III.	33·17	—	18·97	11·21	35·11	2·09	—	100·55
IV.	36·10	trace	4·89	11·81	32·68	15·15	—	100·68

The physical constants (density, crystal-angles, and a selection of the optical constants) of these crystallised materials are compared in the following table:

	D.	(110) : (1$\bar{1}$0).	(021) : (0$\bar{2}$1).	α(Na).	β(Na).	γ(Na).
I.	4·28	49°24′	98°35′	—	1·877	1·886
II.	4·25	49 22	98 37	1·805	1·836	1·846
III.	3·341	47 20	98 21	1·6749	1·7054	1·7105
IV.	3·190	47 5	98 8	—	—	—

Water-clear crystals of melilite gave analyses V (D 2·957) and VI; and the composition is expressed as a mixture of the alumin-

ous gehlenite molecule, $3R''O,R'''_2O_3,2SiO_2$, with the silicate $3R''O,2SiO_2$. The optical constants of these crystals were determined:

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.	Na_2O.	Total.
V.	39·84	4·34	0·12	—	2·30	36·03	10·20	4·37	2·01	99·21
VI.	42·39	1·09	—	1·30	4·38	39·10	12·16	—	—	100·42

L. J. S.

Wolkonskoite. Franz Angel (*Zeitsch. Kryst. Min.*, 1913, **52**, 568—579).—This green, earthy mineral fills nests and veins in calcareous sandstones of Permian age in the governments of Perm and Vyatka, Russia. When placed in water, it absorbs water, and crumbles to scaly fragments, which are optically isotropic, D 2·337. Analyses are given of material from: I, Perm; and II, Echinovka (Perm ?):

	SiO_2.	Cr_2O_3.	Al_2O_3.	Fe_2O_3	FeO.	CaO.	MgO.	H_2O. over 160°.	H_2O. below 160°.	Total.
I.	36·04	24·79	0·63	4·60	4·65	2·33	4·88	6·65	15·17	99·74
II.	37·14	22·77	4·33	2·13	3·46	2·77	4·09	7·38	15·53	99·60

Neglecting water lost below 160°, the formula is

$$(H_2,Mg,Fe,Ca)_3(Cr,Fe,Al)_2Si_3O_{12},$$

which is analogous to the garnet formula.

An artificial material, of similar colloidal nature, was prepared from a solution of sodium silicate and chromium chloride.

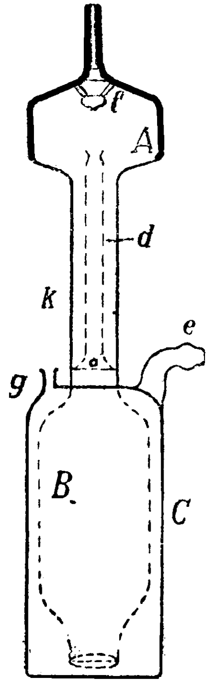
L. J. S.

A New Find of Alkaline Rocks in Timor. H. A. Brouwer (*Centr. Min.*, 1913, 570—576).—Analyses are given of alkali-trachyte and shonkinite. L. J. S.

Weathering of Rock-forming Minerals under the Influence of Sulphurous Acid. H. Lotz (*Jahrb. Min.*, 1913, ii, *Ref.* 180—183; from *Ber. Oberhess. Ges. Natur-Heilkunde, N.F. Naturw. Abt.*, 1910–11, **4**, 70—108, and *Diss.*, Giessen, 1912).—Various rock-forming minerals were exposed to the action of a moist atmosphere containing air (80%), carbon dioxide (19%), and sulphur dioxide (1%). At the same time comparative experiments were made in an atmosphere of air 80% and carbon dioxide 20%. In the latter case there was little or no action, but in the presence of sulphur dioxide small amounts of the bases (especially alkalis, iron, and aluminium) passed into solution, with an enrichment of silica in the residue. Analyses are given of fourteen rock-forming minerals, and of the portions of each that passed into solution. L. J. S.

Analytical Chemistry.

Gas Analysis Apparatus. A. LOMSCHAKOW (*Chem. Zeit.*, 1913, **37**, 1262).—An apparatus for use in gas analysis consists of an absorption vessel *A* (see figure), and two reagent vessels, *B* and *C*. The reagent is introduced into *C* through the opening *g*, which is then closed by a rubber stopper; the vessel *B*, contained in *C*, is open at the bottom, and, by means of a rubber bulb attached to the opening *e*, the reagent may be caused to fill the vessel *A*. The gas under examination is allowed to enter by the capillary at the top of *A*, the reagent being driven back into *B* through the tube *d*, the quantity of solution contained in the space between the walls *d* and *k* passing through the small hole at the bottom of the tube *d*. After the gas has been introduced into the apparatus, the rubber bulb is compressed suddenly, causing a portion of the reagent solution to be expelled up the tube *d* against the plate *f*; this operation is repeated a few times in order to bring the solution in contact with the gas. The residual volume of gas is then driven back into the measuring burette by compressing the bulb, and causing the reagent solution to fill the vessel *A*. W. P. S.



General Remarks on Methods of Volumetric Analysis. M. EMMANUEL POZZI-ESCOT (*Bull. Assoc. chim. Sucr. Dist.*, 1913, **31**, 124—127).—The author advocates the use of normal solutions in volumetric estimations in preference to solutions which have been standardised empirically for one particular purpose. W. P. S.

Use of the Sense of Smell in Volumetric Estimations. JULIUS F. SACHER (*Chem. Zeit.*, 1913, **37**, 1222).—Substances possessing a strong smell, such as *iso*valeric acid, acetic acid, phenol, etc., and the salts of which are odourless, may be titrated without the use of any indicator other than the sense of smell, the disappearance of the odour on the addition of the alkali solution indicating the end-point of the titration. It is advisable, however, to add a slight excess of the alkali, and to titrate this excess with standard acid solution as the neutral point is indicated more sharply by the development of a slight odour than by its disappearance. Hydrolytic action and the action of carbon dioxide derived from the atmosphere influence the results to a certain extent. Similarly, ammonia can be titrated accurately. W. P. S.

An Automatic Pipette. C. H. McCharles (*J. Ind. Eng. Chem*, 1913, **5**, 755—756).—The pipette is similar to that described by Smith (A., 1912, ii, 678), but differs in that the point to which the liquid rises in the capillary is constant. This is attained by having two stock bottles, one being placed higher than the other, and discharging into this through a siphon arrangement, which maintains a constant level of liquid in the lower reservoir from which the pipette is filled. W. P. S.

Estimation of Water of Crystallisation in Sulphates. Simon B. Kuzirian (*Amer. J. Sci.*, 1913, [iv], **36**, 401—405).—When sulphates are fused with sodium paratungstate, no decomposition of the sulphates occurs, reaction taking place in accordance with the equation: $M''SO_4 + Na_2O,12WO_3 = Na_2SO_4 + M''O,12WO_3$. It follows that the water of crystallisation in sulphates may be estimated by fusing them with an excess of the paratungstate. The method was tested on the hydrated sulphates of copper, aluminium, and nickel, and on chrome alum and potassium alum, and found to be quantitative. In these tests the loss in weight of the mixture was determined, and also the water expelled was collected and weighed. It is sufficient to keep the mixture in quiet fusion for fifteen to twenty minutes. T. S. P.

Estimation of Chlorine in the Blood. Ivar Bang (*Biochem. Zeitsch.*, 1913, **56**, 158).—A criticism of the method of Rogée and Fritsch (this vol., ii, 872). S. B. S.

Hydrolytic Action as a Source of Error in the Estimation of Iodine and Bromine in Mineral Waters and Saline Deposits. Paul Kaschinsky (*Zeitsch. angew. Chem.*, 1913, **26**, 492—494).—Magnesium bromide and magnesium iodide are decomposed by water with liberation of the halogen acids, and when the residue obtained on evaporating the water, etc., is heated over a flame, the whole of the iodine and almost all the bromine present may be lost. It is essential in this estimation to precipitate the magnesia by the addition of potassium hydroxide; after the magnesium hydroxide has been separated by filtration, the iodide and bromide are estimated in the usual way. Potassium hydroxide is to be preferred to calcium hydroxide for the removal of the magnesia, as potassium chloride is less soluble than calcium chloride in the alcohol used during the subsequent stages of the estimation. W. P. S.

The Action of Persulphates on Iodates and the Estimation of Periodates in Presence of Persulphates. Erich Müller and Walther Jacob (*Zeitsch. anorg. Chem.*, 1913, **82**, 308—314).—It is known that persulphates and iodates react to form sulphates and periodates, but an analytical method of determining how far the reaction proceeds has been lacking. The reaction $IO'_4 + 2I' + 2H^{\cdot} = IO'_3 + H_2O + I_2$ is quantitative in alkali hydrogen carbonate solution, but proceeds very slowly in alkali hydroxide solution.

When iodide is present, twice as much alkali hydrogen carbonate is added as is required to convert the hydroxide into carbonate, followed by arsenite solution and potassium iodide at 50°, and after cooling the solution is titrated with iodine solution. In this way periodate may be accurately estimated in presence of iodide. In presence of persulphate, however, low values are obtained, as the reaction $3IO'_4 + I' = 4IO'_3$, which does not occur at the ordinary temperature in alkali hydroxide solution, is accelerated by persulphates, hypoiodite being formed as an intermediate product.

A mixture containing only persulphate and periodate is made alkaline with alkali hydroxide, and potassium iodide is added. After boiling and cooling, the solution is acidified with sulphuric acid, and the iodine titrated with thiosulphate, giving the total periodate + persulphate. Another portion is mixed with alkali hydroxide, and reduced by boiling with granulated zinc; after acidifying and adding iodate, the liberated iodine is titrated with arsenite in alkali hydrogen carbonate solution. This gives the periodate oxygen: $IO'_4 = I' + 4O$, and this is subtracted from the total previously obtained. The addition of alkali hydrogen carbonate must be performed in a reflux apparatus to avoid loss of iodine.

It has not been possible to find a reducing agent which acts on either persulphate or periodate, leaving the other intact.

C. H. D.

Volumetric Estimation of Fluorine. ALFRED GREEFF (*Ber.*, 1913, **46**, 2511—2513).—When ferric chloride is added to neutral aqueous solutions of the alkali fluorides, white, crystalline precipitates are formed having the general formula M_3FeF_6, analogous to that of cryolite; the *sodium* and *potassium ferrifluorides* were thus obtained. The existence of a double salt of the formula $2FeCl_3,2KF$ (Guyot, A., 1871, 854) could not be verified.

Sodium ferrifluoride is only very sparingly soluble in water, and does not give a red coloration with thiocyanates. If, however, ferric chloride is run into a solution of an alkali fluoride containing some potassium thiocyanate, excess of the ferric chloride is indicated not by the formation of a red, but by the formation of a yellow, colour. The colour change is not sharp, but can be made more evident by shaking the solution with a mixture of alcohol and ether, the ethereal layer then taking up the red colour of the ferric thiocyanate. The colour change is still not sharp enough for volumetric purposes, but can be made so by diminishing the slight solubility of the alkali ferrifluoride by the addition of sodium chloride. It is necessary that the aqueous solution of the fluoride used should be neutral to phenolphthalein.

The method of estimation is as follows: 0·5 Gram of the substance is dissolved in 25 c.c. of water, 20 grams of sodium chloride and 5 c.c. of potassium thiocyanate solution (1 : 5) are added, and the solution titrated with standard ferric chloride solution until a weak yellow colour is obtained. Ten c.c. of alcohol and 10 c.c. of ether are then added, the solution is well shaken (in a corked

flask), and further titrated with ferric chloride until the red colour persists in the ethereal layer, even after a long time.

The method can be extended to the estimation of commercial sodium fluoride, which generally contains some acid fluoride, NaF,HF, and also sodium silicofluoride. The hot solution is neutralised with standard alkali, using phenolphthalein as indicator, whereby the total quantity of acid fluoride and silicofluoride is obtained; the neutral solution is then titrated with ferric chloride as above. The quantity of acid fluoride present is determined by precipitating the silicofluoride as potassium silicofluoride by the addition of potassium chloride and alcohol, and then titrating with sodium hydroxide. Knowing the total quantity of acid fluoride and silicofluoride present, and also the quantity of acid fluoride, the amount of silicofluoride can be calculated. T. S. P.

Modification of Schulte's Apparatus for the Estimation of Sulphur in Iron and Steel. HANNS FISCHER (*Chem. Zeit.*, 1913, **37**, 1223).—In this method the iron or steel is heated in a flask with hydrochloric acid, and the gases evolved are passed into two absorption flasks containing water and cadmium-zinc acetate solution respectively. In order to prevent the contents of the absorption flasks flowing back into the decomposition flask when the latter is cooled at the end of the operation, two safety bulbs are attached to a side-tube on the delivery tube; the second of these bulbs is partly filled with water, and its outer limb is connected with a vertical tube. The second absorption flask may also be provided with a long, vertical tube, through which the non-absorbed gases may escape. W. P. S.

Fusion Method for the Estimation of Sulphur in Iron and Steel. FREDERICK H. FRANKLIN (*J. Ind. Eng. Chem.*, 1913, **5**, 839—842).—The following method is recommended: Three grams of the sample are dissolved in about 120 c.c. of copper-potassium chloride solution (prepared by dissolving 600 grams of copper-potassium chloride in warm water, adding 30 c.c. of hydrochloric acid and 30 c.c. of 20% barium chloride solution, and diluting the mixture to 1600 c.c.; it should be filtered after twenty-four hours), the insoluble residue is collected on an asbestos filter, washed with dilute hydrochloric acid, and then with water. The residue is separated as far as possible from the asbestos, dried at a temperature slightly under 100°, and then fused with a mixture of 3 grams each of sodium carbonate and sodium peroxide. When cold, the mass is dissolved in hydrochloric acid, the solution is evaporated to dryness, and the residue is treated with water containing a small quantity of hydrochloric acid. The solution is filtered to remove silica, and the sulphuric acid in the filtrate is then precipitated as barium sulphate in the usual way. W. P. S.

Estimation of Sulphur in Pyrites and Other Sulphides. MAX DITTRICH (*Zeitsch. anorg. Chem.*, 1913, **83**, 27—32).—The method of Heczko (A., 1911, ii, 89, 296) may be modified with

advantage by providing the transparent silica tube with ground-on silica connecting tubes, the joints being lubricated with graphite. The escaping gases pass through a long series of absorbing bulbs, containing bromine and bromine water. The finely powdered ore is heated in a porcelain boat. The final heating of the boat, after most of the sulphur dioxide has been driven over, is performed by means of a Teclu burner. The sulphur is estimated as barium sulphate in the usual way. The residue in the boat, which is used for further analysis, should be tested for sulphates. Satisfactory results are readily obtained with pyrites, but zinc sulphide requires very fine powdering, and heating in a long boat to expose a large surface, otherwise sulphur is retained.

Jannasch's method of heating in a stream of oxygen or carbon dioxide laden with bromine, the sulphur being expelled as sulphur bromide, is also successful, but when arsenic, antimony, or other metals forming volatile bromides are used, the exit tube must be wide to avoid stoppage. C. H. D.

Estimation of Sulphur in Pyrites Residues. L. SZNAJDER (*Chem. Zeit.*, 1913, **37**, 1107).—The following volumetric method is proposed: A quantity of 2·5 grams of the sample is heated to redness for thirty minutes with 5 grams of a mixture of sodium carbonate and zinc oxide; after cooling, the mixture is taken up with water, diluted to 250 c.c., and filtered. Two hundred c.c. of the filtrate are heated to boiling, phenolphthalein is added, and dilute hydrochloric acid is run in until the red coloration disappears. Thirty c.c. of $N/5$-barium chloride solution are now added to the hot solution, which is then titrated with $N/5$-sodium carbonate solution. The percentage quantity of sulphur is found from the equation $S = 0{\cdot}16(30 - a)$, a being the number of c.c. of $N/5$-sodium carbonate solution required for the titration.

W. P. S.

Estimation of Sulphur in Organic Compounds. HERMANN APITZSCH (*Zeitsch. angew. Chem.*, 1913, **26**, 503—504).—A piece of combustion tube is drawn out at one end, the narrow tubing so formed opening into an absorption apparatus containing sodium hypobromite solution. The substance containing sulphur is weighed into a porcelain boat and placed in the tube, and on both sides of the boat are placed special spirals of platinum gauze. The substance is burned in a current of oxygen, the platinum acting as a catalytic agent, and the products of combustion collected in the absorbent. When the combustion is complete, the tube is washed out, the washings added to the sodium hypobromite solution, and the sulphur precipitated as sulphate in the usual way. Volatile substances are vaporised outside, and passed through the tube according to the usual method.

The method is accurate, and preferable to the Carius method.

T. S. P.

Estimation of Sulphur in Caoutchouc. ERNST DEUSSEN (*Zeitsch. angew. Chem.*, 1913, **26**, 494—496).—The method described

previously by the author (A., 1910, ii, 750) for the detection of sulphur in organic compounds may be applied to the estimation of sulphur in caoutchouc. The substance is oxidised by repeated evaporation with nitric acid; the residue is then mixed with sodium carbonate, and ignited as described (*loc. cit.*). The sulphide which is obtained in solution on treating the fused mass with water is estimated colorimetrically by comparison with standard solutions prepared by reducing known quantities of sodium sulphate in a similar manner. Alkaline lead acetate solution is employed as the reagent in the colorimetric estimation. W. P. S.

Estimation of Free Anhydride Contained in Fuming Sulphuric Acid by Titration and Determination of Density. P. GAVELLE (*Mon. Sci.*, 1913, **3**, I, 301—308).—A description of two methods for the estimation of sulphur trioxide (by titration) in fuming sulphuric acid; also an account of the determination of the densities at 20° of acids containing 0—30% of sulphur trioxide; the results are tabulated, and a formula for calculating the composition of the acids deduced. F. M. G. M.

Estimation of Ammonia and Nitrogen. HEINRICH HOLTKAMP (*Zeitsch. angew. Chem.*, 1913, **26**, 600).—A simple apparatus is described for the estimation of ammonia by the distillation method. The ordinary bulb trap above the distillation flask is replaced by a wide tube bent in the shape of a swan's neck. This connects, by means of a narrow tube, with a wide vertical tube opening into the absorbent standard acid. T. S. P.

Quantitative Ammonia Distillation by Aeration for Kjeldahl, Urea, and Other Nitrogen Estimations. III. PHILIP A. KOBER and SARA S. GRAVES (*J. Amer. Chem. Soc*, 1913, **35**, 1594—1604. Compare Kober, A., 1910, ii, 651; 1908, ii, 776).—An account of the process described earlier (A., 1908, ii, 776) with a discussion of the theory of the process, and with details of the method. Some additional directions as to manipulation are given, and also the results of experiments proving the trustworthiness of the process. D. F. T.

Colorimetric Estimation of Nitric Acid in Water. J. SILBER (*Zeitsch. Nahr. Genussm.*, 1913, **26**, 282—286).—The phenolsulphonic acid method of Grandval and Lajoux is recommended; the author finds that nitrites do not affect the results obtained, but that, when a large quantity of chloride is present, the water must be treated previously with silver sulphate. The minimum quantity of nitric acid (N_2O_5) which can be estimated by the process is about 0·02 mg. per 50 c.c. of water; when more than 3·0 mg. per 50 c.c. is present the colour comparison is difficult. The author employs a set of comparison tubes, prepared with known amounts of nitric acid, in the estimation (compare A., 1910, ii, 652). W. P. S.

Detection of Nitrous Acid in Presence of Nitric Acid. ANDRÉ LECLÈRE (*J. Pharm. Chim.*, 1913, [vii], **8**, 299).—The test depends on the fact that nitrous acid is liberated from its salts by

citric acid whilst nitric acid is not. The liquid under examination is mixed with its own volume of a syrupy, aqueous solution of citric acid; on this mixture is superposed by means of a pipette a 3 or 4% solution of ferrous ammonium sulphate. If nitrites are present in the liquid a brown ring appears at the surface of contact of the two solutions. If sulphides are present they should first be removed by adding zinc acetate to the solution, the test being then applied to the filtrate. T. A. H.

Nitrates and Nitrites in Milk. GEORGE D. ELSDON and JOHN A. L. SUTCLIFFE (*Analyst*, 1913, **38**, 450—454).—Nitrates have been added to milk as a preservative and to remove any turnip-like taste, whilst nitrites have been added with the object of obscuring the usual tests for formaldehyde when the latter has been introduced into the milk. Since the diphenylamine-sulphuric acid test gives a reaction with both nitrates and nitrites it is not applicable to the detection of nitrates or nitrites in the presence of each other, and, further, is too sensitive for use where relatively large quantities of nitrate are concerned. The brucine-sulphuric acid method is recommended for the purpose. In the absence of nitrites the serum obtained from the milk is treated with the reagent, and the coloration obtained is compared with that produced by known quantities of nitrate. In the presence of nitrites the coloration is produced immediately on the addition of the reagent, and then fades quickly to a certain extent. The bleaching action is independent of the amount of nitrite present, and the comparison solutions are prepared with the addition of 10 parts per 100,000 of sodium nitrite, the comparisons being made after the lapse of three hours. The authors find that potassium nitrate is reduced to nitrite in milk, the quantity of nitrite formed reaching a maximum in about four days, and then decreasing. The Griess-Ilosvay reagent is recommended for the detection and estimation of nitrites. Nitrites act as preservatives when added to milk, but nitrates are inefficient in this respect. W. P. S.

Estimation of Phosphorus in Vanadium S'eel and Ferro-Vanadium. C. F. SIDENER and P. M. SKARTVEDT (*J. Ind. Eng. Chem.*, 1913, **5**, 838—839).—The sample is dissolved in dilute nitric acid, a small quantity of hydrochloric acid being added if necessary, the solution is evaporated to dryness, and the residue is baked until the ferric nitrate is decomposed. The residue is now dissolved in hydrochloric acid, 0·02 gram of aluminium in the form of aluminium chloride is added, the solution is nearly neutralised with ammonia, heated to boiling, and reduced by the addition of an excess of ammonium hydrogen sulphite. Phenylhydrazine is then added; if no precipitate forms, a few drops of ammonia are added, and then more phenylhydrazine. The precipitate obtained is collected, washed with hot water, and dissolved in nitric acid. This solution is treated with hydrogen peroxide and sodium carbonate, boiled, and the aluminium phosphate is precipitated by the addition of nitric acid until the solution is practically neutral to turmeric paper. The precipitate is collected, washed with ammon-

ium nitrate solution, dissolved in nitric acid, and a small quantity of hydrogen peroxide is added. If a pink or red coloration is produced, owing to the presence of vanadium, the precipitation with sodium carbonate and nitric acid must be repeated. The nitric acid solution of the precipitate is then treated with molybdate solution, and the phosphoric acid estimated in the usual way.

W. P. S.

Estimation of Total Phosphoric Acid in Soils. HERMANN FISCHER (*Bied. Zentr.*, 1913, **42**, 585—586; from *Internat. Mitt. Bodenkunde*, 1912, **2**, 541).—The soil (5—10 grams) is treated with about 50 c.c. of aqua regia, and kept covered until evolution of gas nearly ceases, after which it is evaporated to dryness. The residue is ignited, and again treated with the same amount of aqua regia, and evaporated to dryness. Strong nitric acid is added, and then evaporated until the hydrochloric acid is removed, and the residue is extracted with 5 c.c. of nitric acid and hot water. The filtrate, or an aliquot portion, according to the amount of phosphoric acid present, is evaporated down to 25 c.c., and the phosphoric acid estimated by Mitscherlich's method.

The potassium sodium carbonate method is inconvenient when as much as 5 grams of soil is used, owing to the large amounts of salts in the solution; and with less than 5 grams of soil it is difficult to obtain an exact average sample.

N. H. J. M.

The Method of Combustion Calorimetry, and Elementary Analysis by means of the Calorimetric Bomb. M. DIAKOV (*Biochem. Zeitsch.*, 1913, **55**, 116—123).—Attention is called to the difficulties of the correct estimation of nitric acid formed in the combustion. A colorimetric method for the estimation of this acid by means of diphenylamine was not found satisfactory, and the Jodlbauer method was therefore employed. A method is described for estimating the carbon dioxide formed, and the oxygen used during combustion. The amount of oxygen compressed into the bomb is estimated by direct weighing, and from the analysis of this gas (which contains some argon, nitrogen, and carbon dioxide) and of the air, the initial composition of the compressed gaseous contents of the bomb can be found. After the combustion, the gaseous products are passed over adsorption bulbs containing soda-lime, and the carbon dioxide is estimated by weighing. Between the adsorption apparatus and the bomb, however, a T-piece is interposed, leading to a mercury bulb, in which a measured sample of the gas is collected, in which is estimated the carbon dioxide, oxygen, and nitrogen. From this analysis, and the relative amounts of carbon dioxide in this sample to that collected in the absorption bulbs, the amounts of nitrogen and oxygen in the bomb after combustion can be calculated. Correction in estimating the nitrogen must be made, due to the nitric acid formed, which is estimated by Jodlbauer's method.

NATHAN ZUNTZ, in an appended note (*ibid.*, 122), calls attention to the fact that correction must also be made for the argon contained in the commercial oxygen.

S. B. S.

Cerium Dioxide as Contact Substance for the Combustion of Organic Substances. JULIUS BEKK (*Ber.*, 1913, **46**, 2574—2579).—Platinised asbestos, as used by Dennstedt, may be replaced with advantage, by asbestos impregnated with cerium dioxide, prepared by soaking the material in a solution of cerium nitrate and igniting. A layer of about 30 cm. is used in an ordinary combustion tube, and heated to a dull red heat, either in the common form of furnace or in one of the Dennstedt pattern. The substance is placed in a narrow tube, which is drawn out to a jet at the end nearest to the oxygen inlet, whilst the use of a short layer of lead peroxide is recommended in the case of nitrogen or sulphur compounds. As in Dennstedt's process, halogens may be estimated by the increase in weight suffered by a silver spiral or layer of molecular silver. The combustion is complete in fifteen to twenty minutes. Unlike platinised asbestos, the catalyst is not "poisoned" by sulphur dioxide, arsenious acid, or lead peroxide. J. C. W.

The Calorimetric Estimation of Ash. FRITZ (EDLER) VON KONEK-NORWALL (*Chem. Zeit.*, 1913, **37**, 1181—1182).—It is well known that the weight of the ash from a coal burned in a bomb calorimeter may be 4—5% less than the weight obtained in the usual way by ashing the coal in the air in a platinum crucible; also, the weight of the ash may vary considerably in consecutive calorimetric determinations. These differences are only partly due to the fact that some of the ash is blown out of the crucible during the combustion in the calorimeter.

The author finds that the chief cause of these differences is the sulphur-content of the coal. During the combustion in the bomb sulphur trioxide is formed, and gives rise to soluble sulphates by combination with the alkalis, alkaline earths, and iron oxides contained in the ash; these sulphates dissolve in the water in the bomb, and are thus lost in the estimation of the ash. If, now, the contents of the bomb are washed out carefully, the boiling solution neutralised with sodium hydroxide in the presence of phenolphthalein as indicator, a yellowish-white precipitate is obtained, which may be collected, dried, and ashed in the usual way. If the weight of this ash is added to the weight of the calorimetric ash, the differences between consecutive estimations disappear, and the difference between the calorimetric ash and that estimated in the usual way is reduced to 1—1·5%. This remaining difference is probably due to the alkali content of the coal, which remains as soluble sulphates in the wash water, and is lost. T. S. P.

The Electrolysis of Potassium Chloride. HIRAM STANHOPE LUKENS (*J. Amer. Chem. Soc.*, 1913, **35**, 1472—1482).—In the electrolytic estimation of anions, using the Hildebrand cell, only small quantities of salt can be used. The author has investigated the accuracy which is attainable when solutions of potassium chloride containing 1—2 grams of potassium chloride are electrolysed.

It was found that the chief error was caused by the anolyte

creeping into the catholyte under the glass partition (cup) separating the anolyte and catholyte, owing to the fact that the glass is not wetted by the mercury. This could be prevented by platinising the bottom edge and outside of the cup, and then depositing a heavy coating of silver on the platinum. There was still a slight error caused by some decomposition of the amalgam occurring in the inner cell. This was obviated by cutting a section, 8 mm. in height, from the bottom of a beaker 40 mm. in diameter; this was cemented in an inverted position in the centre of the crystallising dish containing the mercury. When the glass cup was then placed in position, the mercury in the anode portion of the cell was confined to an annular space, about 10 mm. wide, between the cup and the section from the beaker, whereby the amalgam was formed close to the outer vessel, into which it quickly made its way and was decomposed.

The results obtained with this apparatus were very accurate, the errors being of the order of 0·0001—0·0003 gram on 0·6 gram of chlorine. 1·09 Grams of potassium chloride could be decomposed in an hour, using 1·6—2 amperes at 6·5—7 volts. T. S. P.

Blacher's Method of Estimating the Hardness of Water. W. HERBIG (*Färberzeitung*, 1913, **24**, 98—101, 113—114).—A discussion on various methods employed for estimating hardness in water. The author confirms the experiments of Blacher, Jacoby, and Koerber (*Zeitsch. angew. Chem.*, 1909, **22**, 967), in which stearic acid is employed, and describes modifications which he considers give more satisfactory results, which are demonstrated in tabular form. F. M. G. M.

Analysis of Alloys of Lead, Tin, Antimony, and Copper. D. J. DEMOREST (*J. Ind. Eng. Chem.*, 1913, **5**, 842—843).—Alloys consisting of these four metals may be analysed by heating the finely divided sample with concentrated sulphuric acid until the lead has been converted into sulphate, and the other metals have dissolved. The lead sulphate is collected and weighed, and the antimony in the filtrate is titrated with potassium permanganate solution. After the titration, the tin is reduced by means of iron in the presence of the antimony, and the stannous salt is titrated with iodine solution. Another portion of the sample is treated with sulphuric acid as before, the lead sulphate is separated, and the copper is precipitated as cuprous thiocyanate either with or without previous titration of the antimony. The cuprous thiocyanate may be titrated with potassium permanganate solution, or the copper estimated by the iodide method after the precipitate has been ignited and the copper oxide dissolved in nitric acid. Full details as to manipulation are given in the original. W. P. S.

Electrolysis of Nitric Acid Solutions of Copper. JOHN H. STANSBIE (*Trans. Faraday Soc*, 1913, **9**, 11—13).—More complete deposition of copper from nitric acid solutions is obtained with a rotating than with a stationary cathode, as in the latter case

nitrous acid may accumulate at the surface of the metal. The addition of sulphuric acid is of advantage in securing complete deposition. When the rotation is stopped, the cathode should be washed before breaking the current. C. H. D.

Electrolytic Estimation of Copper in Solutions containing Nitric Acid. ELIZABETH GILCHRIST and ALEXANDER C. CUMMING (*Trans. Faraday Soc.*, 1913, **9**, 186—187).—The deposition of copper is complete, even in presence of a large excess of nitric acid, if carbamide is added to destroy nitrous acid. C. H. D.

New Method for the Electrolytic Analysis of White Metals for Bearings. I. COMPAGNO (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 221—226).—These alloys contain tin, antimony, and copper, together with lead, arsenic, iron, zinc, nickel, etc., as impurities. The method here described is said to be more exact as well as more rapid than those at present in use. The alloy (1 gram) is treated with 20 c.c. of nitric acid (D 1·4), first for some hours at the ordinary temperature, then for thirty minutes on the boiling water-bath; the tin and antimony then remain undissolved in the form of metastannic and metantimonic acids (which include also a little copper nitrate). After filtration, the copper and, if necessary, the lead are determined electrolytically, and in the remaining solution the other metals may be estimated if required. The precipitate of metastannic and metantimonic acids is then dissolved as directed in a previous paper (A., 1912, ii, 810), and electrolysed as there described. The deposited antimony and copper are weighed together, and the copper present is estimated as follows. The deposit is treated in the warm with 10 c.c. of dilute nitric acid (1 : 2) and 0·3 gram of tartaric acid; the solution is evaporated to dryness, redissolved in 20 c.c. of water, made alkaline with sodium hydroxide, and treated with 1—2 c.c. of potassium sodium tartrate solution (10%), and with about 0·3 gram of dextrose. After boiling, the cuprous oxide is dissolved in nitric acid, and the copper in the solution estimated (after addition of 2 c.c. of concentrated sulphuric acid) electrolytically. The liquid from which the antimony and copper have been removed is heated almost to boiling, and treated very cautiously with 120 c.c. of hydrochloric acid (D 1·19). Boiling is continued until the tin sulphide at first precipitated is entirely decomposed, and the liquid is then concentrated and heated for a few minutes with a few drops of hydrogen peroxide. After addition of 20 grams of pure oxalic acid and dilution to 500 c.c., the tin is deposited electrolytically, preferably in an apparatus described, which is especially adapted for operations in the warm with rotating electrodes. R. V. S.

Estimation of Small Quantities of Mercury in Organic Substances. SVEND LOMHOLT and J. A. CHRISTIANSEN (*Biochem. Zeitsch.*, 1913, **55**, 216—223).—The organic material is first destroyed in the presence of sulphuric or nitric acid and potassium per-

manganate. A small amount of copper sulphate is then added, and the copper and mercury are precipitated together by hydrogen sulphide. The sulphide is filtered off on to a Gooch crucible, and dissolved in a mixture of 5 c.c. of concentrated nitric acid and 1·5 c.c. of 1% hydrochloric acid. (This ratio of acids must not be departed from.) From the solution thus obtained, the mercury is separated by electrolysis after dilution to 40 c.c., using platinum wire for an anode, and a gold plate for cathode and a tension of 1·5 volts. After eight hours, the cathode is removed, dried, and weighed. It is then heated in a current of hydrogen to volatilise the mercury, and weighed again. The difference gives the amount of mercury. S. B. S.

The Chemical Investigation of Aluminium. J. CZOCHRALSKI (*Zeitsch. angew. Chem*, 1913, **26**, 501—503).—The analysis of aluminium, and of alloys rich in aluminium, is best carried out as follows: Two grams of borings are dissolved in a mixture of 40 c.c. of water, 40 c.c. of concentrated sulphuric acid, and 2 c.c. of nitric acid (D 1·48). The solution is diluted to 300 c.c., and warmed for some time at 80° in order to make the silicic acid ball together, after which the undissolved matter is collected, dried, and weighed. The residue is tested for purity with hydrofluoric and sulphuric acid, and if large it is fused with sodium carbonate-sulphur mixture, and further investigated for tin, antimony, and lead. If arsenic, bismuth, etc., are to be estimated in the filtrate, they are precipitated with hydrogen sulphide, otherwise the copper, and any traces of lead, are estimated electrolytically. To the filtrate from the metals of the hydrogen sulphide group are then added 20 grams of ammonium tartrate dissolved in 100 c.c. of water, the solution is made alkaline, and the iron, nickel, manganese, and zinc precipitated with ammonium sulphide; magnesium is precipitated from the filtrate as magnesium ammonium phosphate. The iron, nickel, etc., are separated in the usual way, the nickel and zinc being estimated electrolytically.

Special methods are described for the estimation of any particular impurity which may be present.

Microphotographs are given of aluminium containing impurities and of aluminium alloys. T. S. P.

The Increase in the Oxidising Potential of Dichromate Ion on Platinum caused by Certain Reducing Agents. An Improved Method for the Electrometric Titration of Ferrous Salts. GEORGE S. FORBES and EDWARD PAYSON BARTLETT (*J. Amer. Chem. Soc.*, 1913, **35**, 1527—1538).—It is found that certain reducing agents, as, for example, ferrous sulphate, arsenious acid, chromous sulphate, and potassium ferrocyanide, increase the oxidising potential of the dichromate ion on platinum by amounts up to 0·2 volt. No other oxidising agent has been found to give a similar effect.

The potential increases continuously up to the point where all the dichromate is reduced, and then drops suddenly when excess

of the reducing agent is added. An excess of one drop of a $0{\cdot}1N$-solution of the reducing agent often depresses the potential by 0·5 volt, so that the method can be used for titrating a dichromate solution with a ferrous salt; the end-point reaction is much more delicate than with the ferrocyanide indicator.

The duration of the effect varies with the reducing agent used, from a few seconds to many hours; chlorides are fatal to the permanency, owing apparently to a side-reaction.

The authors suppose that the phenomenon is catalytic in nature, but direct tests of their hypothesis could not be devised.

T. S. P.

Estimation of Cobalt and Uranium in Steel. HEINRICH KÖNIG (*Chem. Zeit.*, 1913, **37**, 1106—1107).—The estimation of cobalt in steel entails a separation of this metal from nickel, as the two are always present together. The iron, nickel, and cobalt are first estimated electrolytically from an ammonium oxalate solution; the iron and nickel are then estimated separately, and the quantity of cobalt is found by difference. For the estimation of the nickel, the hydrochloric acid solution of the steel, after the removal of tungstic acid, is shaken with ether to separate the greater part of the iron. The acid solution is then heated to expel the ether, the iron is reduced by the addition of sulphurous acid, and the solution is neutralised with alkali solution. Potassium cyanide is now added, the separated chromium precipitate is removed by filtration, and the filtrate is boiled. The cobalt is thus converted into the complex potassium cobalticyanide, which remains in solution when the nickel is precipitated as hydroxide by the addition of potassium hydroxide and bromine. The nickel hydroxide is then collected, dissolved in hydrochloric acid, and the nickel estimated by the dimethylglyoxime method. The uranium is estimated as follows: The hydrochloric acid solution of the steel, after the removal of tungstic acid, is evaporated with sulphuric acid, the solution is diluted with water, nearly neutralised with ammonia, and the iron is electrolytically deposited from an ammonium oxalate solution. The electrolysis is continued until the ammonium oxalate has been converted into carbonate, and a precipitate consisting of the chromates, vanadates, and hydroxides of uranium, aluminium, and manganese is obtained. The uranium is, however, precipitated completely only when the ammonium carbonate has been decomposed by boiling the solution. When this has been done, the precipitate is collected, washed with dilute ammonium chloride solution, dissolved in hydrochloric acid, chromates are reduced by the addition of a few drops of alcohol, and the solution is oxidised with nitric acid. After iron, chromium, manganese, and aluminium have been precipitated by the addition of ammonium carbonate and sulphide, the solution containing the uranium and vanadium is acidified with acetic acid, boiled, and the vanadium sulphide removed by filtration. The filtrate is oxidised with nitric acid, and the uranium is precipitated by the addition of ammonia; the precipitate is washed with ammonium

chloride solution, ignited in a current of hydrogen, and weighed as UO_2. W. P. S.

Action of an Excess of a Soluble Ferrocyanide on Solutions of Zinc, Copper, and Nickel, and the Volumetric Estimation of the Latter. RAOUL MEURICE (*Ann. Chim. anal.*, 1913, **18**, 342—345).—When zinc salts are treated in solution with an excess of potassium ferrocyanide, the precipitate obtained has the formula $Zn_3K_2[Fe(CN)_6]_2$, and its formation may be utilised as a means of estimating zinc volumetrically. The zinc solution is treated with an excess of standard potassium ferrocyanide solution, and the excess of the latter is then titrated with permanganate solution in a portion of the clear solution after the addition of sulphuric acid. In the case of copper salts, the ferrocyanide formed varies in composition with the concentration of the solution, and is slightly soluble; the ferrocyanide method cannot, therefore, be used for the volumetric estimation of copper. Nickel yields a definite ferrocyanide in the presence of an excess of potassium ferrocyanide and ammonium sulphate. For the estimation of this metal the solution (containing about 0·1 gram of the metal) is treated with 100 c.c. of 3·5% potassium ferrocyanide solution, 5 grams of ammonium sulphate are added, and the mixture is diluted to 200 c.c. After filtration, 100 c.c. of the filtrate are diluted to about 800 c.c., acidified with sulphuric acid, and titrated with permanganate solution. The potassium ferrocyanide solution is standardised against the permanganate solution, and this in turn against sodium oxalate; the iron equivalent of the permanganate is thus obtained, and 1 atom of iron is equivalent to 1 atom of nickel. W. P. S.

Detection of Potassium Dichromate in Milk. B. GREWING (*Zeitsch. Nahr. Genussm.*, 1913, **26**, 287).—Ten c.c. of the milk are mixed with 4 c.c. of a 3% aniline solution, and the mixture is allowed to flow on to the surface of 3 c.c. of concentrated sulphuric acid. A blue-coloured zone appears at the junction of the liquids if the milk contains dichromate. The test will detect as little as 0·01 gram of dichromate per litre, but in this case the colour obtained is reddish-violet, and does not develop until after the lapse of about eight minutes. Nitrates, formaldehyde, and hydrogen peroxide do not interfere with the reaction. W. P. S.

Colorimetric Estimation of Titanium in Iron and Steel. CHARLES R. MCCABE (*J. Ind. Eng. Chem.*, 1913, **5**, 735—736).—Two grams of the sample and 2 grams of non-titanium steel are dissolved separately in dilute sulphuric acid, and the solutions are oxidised with nitric acid. The solutions are now transferred to graduated tubes, diluted to the same volume, and compared. Having obtained solutions showing the same colour in equal volumes, hydrogen peroxide is added to each tube, and if any deepening of colour is observed in the solution of the sample, standard titanium solution is added to the other tube until the

tints are equal. When the iron or steel contains less than 0·02% of titanium the oxidised hydrochloric acid solution of both the sample and the non-titanium steel are extracted with ether to remove the greater part of the iron; the acid solutions are then boiled, ammonia is added, the precipitates are collected, dissolved in sulphuric acid, and the titanium is estimated by comparison, as described previously. W. P. S.

Estimation of Vanadium in Steel by the Hydrogen Peroxide Colorimetric Method. CHARLES R. MCCABE (*J. Ind. Eng. Chem.*, 1913, **5**, 736—737).—The method consists in treating a non-vanadium steel in precisely the same way as the sample, the colour of the latter solution being then imitated by the addition of a standard vanadium solution to the non-vanadium steel solution, the final comparison being made at equal volumes. Two grams each of the sample and a non-vanadium steel are dissolved in 40 c.c. of nitric acid, D 1·2, 0·1 gram of potassium permanganate is added to each solution, and, after two minutes' heating, the solutions are clarified by the addition of ammonium hydrogen sulphite. Excess of sulphur dioxide is expelled by heating, and the colours of the solutions are then matched. One c.c. of a 3% hydrogen peroxide solution is now added to each tube, and standard vanadium solution is run into the non-vanadium steel solution until the desired coloration is obtained at equal volumes. In the case of steels containing chromium, a quantity of potassium dichromate corresponding with the amount of chromium in the steel must be added to the non-vanadium steel. W. P. S.

Electrolytic Deposition of Antimony. NEWCOMB K. CHANEY (*J. Amer. Chem. Soc.*, 1913, **35**, 1482—1490).—Antimony may be deposited, but not quantitatively, from electrolytes containing ammonium, sodium, and barium lactates; tin is not deposited from these electrolytes.

The conditions for the quantitative deposition of antimony from an ammonium sulphide electrolyte were worked out. It was found that incomplete deposition is due to the fact that antimony is appreciably soluble in colourless ammonium sulphide, and therefore, for complete deposition, it is necessary for the concentration of ammonia and ammonium sulphide to be made negligible towards the end of the electrolysis. This can be effected by electrolysing at boiling temperature, the ammonia and ammonium sulphide being thus expelled or oxidised to ammonium sulphate. The deposits of antimony thus obtained are like polished platinum in appearance. An essential condition for the satisfactory progress of the electrolysis is the proper initial concentration of the ammonium polysulphide. This is best obtained by making two solutions: (*A*) Concentrated aqueous ammonia is saturated with hydrogen sulphide in the presence of powdered sulphur, the excess of which is filtered off after long shaking. (*B*) A concentrated solution of ammonia is saturated with hydrogen sulphide. For the electrolysis, one volume of *A* is mixed with six volumes of *B*, and added drop by drop to

the antimony solution until a clear liquid is obtained. With rotating electrodes 0·24 gram of antimony can be deposited in an hour, using a current density of 1 ampere per sq. dcm. Since tin may be deposited from the same electrolyte, a method of estimating the total tin and antimony is given.

Of the alkaline earth sulphides, that of calcium was found to be best suited for the deposition of antimony. Details of the method are given, but it is somewhat cumbersome, and is liable to give high results. It was found possible to separate tin from antimony by the precipitation of the tin as stannic hydroxide and electro-deposition of the antimony in a solution of calcium sulphide, but further work is necessary before the method can be depended on.

Quantitative results for antimony could not be obtained from ammonium, sodium, and potassium tartrate, or tartaric acid electrolytes. T. S. P.

Volumetric Method for Estimating *o*-, *m*-, and *p*-Cresols, Thymol, and Phenol. L. V. Redman, A. J. Weith, and F. P. Brock (*J. Ind. Eng. Chem.*, 1913, 5, 831—830).—Rapid and trustworthy estimations of *o*-, *m*-, and *p*-cresol, phenol, and thymol may be made by treating their dilute solution with *N*/30-iodine solution, adding sodium hydrogen carbonate until the mixture is about *N*/2 (compare A., 1911, ii, 546), shaking the mixture for one minute, acidifying the solution, and titrating back the excess of iodine. A series of equations is given for calculatng the quantity of phenol, *m*-cresol, and the sum of the *o*- and *p*-cresols in the presence of each other in any combination or proportion if two quantities are known. namely, the weight of the mixture taken and the amount of iodine absorbed. The error is about 0·2% for each substance present. W. P. S.

Detection of Small Amounts of Dextrose in Urine. Sydney W. Cole (*Lancet*, 1913, Reprint, 6 pp.).—The method is based on the reducing power of dextrose after other reducing substances and lactose have been removed by treatment with charcoal. Ten c.c. of the urine are boiled with 1 gram of pure blood-charcoal, then cooled, shaken for about five minutes, and filtered. The filtrate is received in a test-tube containing 0·5 gram of anhydrous sodium carbonate, and, after the addition of six drops of glycerol, the mixture is boiled for fifty seconds. Four drops of a 5% copper sulphate solution are now added, and the mixture is left without further heating for one minute. With normal urine, the solution retains its blue colour, a small amount of phosphates being precipitated. If dextrose is present to the extent of 0·02%, or more, above the average normal amount, the blue colour is discharged, and a yellow precipitate of cuprous hydroxide forms. In the case of urines containing much lactose, the treatment with blood-charcoal must be repeated in order to remove this sugar. Lactose may be detected by heating the urine with blood-charcoal, collecting the latter, and extracting it with hot acetic acid. The acetic acid solution is then used for the preparation of the lactosazone, m. p. 200°. W. P. S.

Method of Estimating Sugar in the Blood. IVAR BANG (*Biochem. Zeitsch.*, 1913, **56**, 159).—A reply to Hatta's criticisms (this vol., ii, 735) on the author's method of sugar estimation. S. B. S.

Quantitative Estimation of Mannitol. JAN SMIT (*Chem. Weekblad*, 1913, **10**, 894—907).—An application of Wagenaar's glycerol estimation process (A., 1911, ii, 663) to the quantitative estimation of mannitol. The experimental details are similar. Ammonium compounds must be eliminated by boiling with alkali; amino-acids by precipitation with phosphotungstic acid, or by transformation into hydroxy-acids by means of nitric acid; sugars by fermentation with an appropriate culture; hydroxy-acids by precipitation as calcium or lead salt; glycerol by extraction with a mixture of alcohol (1 vol.) and ether ($1\frac{1}{2}$ vols.); hexitols, such as sorbitol and dulcitol, by the formation of an acetal derivative with benzaldehyde. The amount of mannitol is not strictly proportional to the cupric hydroxide dissolved, but an empirical table is given showing the proportions of mannitol corresponding with 0·25 to 29·1 c.c. of $N/10$-thiosulphate. It is important to have the concentration of the alkali $4N$, but the temperature has little influence on the results obtained. A. J. W.

Estimation of *d*-Lactic Acid in Body Fluids and Organs JUNJI YOSHIKAWA (*Zeitsch. physiol. Chem.*, 1913, **87**, 382—417).—The relation between the rotatory power and concentration of solutions of lithium lactate is established. Solutions of zinc lactate are warmed with lithium carbonate, filtered, and polarised, when the *d*-lactic acid present is accurately estimated. The presence of *dl*-lactic acid does not disturb the polarisation, neither does lithium acetate have any effect. Normal urine contains no *d*-lactic acid. Added lactic acid can be determined in urine by the polarimetric method, treatment with lead carbonate being unnecessary. The best results are obtained when the lactic acid is extracted with ether from the urine made acid with phosphoric acid. In muscle about 94% of added *d*-lactic acid is indicated by the polarimetric method. *d*-Lactic acid is formed on autolysis of muscle without the intervention of micro-organisms. Similar results were obtained with the liver. E. F. A.

Detection and Identification of Malonic Acid. J. BOUGAULT (*J. Pharm. Chim.*, 1913, [vii], **8**, 289—294).—The formation of cinnamylidenemalonic acid is suggested as a means of identifying malonic acid in a mixture of oxidation products. Particulars are first given of the yields of cinnamylidenemalonic acid obtained when free malonic acid or its sodium or calcium salt is treated with cinnamaldehyde in presence of acetic acid, and it is shown that the inorganic salts and organic acids, likely to occur with malonic acid in mixtures resulting from oxidation experiments, do not seriously interfere with this condensation.

The solution resulting from the oxidation is treated with excess of sodium carbonate, the filtrate, after neutralisation with acetic

acid, evaporated to dryness, and the residue washed with 60° alcohol. The residue left on evaporating this solution is treated with 60° alcohol, and the residue from this solution is mixed with cinnamaldehyde and acetic acid and heated in a closed tube during ten hours. The product is then saturated with sodium carbonate, the solution filtered, and the cinnamylidenemalonic acid isolated by adding hydrochloric acid (compare Riiber, A., 1904, i, 894).

T. A. H.

Estimation of Fixed Organic Acids and a New Method for the Estimation of Citric Acid in Wines and Musts. L. Mathieu and L. Ferré (*Ann. Chim. anal.*, 1913, **18**, 352—355).—The following procedure is recommended for the estimation of tartaric, malic, and citric acids: (1) Separation of the mixed acids by the process described by Mestrezat (A., 1906, ii, 635), and estimation of the lactic acid by Moeslinger's method. (2) Estimation of the tartaric acid by Kling's method (A., 1912, ii, 1006). (3) Oxidation of the mixture of the three acids by permanganate in both acid and alkaline solution. In acid solution, 1 gram of potassium permanganate oxidises 1·447 grams of tartaric acid, 2·078 grams of malic acid, or 1·820 grams of citric acid, whilst in alkaline solution the same quantity of permanganate oxidises 0·620 gram of tartaric acid, 0·615 gram of malic acid, or 0·380 gram of citric acid.

W. P. S.

A Microchemical Method for the Determination of α- and β-Amino-acids and Certain Derivatives: in Proteolysis, Blood and Urine. Philip A. Kober and Kanematsu Sugiura (*J. Amer. Chem. Soc.*, 1913, **35**, 1546—1584. Compare A., 1912, 952, 953).—The method described earlier for the formation of complex copper compounds by the interaction of copper hydroxide and an amino-acid, peptide, or peptone in neutral or slightly alkaline solution has been increased in accuracy by the addition of a suitable solution of sodium borate and boric acid, which prevents the otherwise slightly excessive precipitation of copper.

It is shown that the process can be applied to the accurate and rapid estimation of amino-acids, peptides, and peptones in physiological material.

The copper complexes of amino-*n*-hexoic acid and of phenylglycine are exceedingly sparingly soluble, and, indeed, these acids will precipitate the copper from solutions of all the other complexes examined excepting that of histidine; small quantities of this substance can therefore be readily estimated in mixtures.

D. F. T.

Estimation of Formaldehyde in Fumigators and Commercial Solutions. Jack J. Hinman (*J. Ind. Eng. Chem.*, 1913, **5**, 752—755).—A comparison of various methods which have been proposed for the estimation of formaldehyde and its isomerides showed that the method of Haywood and Smith (A., 1905, ii, 771) and that of Seyewetz and Gibello (A., 1904, ii, 521) are the most

trustworthy. Kleber's method (A., 1904, ii, 371) may also be used, and will be found convenient when a considerable number of estimations have to be made. Legler's ammonia method yields low results (compare A., 1904, ii, 98). W. P. S.

A New Method of Estimation of Urea in Blood. ELI K. MARSHALL, jun. (*J. Biol. Chem.*, 1913, **15**, 487—494).—The method adopted is to convert urea into ammonium carbonate by the urease of soja-bean, and then to estimate the alkalinity. If the ammonia is removed by an air current as in Folin's method, satisfactory results are obtained without a preliminary removal of the proteins. W. D. H.

Estimation of Urea in Urine. ELI K. MARSHALL, jun. (*J. Biol. Chem.*, 1913, **15**, 495—496).—The same method (preceding abstract) may be employed for the urine, and gives better results than the rapid clinical method previously recommended. W. D. H.

Plant Micro-chemistry. Identification of Alkaloids in Sublimates. OTTO TUNMANN (*Pharm. Zentr.-h.*, 1913, **54**, 1065—1068. Compare this vol., ii, 351).—Reactions are given for distinguishing caffeine from theobromine when these alkaloids have been obtained as sublimates. If the sublimate is submitted to the vapours of hydrochloric acid, caffeine yields a crop of crystals within a few minutes, whilst theobromine remains as a white powder. A 10% tartaric acid solution dissolves caffeine readily, but theobromine remains insoluble. Caffeine also dissolves in a concentrated aqueous chloral hydrate solution; theobromine, only when the mixture is heated. These chloral hydrate solutions of the two alkaloids deposit characteristic crystals; in the case of theobromine the crystals appear as spherical masses of needles, whilst caffeine yields hexagonal plates, with needle-shaped crystals developing on the edges of the plates. W. P. S.

The Use of the Folin Method for the Estimation of Creatine and Creatinine. WILLIAM H. THOMPSON, THOMAS A. WALLACE, and HAROLD R. S. CLOTWORTHY (*Biochem. J.*, 1913, **7**, 445—465).—The degree of conversion of creatine into creatinine by boiling with hydrochloric acid is inconstant; it is therefore better to use creatinine picrate for the preparation of the control of the standard dichromate solution. In development of the colour in the Folin method, the optimum time and temperature is seven to twenty-five minutes at 117—120°. The amount of alkali found best is that recommended by Folin.

In urine the darkening of the pigments by acid introduces an error, which in dog's urine may be as high as 10%. Dextrose up to 10% does not affect the estimation. Phosphoric is not superior to hydrochloric acid in the presence of dextrose. The recovery of creatine from diabetic urine is accompanied by a loss of 5%; this is attributed to the effect of acetoacetic acid. W. D. H.

Precipitation by Zinc Salts of the Purine Bases from Urine and Meat Extracts. ERNST SALKOWSKI (*Biochem. Zeitsch.*, 1913, **55**, 254—259).—The author emphasises the value of his process for separation of the purine substances (this vol., ii, 639) by zinc chloride. The precipitate does not yield the purine substances directly after decomposition of the zinc compounds with hydrogen sulphide. If, however, the zinc salt is first treated with warm nitric acid in the presence of urea, the bases can be precipitated with silver nitrate. The failure to obtain the purine bases directly is due, either to the presence of albumoses, which inhibit the precipitation, or to the fact that the purine substances are in some form of combination, from which they are only set free after treatment with the hot acid. It is shown by the author that the purine bases can also be nearly quantitatively precipitated by zinc salts even without previous removal of phosphates by calcium chloride and ammonia. Purine substances are not carried down as zinc salts in Böhmer's process for separation of albumoses, owing to the large amount of sulphuric acid present. The author replies to certain recent criticisms of his method (compare Thar and Beneslawski, this vol., i, 935). S. B. S.

The Colour Reactions of Triketohydrindene Hydrate (Ninhydrin). W. HALLE, ERNST LOEWENSTEIN and EGON PŘIBRAM (*Biochem. Zeitsch.*, 1913, **55**, 357—369).—A number of substances containing alcohol, aldehyde, or keto-groups, such as glycerol, ethylene glycol, erythrol, glyceraldehyde, acetone, as well as certain sugars, gives the ninhydrin colour reaction, a fact which depends on the existence of a reducing group. The production of the colour is facilitated by the presence of free hydroxyl ions, and in the presence of alkali, dextrose can give the reaction in the dilution 1 : 100,000. The shade of colour produced depends on the strength of the alkali, and the medium of the reaction. Hydrindantin is an intermediate product, and it is an extremely sensitive indicator for hydroxyl ions. The colour produced by amino-acids with ninhydrin differs from that obtained from the above-mentioned substances, in that it is produced in the cold, in the absence of oxygen, and its intensity is not increased on the addition of alkali. Hydrindantin also gives a blue colour with amino-acids. The mechanism of the two classes of reactions is not clearly explained. The colouring matter produced from ninhydrin is in all cases of colloidal character, and it is influenced by the presence of inorganic salts, the cation playing the chief rôle in the changes produced.

S. B. S.

General and Physical Chemistry.

Refraction and Dispersion of Gaseous Nitrogen Peroxide. CLIVE CUTHBERTSON and MAUDE CUTHBERTSON (*Proc. Roy. Soc.*, 1913, *A*, **89**, 361—369).—In order to ascertain the influence of polymerisation on refractivity and dispersive power, the authors have made measurements of the refractive index and dispersion of gaseous nitrogen peroxide at different temperatures and pressures. If the refractivity, reduced to normal temperature and pressure on the assumption that the dissociation equilibrium remains unchanged, is plotted against the corresponding reduced density, it is found that the points fall on a straight line. By extrapolation, this leads to the values 0·000509 and 0·001123 for the refractivity of NO_2 and N_2O_4 respectively. It thus appears that polymerisation increases the refractivity by about 10·5%. In comparison with the refractivities of the constituent elements, that of a molecule of NO_2 is greater by about 21%.

The dispersion measurements show that the dispersive power of a molecule of NO_2 in the red and green is considerably greater than that of a molecule of N_2O_4. H. M. D.

Optical Properties of the Four Carbon-atom Ring. SERGEI V. LEBEDEV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1388—1390. Compare this vol., i, 1285).—The author has measured the refractivities of a number of *cyclo*butane derivatives, including several spirans. In order to obtain the value of the optical exaltation of the four carbon-atom ring, the exaltation of the unsaturated compound is diminished by 0·51, which Auwers and Ellinger (A., 1912, i, 187) found to be the mean value of the exaltation for the *D*-line caused by the presence of a semicyclic linking; this difference is then divided by the number of rings. With hydrogenised hydrocarbons, the magnitude of the exaltation is divided directly by the number of rings. The values thus obtained are as follows: From the trimeride of *as*-dimethylallene, 0·63; second tetrameride of allene, 0·44; pentameride of allene, 0·47; hexameride of allene, 0·52; 1 : 2-di*iso*propyl*cyclo*butane, 0·40; 1 : 1 : 2-trimethyl-3-*iso*propyl*cyclo*butane, 0·60; 2-*iso*propyl*cyclo*butanone, 0·71; hydrogenised trimeride of allene, 0·62; hydrogenised trimeride of *as*-dimethylallene, 0·75; hydrogenised first tetrameride of allene, 0·75; hydrogenised second tetrameride of allene, 0·67; hydrogenised pentameride of allene, 0·60. The mean of these twelve values is 0·60 (compare Östling, T., 1912, **101**, 457). T. H. P.

Refractive Indices of Certain Liquid Crystals. WALTHER KREIDE (*Physikal. Zeitsch.*, 1913, **14**, 979—981).—Measurements have been made of the refractive indices of cholesteryl chloride and cholesteryl nitrobenzoate in the liquid crystalline condition. Data are recorded for a series of temperatures and for the red

lithium, the yellow sodium, and the green and blue mercury lines. The index of refraction varies with the temperature according to a linear formula. The light which is transmitted by a layer of the liquid-crystalline substances at grazing incidence is found to be polarised. H. M. D.

Refractive Indices of Gelatin Sols and Gels. GEORGE S. WALPOLE (*Kolloid. Zeitsch.*, 1913, **13**, 241—248).—Experiments have been made to ascertain the influence of concentration, temperature, electrolytes, and gel formation on the refractive index of gelatin. At constant temperature, the value of $(n-n')/g$, where n and n' are the refractive indices of the gelatin solution and of water respectively, and g is the number of grams of gelatin per 100 c.c. of solution, is constant and independent of the concentration of the gelatin. It is calculated that the value of $(n-n')/g$ for dry, ash-free, commercial gelatin is 0·001824 at 17·5°. The addition of salts, acids, and bases is without influence on the refractive index of the gelatin, as is shown by observations on solutions containing ammonium chloride, sulphate, and thiocyanate, hydrochloric acid, and sodium hydroxide. The transition from the sol to the gel condition is also unaccompanied by any change in the refractive index of the gelatin when this is measured by means of the quantity $(n-n')/g$. The conclusions drawn by Frei (A., 1910, ii, 365) from a series of similar experiments are adversely criticised. H. M. D.

Refraction and Magnetic Rotation of Compounds with Acetylenic Function. CHARLES MOURÈU, PAUL TH. MULLER and J. VARIN (*Compt. rend.*, 1913, **157**, 679—682. Compare Moureu, A., 1906, ii, 1).—A study of the magnetic rotation and refraction of a number of aliphatic and aromatic substances containing an acetylene linking in varying proximity to a substituted negative group. The values for the triple linking have been obtained from the values found and calculated for heptinene and octinene. The results are in accord with those previously obtained by Moureu for the refraction and molecular dispersion (compare *loc. cit.*). The proximity of the triple linking and a negative radicle produce a more or less marked rise in the refraction in the aliphatic series, this being much accentuated in the aromatic series by the proximity of the phenyl group to the acetylene linking. The magnetic rotation is affected qualitatively in the same manner except in the case of acetylene diacetal, $CH(OEt)_2 \cdot C\vdots C \cdot CH(OEt)_2$. The magnetic rotation is more sensitive than the refraction to the reciprocal influence of the triple linking and the negative or unsaturated groups, this being particularly manifest in the aromatic compounds, where there is a conjugation of the double linking in the phenyl group and the acetylene linking. W. G.

Resonance Spectra of Iodine under High Dispersion. ROBERT W. WOOD (*Phil. Mag.*, 1913, [vi], **26**, 828—846.* Compare A., 1912, ii, 1018).—The resonance spectra of iodine excited by the

* and *Physikal. Zeitsch.*, 1913, **14**, 1189—1200.

green and yellow lines of mercury have been further examined. Improvements in the method of utilising the exciting light have made it possible to photograph the resonance spectra in the fourth order spectrum given by a large plane grating with an exposure of only twenty-four hours. By operating the mercury vapour lamp with different resistances in circuit, it was found possible to vary the width of the exciting line so as to cover a variable number of iodine absorption lines, and the resonance spectra obtained under these conditions have been carefully compared.

In the earlier work it was assumed that each of the bright resonance lines coincided with one or other of the numerous absorption lines, but it is now found that this is not the case. The vapour always emits a line, the wave-length of which is identical with that of the exciting light. This line, termed the resonance radiation line, is accompanied by companion lines which form a group very similar in appearance to the other groups which appear at intervals along the spectrum. The width of this group of lines is about thirty times the width of the group of absorption lines, which are covered by the mercury exciting line. This indicates that each one of the absorption lines must be responsible for more than one line in each resonance group. From the fact that the characteristic resonance group forms a cluster round the exciting line, and that the widths of the different groups are sensibly the same, it appears probable that each absorption line gives rise to a series of equidistant lines, which are superposed and form the cores of the different groups. These lines are accompanied by companion lines, the position of which depends on the absorption lines which are excited, but for any given absorption line, the position of the companion line and its distance from the core remains constant. By reducing the density of the iodine vapour in the resonance tube, it is found that the band spectrum is emitted. This spectrum is more strongly absorbed by the iodine vapour than the lines of the resonance groups.

There is apparently no phosphorescent effect in the emission of the resonance spectrum. H. M. D.

The Arc and Spark Spectrum of Aluminium in International Normals. RAINER GRÜNTER (*Zeitsch. wiss. Photochem.*, 1913, **13**, 1—19).—Wave-length measurements have been made in the arc and spark spectra of aluminium. The recorded observations, which extend from $\lambda = 2100$ to $\lambda = 6700$, are expressed in terms of the international normal lines, and compared with the data obtained by Kayser and Runge and by Exner and Haschek. In addition to the line spectrum, aluminium gives a characteristic band spectrum, in which the bands are shaded off towards the red end of the spectrum. H. M. D.

Measurements in the Ultra-violet Spark Spectrum of Metals According to the International System. JOSEF M. EDER (*Zeitsch. wiss. Photochem.*, 1913, **13**, 20—40).—Accurate wave-length measurements have been made of the lines in the ultra-violet spark

spectra of silver, aluminium, arsenic, gold, barium, bismuth, carbon, calcium, cadmium, copper, lead, antimony, tin, strontium, thallium, and zinc between λ 1900 and λ 2400. It is estimated that the wave-lengths of the sharp lines are accurate to 0·01 Å, whilst the weaker lines are probably correct to 0·02 Å.

The wave-lengths of the sharper lines in the ultra-violet spectrum of copper were determined in the first instance in terms of the international scale and by the use of copper alloys as electrodes; the spectra of the other elements were referred to the copper standards. In some cases the spark discharge was allowed to take place between a copper electrode and an electrode of the metal under investigation.

It is claimed that the measurements afford more accurate wave-length data than have hitherto been available for the region examined, and that the accuracy with which dispersion formulæ for quartz prisms may be determined has been considerably increased.

H. M. D.

New Measurements of the Arc Spectra below $\lambda = 3200$ for Several Metals. WILHELM HUPPERS (*Zeitsch. wiss. Photochem.*, 1913, **13**, 46—88).—The arc spectra below $\lambda = 3200$ of the metals zinc, lead, calcium, thallium, cadmium, magnesium, aluminium, copper, silver, and lithium have been measured by means of a quartz spectrograph. The Hartmann formula was used to calculate the wave-lengths of the various lines, and values are obtained of an accuracy of $\pm$0·01 Å. The stronger spark lines, particularly in the cases of silver and copper, make their appearance in the ultra-violet spectrum. A large number of hitherto unmeasured lines are recorded, the more particularly in the case of cadmium. Many of these new lines can be placed in the various series, or can be classified as combination lines. The thallium spectrum is remarkable for the unsharp nature of the lines and the partition of their intensities. The reversals of the lines λ 2379 and λ 2767 are observed in the photographs, but other reversals are not visible in the photographs. Reproductions of portions of the cadmium and thallium spectra are appended to the paper. J. F. S.

Investigations in the Extreme Ultra-violet. KARL WOLFF (*Ann. Physik*, 1913, [iv], **42**, 825—839).—A new form of quartz arc lamp is described, by means of which the author has investigated the arc spectra of zinc, cadmium, and mercury in the extreme ultra-violet region, the observations extending up to the limit fixed by the transparency of fluorite. The series lines anticipated by Paschen (A., 1911, ii, 133) have been actually observed, and from comparative observations on the hydrogen spectrum in the Schumann region, it has been possible to assign wave-lengths to several hydrogen lines with an accuracy of the order of 0·02 Ångström. These lines and the new lines belonging to zinc, cadmium, and mercury may be utilised as normal lines in the investigation of this region of the spectrum.

Certain lines belonging to carbon and silicon have also been

measured, and Lyman's observation that the helium spectrum contains no lines between $\lambda=1850$ and $\lambda=1402$ is confirmed.

H. M. D.

[Investigations in the Extreme Ultra-violet.] FRIEDRICH PASCHEN (*Ann. Physik*, 1913, [iv], **42**, 840—842).—The nature of the ultra-violet series of lines found by Wolff (preceding paper) in the spectra of zinc, cadmium, and mercury is discussed with reference to the author's formulæ for principal and combination series of lines.

H. M. D.

Influence of Self-induction on the Spark Spectra of Certain Non-metallic Elements. GENEVIEVE V. MORROW (*Sci. Proc. Roy. Dubl. Soc.*, 1913, **13**, 607—620).—The spectra obtained by sparking gold and carbon electrodes, with and without self-induction, have been examined in an atmosphere of nitrogen, oxygen, hydrogen, chlorine, bromine, iodine, sulphur, phosphorus, boron trichloride, silicon tetrachloride, sulphur dioxide, hydrogen sulphide, carbon dioxide, carbon monoxide, and hydrogen chloride.

It is found that the principal lines of the line spectra of the elements present in the gaseous atmosphere are obtained, and, as a general rule, the intensity of the lines is greatest when self-induction is not introduced. In the case of compounds, only the line spectra of the component elements are observed, the band spectra of the compounds not being seen except in the case of cyanogen. With hydrogen, which was the only electropositive gas examined, the effect of self-induction is to intensify and sharpen the hydrogen lines, and to remove, more or less completely, the lines of gold and carbon. On the other hand, with electronegative gases, such as oxygen and nitrogen, self-induction removes the gas lines and leaves the gold or carbon spectrum more or less unchanged. With chlorine, bromine, and iodine, the effects of self-induction are not so pronounced.

When carbon electrodes are employed, the three bands attributed to cyanogen are seen in almost any atmosphere except hydrogen if self-induction is introduced into the circuit. Without self-induction, only the one band at λ 3883·6 is observed, and this is also found in any atmosphere except hydrogen.

H. M. D.

New Burner for Spectroscopic Use. ERNST H. RIESENFELD (*Chem. Zeit.*, 1913, **37**, 1372).—The relative advantages of burners in which a spray of the solution to be investigated is carried by the air into the interior of a Bunsen flame (such spray being obtained by the chemical [Beckmann, A., 1907, ii, 209] or electrolytic [Riesenfeld and Wohlers, A., 1906, ii, 593] evolution of gas in the solution) are discussed. Preference is given to the latter method, for which a greater constancy in the intensity of illumination as well as a greater range in the latter are claimed.

A new burner is described in which the solution to be investigated (about 1 c.c.) is placed in a small glass cup inside the tube of a Bunsen burner, the upper portion of which is preferably made

of glass. About 1 c.c. of nitric acid (10 per cent.) is added, and a particle of granulated zinc. For a sodium flame, it is advisable to use sodium nitrate solution (20%). Fracture of the burner owing to heat is unlikely, provided the flame is prevented from striking back. The flame is not coloured by the constituents of the glass, and, when the cup is not charged, shows only the Swan spectrum and the sodium lines. H. W.

Influence of Neutral Gases on the Absorption of Sodium Vapour. (A Correction.) KARL FREDENHAGEN (*Physikal. Zeitsch.*, 1913, **14**, 1047—1049. Compare A., 1911, ii, 571; A., 1912, ii, 517).—The very considerable variations in the absorption and dispersion of sodium vapour, which are observed when the pressure in the tube containing the vapour is changed, have been previously attributed to the influence of traces of foreign gases on the sodium vapour. Experiments are now described in which sodium was heated in highly exhausted tubes on the one hand, and in tubes containing helium on the other. Some of these tubes were heated as uniformly as possible, at about 400°, whilst others were only partly immersed in the heating jacket, and the absorption in the different tubes was compared. The observations indicate clearly that the presence of the helium is without influence on the absorption of the sodium vapour, and that the above-mentioned changes in the optical properties are to be attributed to changes in the density resulting from the pressure variations. H. M. D.

A Quantitative Study of Absorption Spectra by means of the Radiomicrometer. J. SAM GUY and HARRY C. JONES (*Amer. Chem. J.*, 1913, **50**, 257—308. Compare A., 1909, ii, 197, 359, 775; 1910, ii, 87, 172, 246; 1911, ii, 166; 1912, ii, 216, 507, 711; this vol., ii, 362).—The authors have studied the absorption spectra of salts of neodymium, praseodymium, nickel, and cobalt over the range λ 6800 to λ 10,000, and at several concentrations by means of a radiomicrometer specially constructed by them. The results are plotted as transmission curves; it is shown that in general the more concentrated the solutions the less the transparency and the broader the absorption bands, but in the more dilute solutions the intensity of the bands was greater, and there is a shifting of the middle of the bands toward the region of greater wave-length on dilution. In the case of salts of neodymium, three bands are observed with their centres at λ 7300, λ 7950, and λ 8700, and two other bands at λ 7150 and λ 9000, which are probably due to the solvent. The reason for increase in the intensity of the bands on dilution is explained on a theory of resonance. It is noticed in many cases that the aqueous solutions of hydrated salts are often more transparent than pure water. This point is carefully studied, and it is shown that the absorption of light by solutions of non-hydrated salts is the same as that of the water contained in the solution, providing that the salt itself has no specific absorption, but in the case of highly hydrated salts the

absorption of the solution is less than that of the pure water. It is thus shown that free water and combined water have different absorptive effects on infra-red rays. The maximum transmission of neodymium salt solutions lies at λ 7600 and λ 8400. Solutions of praseodymium salts are transparent in the infra-red as far as 1·5μ; there are two groups of bands, one in the green near λ 4600, and another near λ 5900. Solutions of nickel chloride show an increasing absorption from λ 5200 to λ 6300, where it becomes complete; from here there is complete absorption to λ 7200, and then the transmission steadily increases to λ 9000 and then decreases to zero at λ 10,000. The absorption of nickel nitrate solutions resembles that of the chloride, but in the case of the sulphate there is no region of complete absorption. The maxima of transmission lie at λ 5400 and λ 9000, and the minima at λ 6900 and λ 11,000. Salts of cobalt have strong ultra-violet absorption, and there is a band in the orange near λ 5000 with increasing transmission toward the red. The infra-red absorption curves of cobalt chloride, nitrate, bromide, sulphate, and acetate have maxima of transmission at λ 5950, λ 7800, λ 9100, and λ 10,600. The transmission curves of all the salts of cobalt studied rise rapidly from λ 5000 to λ 5900; they show a broad, slight absorption over the region near λ 6500, and reach a maximum transmission from λ 7000 to λ 8000. There is a series of small absorption regions near λ 8400, λ 8900, and λ 9800. Beyond λ 10,900 the absorption increases rapidly to the region where water is practically opaque. Beer's law is shown to hold for the infra-red absorption of solutions of neodymium chloride and praseodymium chloride. J. F. S.

Spectro-chemistry of the Cobalt Complexes. YUGI SHIBATA and GEORGES URBAIN (*Compt. rend.*, 1913, **157**, 593—595).—A study of the absorption spectra of solutions (*N*/100 and *N*/1000) of twenty-four complex cobalt salts in the visible and ultra-violet portions of the spectrum, the results pointing towards certain relations between the constitutions of the complex salts and their absorption. Curves obtained by plotting the thickness of the solutions against the frequency limits of absorption show two decided minima in the neighbourhoods of λ 2000 and 3000. These two bands seem to be characteristic of the tervalent cobalt atom, functioning as chromophore. In general, with the exception of the group NO_2, the negative radicles provoke a displacement of the less refrangible band towards the red. The effect of the relative changes in intensity of the two bands is almost always more marked than the displacement effect in the frequency scale. W. G.

Ultra-violet Absorption of Pure Acetone above λ 332 $\mu\mu$. HANS T. CLARKE and ALFRED W. STEWART (*Physikal. Zeitsch.*, 1913, **14**, 1049—1050. Compare Gelbke, A., 1912, ii, 713).—The absorption of ultra-violet light by pure acetone has been investigated by experiments with layers of thickness ranging from 50 to 400 mm. The curve which is obtained when the wave-length of the limiting transmitted light is plotted against the thickness of the absorbing

layer exhibits no minimum above λ 332$\mu\mu$, although there is a change in the slope of the curve at λ 336·5$\mu\mu$.

In a note added by JOHANNES STARK it is claimed that this affords clear evidence of the long-waved ultra-violet band, the existence of which he has previously anticipated. H. M. D.

Fluorescence of the Elements of the Sixth Group of the Periodic System. F. DIESTELMEIER (*Physikal. Zeitsch.*, 1913, **14**, 1000).—A claim of priority against Steubing (this vol., ii, 816), in reference to the fluorescence spectrum of sulphur and selenium. H. M. D.

Some Decompositions in Ultra-violet Light. ANTON KAILAN (*Monatsh.*, 1913, **34**, 1209—1244).—The action of a quartz-mercury lamp at a distance of 8 cm. on *N*/2- to 2*N*-solutions of acetic, oxalic, malonic, succinic, malic, and tartaric acids in quartz vessels produced in all cases decomposition, as shown by diminution of the titre with alkali. Acetic acid was decomposed to the greatest extent, and oxalic acid to the least. The presence of the hydroxyl group in the molecule increased the rate of decomposition. The decomposition in *N*-acetic acid solution amounted to 3·5% after three hours' exposure. No effect was observed in transparent glass vessels. The reaction velocity increases with the time of exposure and with the concentration, although less rapidly than in proportion to the latter, the departure from proportionality being smaller than is the case in the decomposition of iodides and the oxidation of aldehyde. Dissolved oxygen produces little, if any, effect.

No effect was produced on the rotation of fermentation amyl alcohol. In neutral *N*/10-solution, potassium and sodium iodides are less decomposed than the iodides of barium and strontium, but in *N*/160-hydrochloric acid, these iodides and that of magnesium are decomposed to the same extent. The acid increases the rate of decomposition up to *N*/800, but after that only produces a slight effect. Dissolved oxygen is responsible for the liberation of the iodine. In a vacuum, the decomposition may be reduced to less than one-half. The presence of thiosulphate and rise of temperature are without effect, and the liberation of iodine through the formation of hydrogen peroxide plays no important part. Potassium fluoride is not decomposed under these conditions. F. S.

The Physical Chemistry of Photographic Development. C. E. KENNETH MEES (*J. Amer. Chem. Soc.*, 1913, **35**, 1727—1732).—A paper read at the Rochester meeting of the American Chemical Society, 1913. It consists of a review of the physical chemistry of photographic development. T. S. P.

Physico-chemical Studies on Photographic Developers. III. NIKOLAI SCHILOV and EUG. TIMTSCHENKO (*Zeitsch. Elektrochem.*, 1913, **19**, 816—819. Compare A., 1912, i, 966; this vol., ii, 371; also Pinnow, this vol., ii, 398).—In the previous papers it is shown that sodium sulphite plays a definite rôle in the oxidation of quinol,

in that it first functions as an acceptor for the peroxide oxygen, and later forms complex additive compounds with the quinol, which are oxidised regularly and slowly without the formation of tarry matter. In the present paper the sulphite is replaced by other reducing agents. Sodium arsenite is first investigated, and it is shown that it acts mainly as an acceptor for the oxygen and uses up about one-half of the oxygen, but probably forms no complex compounds with the quinol. Experiments were made also with hydroxylamine and with hydrazine. Both these substances regulate the oxidation of the quinol in exactly the same way as sodium sulphite, inasmuch as they form a series of complex additive compounds. It is shown that a photographic plate can be developed by quinol in the presence of hydroxylamine. J. F. S.

Oxidation and Preservation of [Sodium] Sulphite–Quinol Solutions. JOHANNES PINNOW (*Zeitsch. wiss. Photochem.*, 1913, **13**, 41—45. Compare this vol., ii, 398).—It is shown that the sodium salt of quinolmonosulphonic acid is the chief product of the first oxidation of sodium sulphite–quinol solutions. This salt has been isolated, and is described as crystallising in small, thin leaflets from methyl alcohol solution. It is also shown that by the addition of 0·05 mol. acetic acid per litre the ordinary quinol–sulphite developer can be preserved for four times the ordinary length of time. In using the acidified developer it is necessary to add twice as much soda solution as is required to neutralise the acid which has been added. J. F. S.

Luminescence. EARL F. FARNAU (*J. Physical Chem.*, 1913, **17**, 637—656).—The luminescence produced by a number of substances under a series of conditions have been determined by the author. The experiments include observations on the cathodo-luminescence, canal ray luminescence, ultra-violet luminescence, luminescence by heating, luminescence by trituration, chemi-luminescence, and crystallo-luminescence of a series of the haloids of sodium, potassium, cadmium, zinc, mercury, lithium, rubidium, and cæsium, together with, in a few cases, the carbonates and sulphates. The author draws the conclusion that luminescence of all kinds is due to a chemical reaction. Increase in the rate of the reaction, brought about either by a catalytic agent or by increase in the temperature, increases the luminescence. The nature of the luminescence is but slightly altered by the nature of the catalyst or the temperature change. The nature of the luminescence in most cases depends only on the metal of the salts, but in a few cases the acid radicle has an influence. The nature of the luminescence is the same no matter how it is produced. J. F. S.

Absorption Measurement of β-Rays. HERMANN STARKE (*Physikal. Zeitsch.*, 1913, **14**, 1037—1038).—Position of the absorption screen with reference to the radioactive preparation and the measuring instrument affects measurements of β-rays, and it is recommended that the screen be placed directly against the ionisation chamber. F. S.

The Excitation of γ-Rays by β-Rays. HERMANN STARKE (*Physikal. Zeitsch.*, 1913, **14**, 1033—1038).—The secondary γ-rays excited by the β-rays of mesothorium were put in evidence by concentrating the β-radiation on to a reflecting plate by means of a powerful magnet. The mesothorium was placed near one pole, and the reflector near the other pole, a sensitive ionisation chamber being placed so that it was screened from direct radiation by a lead block, but not from the reflected radiation. Excitation of the magnet showed a distinct but small effect, which was estimated to be about one-thousandth part of that due to the primary γ-rays. Only those γ-rays capable of penetrating 3 mm. of aluminium could be looked for by this method. F. S.

Determination of Radium by the γ-Ray Method. VIKTOR F. HESS (*Ber. Deut. physikal. Ges.*, 1913, **15**, 1002—1016; *Physikal. Zeitsch.*, 1913, **14**, 1135—1141).—A modified form of Wulf's γ-ray electrometer is described. Observations made with this instrument and a standard radium preparation placed at a fixed distance from the electrometer chamber show that the ionisation current increases as the source of the rays is gradually moved from the middle of the room into close proximity with one of the surrounding walls. When this distance was reduced to 2 cm., the ionisation was found to increase to the extent of 17%. The increase is due to the secondary γ-rays which are emitted by the adjacent wall. The fact that the same increase in ionisation is observed when the radium preparation is enclosed in a lead capsule, indicates that these secondary γ-rays are produced by the primary γ-rays emitted by the active substance. The importance of this effect in connexion with the standardisation of γ-ray electrometers is referred to.

A new compensation method for the rapid evaluation of radium preparations according to γ-ray method is also described. The arrangement resembled that previously described by Bronson, with the exception that the ionised air resistance is replaced by a liquid resistance prepared by mixing xylene and ethyl alcohol in the ratio of 10 volumes to 1, as recommended by Campbell (*Phil. Mag.*, 1912, [vi], **23**, 668). H. M. D.

The Influence of Penetrating Radium-rays upon the Iodides of Alkaline Earth Elements. ANTON KAILAN (*Monatsh.*, 1913, **34**, 1245—1268. Compare A., 1912, ii, 522).—The decomposition of the iodides of magnesium, calcium, strontium, and barium in neutral and in feebly and strongly acid aqueous solutions by the penetrating rays of radium is analogous to that of the alkali-metal iodides. Both in neutral and acid solutions, in absolute alcohol magnesium iodide is decomposed more quickly than in water. No connexion was found between the molecular weight and speed of decomposition. The penetrating rays from preparations containing from 80 to 200 mg. of radium (element) produce only from 1/200 to 1/800th of the effect of a quartz mercury lamp at 8 cm. distance, but in spite of the different orders of magnitude, the general reactions appear to be the same in the two cases. F. S.

The Chemical Action of Penetrating Radium Rays. ANTON KAILAN (*Monatsh.*, 1913, **34**, 1269—1289).—No effect within the error of measurement was produced during 2850 hours by the penetrating rays from 106 mg. radium chloride on the rotation of 200 c.c. of a normal aqueous solution of dextrose at 5° to 10°. Small changes were traced to the influence of the acids formed, which occurs to a greater extent with dextrose than with sucrose. Absolute alcohol is oxidised to aldehyde and acid, and there results in addition a formation of water, for the most part not produced by oxidation, but by decomposition of the alcohol. On succinic and malonic acid solutions the penetrating radium rays produce only an exceedingly slight decomposition, of the same order, compared with that produced by ultra-violet light, as in the decomposition of iodides. No changes could be established in the electric conductivity and dissociation constants of these acids.

The penetrating rays from 42 mg. of radium chloride, acting for 4000 hours on 5 grams of silver nitrate in $N/4$-solution in the dark, reduced about one-thousandth part to metallic silver.

F. S.

Comparison of the Results of the Electromagnetic and the Spectral Analysis of Canal Rays. JOHANNES STARK (*Physikal. Zeitsch.*, 1913, **14**, 961—965).—A comparison is made of the results which have been obtained by the electromagnetic and spectral methods in their application to the analysis of canal rays. Both methods agree in that they show the existence of hydrogen, helium, carbon, nitrogen, oxygen, chlorine, argon, iodine, and mercury ions carrying a single positive charge; of helium, carbon, nitrogen, oxygen, chlorine, argon, and mercury ions with a double charge; of argon, nitrogen, and mercury ions with three charges; and mercury ions with four charges. On the other hand, the existence of sulphur and iodine ions with two charges, and of oxygen, sulphur, and chlorine ions with three charges, is only revealed by the spectral method of analysis, whilst mercury ions carrying five, six, and seven charges are only shown by the electromagnetic method.

It is pointed out that the experimental conditions obtaining in the spectral method of analysis are, generally speaking, more favourable as regards the formation of ions with multiple charges than the conditions which obtain in the electromagnetic method.

H. M. D.

The Multiple Positive Charge of Chemical Atoms. JOHANNES STARK (*Physikal. Zeitsch.*, 1913, **14**, 965—969. Compare preceding abstract).—A theoretical paper, in which the author discusses the mechanism by which positive ions carrying a multiple charge are produced. It is considered that such ions may either be produced directly as the result of a single collision, or indirectly as the result of a series of collisions in each of which an electron is displaced. Since the energy required for the simultaneous expulsion of several electrons from an atom is much greater than that required for the removal of a single electron, it is probable

that high speed rays are favourable to the formation of multiply charged ions according to the former process. Since the ratio of the number of singly charged ions to neutral atoms is very small, it is further probable that the production of multiply charged ions as the result of a single collision with high speed cathode or canal rays is more frequent than the production by the alternative method.

Since the number of positive charges which an atom can take up is in general greater than the number of valency electrons, it must be assumed that electrons which are more intimately associated with the positive nucleus than the valency electrons, can be expelled under favourable conditions, such as are obtained when a gas is subjected to the influence of canal rays. The energy required for the expulsion of the interior electrons is probably much greater than that which suffices for the liberation of the valency electrons.

H. M. D.

[Canal Ray Spectrum of Hydrogen.] ERNST GEHRCKE and OTTO REICHENHEIM (*Ber. Deut. physikal. Ges.*, 1913, **15**, 1063—1064).—The authors criticise the interpretation of the Doppler effect in the canal rays spectrum of hydrogen given by Stark (this vol., ii, 907), and suggest that the outermost maximum on the displacement curve is due to hydrogen atoms carrying two positive charges. This would fit in with the view that the innermost maximum is due to hydrogen molecules carrying a single charge, and the middle maximum to hydrogen atoms with a single charge. H. M. D.

[Lines in the Canal Ray Spectrum of Argon Corresponding with Ions Carrying One, Two, and Three Charges.] JOHANNES STARK and H. KIRSCHBAUM (*Sitzungsber. K. Akad. München*, 1913, 331—353).—From observations of the Doppler effect in the canal ray spectrum of argon, it is shown that the lines in the red spectrum are due to positively charged atoms carrying a single unit of charge. The lines in the blue spectrum are mainly due to doubly charged atoms, but to a certain extent the blue emission is due to atoms carrying three charges. Low speed cathode rays give rise in general to the carriers of the red spectrum, whilst the production of multiply charged carriers is brought about by high speed rays. The transition from the one type of carrier to the others represents a reversible process, and a condition of equilibrium is set up when the conditions of the discharge are kept constant. H. M. D.

The Energy of the Electron Emission of Strongly Heated Substances. ARTHUR WEHNELT and ERIK LIEBREICH (*Ber. Deut. physikal. Ges.*, 1913, **15**, 1057—1062).—Measurements have been made of the saturation currents which are obtained as a result of the emission of electrons by strongly heated platinum wires covered with a layer of calcium oxide, the observations extending over an interval of twenty-four hours. The saturation current is by no means constant, but rises to a maximum, and this is followed by a gradual fall to a much smaller value. The time required for the

attainment of the maximum current diminishes as the temperature is increased. The final value to which the current falls corresponds with the electron emissive power of pure platinum, indicating that the oxide film gradually disappears. These observations afford an explanation of the fact, established by previous experiments, that the emission of electrons by a platinum electrode coated with a film of oxide is not in agreement with Richardson's formula.

H. M. D.

Cause of the Emission of Electrons by Oxide Cathodes. A. GEHRTS (*Ber. Deut. physikal. Ges.*, 1913, **15**, 1047—1056).—The fact that strongly heated electrodes covered with a thin layer of an alkaline earth metal oxide emit large quantities of electrons has been known for some time, and Fredenhagen (*Physikal. Zeitsch.*, 1912, **13**, 539) has suggested that the oxides are decomposed by the current, and that the emission of electrons is a consequence of the chemical recombination of the oxygen with the alkaline earth metal. In the author's opinion the separation of the oxygen is mainly due to thermal dissociation of the oxide, although there may be a certain amount of oxygen liberated as a result of electrolysis. In other respects the author's theory agrees with that put forward by Fredenhagen.

In the absence of a potential difference the dissociated oxygen recombines quantitatively with the alkaline earth metal, but in an electric field some of the oxygen atoms are converted into ions by combination with electrons, and are thus transported to the anode. The fact that the life of an oxide cathode diminishes as the intensity of the discharge increases is quite in accordance with this hypothesis.

Further evidence in support of it has been obtained in a series of experiments with electrodes of platinum, iridium, tantalum, carbon, and tungsten, each covered with a layer of calcium oxide. After employment as cathodes for some time, the layer of oxide was removed, and the surface of the electrode examined with the aid of a binocular microscope. In the case of platinum and iridium, evidence was obtained of the formation of calcium alloys, whilst tantalum is oxidised to the dioxide and carbon gives rise to carbon monoxide. Tungsten proved to be unsuitable for the experiments, for the oxide film becomes detached as soon as the current is passed between the electrodes. These chemical changes are regarded as distinctly favourable to the author's view of the activity of the oxide-covered electrodes. H. M. D.

Origin of Thermal Ionisation from Carbon. JOHN N. PRING (*Proc. Roy. Soc.*, 1913, *A*, **89**, 344—360. Compare A., 1912, ii, 115).—Further experiments have been made to ascertain whether electronic emission can be attributed to incandescent carbon, the conditions being modified so as to eliminate more completely the large ionisation effects which were found in the earlier work to be due to chemical action. For this purpose, the purification of the carbon and the exhaustion of the surrounding vessel were carried out more perfectly, and the effect of this on the ionisation

was examined at a series of definite temperatures. Experiments were also made, in which small quantities of highly purified helium, argon, nitrogen, hydrogen, carbon monoxide, and carbon dioxide were admitted into the apparatus at known pressures.

The conclusions drawn from the previous observations (*loc. cit.*) are confirmed by the results obtained in the present work. It is found that the more complete removal of absorbed gases from the carbon leads to a further large reduction in the ionisation. From the observations made after the admission of the different gases, it appears that the ionisation increases with the chemical activity in the order: helium and argon, nitrogen, hydrogen, carbon monoxide, and carbon dioxide. It was found possible to trace the absorption and evolution of gas by the carbon by means of the ionisation currents.

The experiments show that the thermal ionisation of carbon is due to chemical reaction between the carbon and the surrounding gas. If electronic emission occurs at all, the effect must be very small in comparison with that which can be attributed to chemical action. H. M. D.

Photo-electric Emission of Electrons. ROBERT POHL and P. PRINGSHEIM (*Physikal. Zeitsch.*, 1913, **14**, 1112—1114. Compare A., 1912, ii, 317, 618).—From the data for lithium, sodium, potassium, and rubidium, it appears that the wave-length corresponding with the maximum of the selective photo-electric effect is approximately inversely proportional to the radius of the atom. The resonance frequency is, however, not entirely determined by the properties of the atom, for it has been found that the superficial oxidation of a layer of colloidal potassium is accompanied by a shift of the resonance maximum to the extent of $20\mu\mu$. On reduction by hydrogen, the original resonance maximum is observed. Other electronegative gases exert a similar effect in shifting the position of the resonance maximum.

The normal photo-electric effect is also influenced by factors, the nature of which is as yet unknown. From observations on the photo-electric emissive power of a calcium amalgam, it has been found that the emission of electrons commences at about $\lambda\, 365\mu\mu$ in the case of a freshly prepared liquid surface. At the end of an hour, the limiting wave-length has shifted its position about an octave, and is situated in the ultra-red region. H. M. D.

The Photo-electric Effect of Metallic Compounds. B. A. DIMA (*Compt. rend.*, 1913, **157**, 590—593. Compare this vol., ii, 465).—The author has confirmed his previous results that the photo-electrical effect of similar compounds of the same metal diminishes with increase in valency of the metal, by studying the oxides of molybdenum and manganese. It is necessary to use the anhydrous oxides, as their hydrates produce a much feebler emission. From a study of numerous series of oxides he draws the conclusion that the phenomenon of photo-electrical fatigue is only exhibited very slightly by the highest oxides, but to a greater extent by the lower

oxides. In the case of molybdenum trioxide, an increase of 25% was noticed in the emission by prolonging the exposure to ultra-violet light for two hours. At the same time reduction appeared to have taken place at the surfaces exposed to the light. Bromides give a photo-electrical effect intermediate between those of the corresponding chlorides and iodides, and, except in the case of cadmium salts, the effect is increased with increase in the atomic weight of the halogen. W. G.

Connexion Between Ionisation by Collision and Electron Affinity. J. FRANCK and G. HERTZ (*Ber. Deut. physikal. Ges.*, 1913, **15**, 929—934; *Physikal. Zeitsch.*, 1913, **14**, 1115—1117).—In order to account for the phenomena of electric discharge through the inert gases, it is necessary to assume that the collisions between the molecules and the electrons are elastic in character. For other gases the elastic nature of the collisions will decrease as the electro-negative character of the gas increases. Observations on the reflexion of electrons by gas molecules indicate that all electrons with speeds smaller than that corresponding with the ionisation potential undergo reflexion in the case of helium. Similar experiments with hydrogen show that only a certain proportion of the electrons are reflected, and in the case of oxygen the reflected electrons are very small in number. These facts indicate that the phenomenon of ionisation by collision is intimately connected with the affinity of the gas molecules for electrons.

In view of the elastic nature of the collisions in the case of the inert gases, the authors draw the conclusion that the influence of an electric field on the electrons present in such a gas is not determined by the length of the free path, but that the accelerating influence of the field is cumulative in its action when the electrons are subjected to a succession of collisions. Ionisation by collision will take place as soon as the potential difference at the electrodes exceeds the ionisation potential. The current potential curves for helium and neon have been examined, and the fact that the curves show a series of breaks at intervals equal to the ionisation potential is quite in accord with the authors' views on the nature of ionisation by collision in the case of these inert gases. H. M. D.

Radium and Radium-emanation in the Water and Deposits of Lake Balaton, Hungary. D. V. LENKEI (*Zeitsch. Kryst. Min.*, 1913, **53**, 65; from *Magyar.-balneolog. Értesitö*, 1910, **3**, Nos. 5 and 6).—As determined with the electrometer, the water contains 0·0064—0·0224 millionth of a cubic millimetre of emanation per litre; and the mud and sand 0·13—0·85 millionth mg. of radium per kilogram. L. J. S.

Quantitative Estimation of Radium by the Emanation Method. ERICH EBLER (*Zeitsch. angew. Chem.*, 1913, **26**, 658—661). —An apparatus is described for estimating the amount of radium in solutions by the emanation method, consisting essentially of the flask to hold the solution, with capillary leading-in tube and tap,

ground to a small condenser provided at the upper end with a tap, which in turn is ground to one end of a bulb closed by two taps. The solution is boiled in a partial vacuum, and, when the emanation is driven out, saturated salt solution is admitted through the leading-in tube to drive all the emanation into the bulb, which is then detached, and the emanation admitted to the ionisation chamber of an electroscope. The measurement follows the usual method. F. S.

Determination of Valency of Radium by means of Electric Endosmose. HERBERT FREUNDLICH and G. VON ELISSAFOFF (*Physikal. Zeitsch.*, 1913, **14**, 1052—1057. Compare A., 1912, ii, 419).—The electric endosmose method allows the valency of a metal to be determined in excessively small quantity. With a concentration of 50 micromols., the difference between uni-, bi-, and ter-valent ions can be determined with from 0·01 to 0·001 mg. Curves, in which the volume of liquid transported is plotted against concentration, show that radium clearly is bivalent, and accords with magnesium and barium, when the behaviour of these ions is compared with that of sodium on the one hand, and chromium, aluminium, and zirconium on the other. No disturbing effects were observed due to the action of the rays on the electric double layer, the behaviour of radium being quite analogous to that of barium. An attempt was made similarly to find the valency of actinium-*X*, but, although the measurements indicated that it was bivalent, later observation showed that an impurity must have been present. F. S.

Attempts to Separate Radium-*D* from Lead. FRITZ PANETH and GEORG VON HEVESY (*Monatsh.*, 1913, **34**, 1393—1400).—Even although no practical separation of lead from radium-*D* were possible, a slight enrichment of the radioactive constituent would be of great theoretical importance. Numerous attempts have been made in this direction with results completely negative. Earlier observations which apparently gave positive results may be ascribed to the separation of the later products, radium-*E* and -*F*. Among the methods unsuccessfully tried were (1) by precipitation of lead chloride solution at 100° with dilute sodium thiosulphate and with hydrofluoric acid; (2) with quadrivalent lead compounds, by precipitation of a lead chloride solution, saturated with chlorine, with ammonium chloride, whereby ammonium plumbichloride is precipitated; by passing carbon dioxide through a solution saturated with lead chloride and hydrogen chloride (H_2PbCl_6), whereby the lead chloride is fractionally precipitated; and by precipitation of lead dioxide by addition of hydrogen dioxide or bromine water to a solution of lead hydroxide in sodium hydroxide, or of bromine water to lead acetate; (3) by adsorption methods, as by precipitation of barium sulphate or silicofluoride in lead nitrate solution, or barium chloride in a lead chloride solution by saturating with hydrogen chloride; also by separating iron from lead chloride solution by the acetate precipitation, by adding potassium per-

manganate and alcohol to lead chloride solution, and by boiling the latter with flowers of sulphur; (4) by distillation of lead chloride in carbon dioxide at 1000°; (5) by electrolysis in solution, under varying conditions, so that part of the lead separates on the cathode and part on the anode as dioxide, and of molten lead chloride, pure or mixed with potassium chloride; (6) by dialysis of lead nitrate through parchment paper or animal membrane and diffusion of lead chloride solution. The causes of error (presence of radium in the radio-lead, variation in the β-rays of radium-*E* used in the measurements, due to absorption in the material and secondary radiation) are briefly pointed out. F. S.

The Electrochemical Identity (Vertretbarkeit) of Radio-elements. FRITZ PANETH and GEORG VON HEVESY (*Monatsh.*, 1913, **34**, 1593—1603).—The question was examined whether the chemical identity of groups of radio-elements with other elements and among themselves would extend to the electro-chemical behaviour and explain the open questions, such as the frequent activisation of the anode and sharp separation of the *B*-products by an extraordinarily "noble" potential. The electro-chemical behaviour of radium-*E* and thorium-*C* with respect to bismuth, of thorium-*B* with respect to lead and of radium-*A*, -*B*, and -*C* with reference to bismuth, lead, and polonium respectively, supports this extension. The amount of thorium-*C* deposited on a platinum plate, kept $+0\cdot6V$ with reference to a *N*-calomel electrode, in $N/100$-nitric acid solution, is greatly reduced by the presence of a few mg. of bismuth. Decomposition voltages for the radio-elements cannot be determined as a function of the current flowing, for the quantity of the radio-ion is insufficient to carry the whole of the current. They were determined by plotting the amount of radio-element deposited during one hour as function of the cathode potential, and in this method a sudden increase in the amount deposited, instead of a sudden increase of current strength, indicates the decomposition voltage. By this means the progress of deposition at potentials higher than the decomposition voltage may be determined. For thorium-*C*, in presence of bismuth, the sudden increase occurs at $-0\cdot08V$, an immersed bismuth plate showing the potential $-0\cdot082V$. For thorium-*B*, in presence of lead, deposition occurs with perceptible amounts of lead at $-0\cdot44V$, but in absence of lead already at $-0\cdot33V$. The anodic deposition of thorium-*B* in absence of lead showed a sudden deposition between $1\cdot0$ and $1\cdot1V$, which is very near to that of lead dioxide. The thorium-*B* is deposited no longer as metal, but as dioxide.

For the radio-elements, electrode potential is of the first importance, the passage of the current, and hence the difference between anode and cathode, is quite a secondary consideration. With three platinum electrodes in a solution of thorium-*B* + -*C*, an anode, a cathode, and a third currentless electrode, and a feeble current strength arranged to give an anode potential the same as that between the third electrode and the solution, there is no difference in the amounts of radioactive matter deposited on the

anode and the third electrode. By gradually increasing the current strength, the potential of the cathode to the solution may be changed from positive to negative, with reference to the calomel electrode, and so a continuous series of potential differences may be obtained. In the anodic metallic deposition of the radio-elements, the anode behaves as a strongly positively polarised cathode, and this explains the anodic deposition of polonium. When the separation of a radio-element from another in a high state of purity is desired, the addition of an appreciable quantity of an element "identical" with the other element is recommended, for example, in separation of pure thorium-*C* from thorium-*B*+-*C*, lead should be added, the action being analogous to the prevention of adsorption of uranium-*X*, for example, by presence of thorium.

F. S.

Behaviour of Radio-elements in Precipitation Reactions. KASIMIR FAJANS and PAUL BEER (*Ber.*, 1913, **46**, 3486—3497).—A detailed discussion is given of the evidence that a radio-element in infinitesimal amount is precipitated with a filterable quantity of the precipitate of a common element whenever under the conditions the radio-element itself would be precipitated were it present in precipitable amount. The determination of the chemical nature of a radio-element, not identical in properties with any of the common elements, depends on this behaviour, which, although generally considered obvious, is shown to be difficult to account for. Abnormal adsorption phenomena appear to influence the precipitation less than might be expected.

Although radium-*A* is precipitated with mercury as sulphide and chromate, it is distinguished from mercury by being precipitated with bismuth in strongly acid solution as phosphate. Radium-*A* is distinguished from tellurium by the fact that when precipitated with copper and tellurium sulphide, it is not dissolved from the precipitate by ammonium sulphide, but remains undissolved with the copper sulphide. This difference is analogous to that between antimony and bismuth. Were it possible to obtain radium-*A* (or polonium, with which it is identical) in weighable amounts, it would, unlike tellurium, give a sparingly soluble chromate and phosphate.

The precipitation of radio-elements with other precipitates shows that the solubility product need not be attained before precipitation takes place. The influence of adsorption and the possibility that the radio-elements are present as colloidal solutions (Paneth) require further investigation.

F. S.

Measurement of Radioactive Substances in the Guard-ring Plate Condensor. L. FLAMM (*Physikal. Zeitsch.*, 1913, **14**, 1122—1125).—The mathematical expressions connecting the ionisation with the distance apart of the two plates of a guard-ring plate condensor are developed with special reference to the case where the space is uniformly filled with emanation, with a view to the ultimate construction of a standard form of measuring

apparatus, which will enable absolute measurements of quantities of emanation to be undertaken without the uncertainty attaching to the employment of standard solutions of radium. Tables are supplied for some of the quantities entering into the mathematical expressions. Experiments, with one plate uniformly covered with a layer of polonium, on the variation of the ionisation current with distance between the plates, are shown to agree with the calculated ionisation currents when corrected for a certain small loss of ionisation due to the absorption of the α-rays in the layer of polonium itself. Possibly there is a small effect due to condensed films of moisture. F. S.

The Extraction of Polonium. FRITZ PANETH and GEORG VON HEVESY (*Monatsh.*, 1913, **34**, 1605—1608).—Radio-lead from pitchblende serves as a raw material for the extraction of polonium. The hot saturated solution of the lead nitrate is left to crystallise, the mother liquor is separated by centrifuging, and after being slightly diluted is electrolysed with platinum electrodes and a feeble current, a few mg. of bismuth being added to diminish the separation of radium-*E*. The cathode potential must not exceed $-0{\cdot}8V$, which corresponds, in the solution described, with 0·16 milliampere per cm.^{2}, but if freedom from radium-*E* is desired, a potential of $-0{\cdot}5V$ or 0·4 ma. per cm.^{2} may be used. Stirring is advantageous both in electrolysis and also in deposition on copper, which is an equally good method. If polonium free from lead and radium-*D*, but not from radium-*E*, is required, so much concentrated nitric acid is added that lead is no longer cathodically deposited. Under these conditions most of the polonium can still be separated at the cathode. By volatilisation at 1000°, all but 0·1% of the polonium may be removed from the electrodes, which is difficult to do by boiling with acids. The polonium vapour condenses preferably on palladium and platinum, in special degree on the former, rather than on gold, copper, nickel, or the walls of a quartz tube. F. S.

The Solutions of Radioactive Products. TADEUSZ GODLEWSKI (*Le Radium*, 1913, **10**, 250—264).—A platinum plate, coated with the active deposit of actinium (by immersion, negatively charged, in the emanation) was made the anode in purified water, a similar platinum plate being the cathode. A notable proportion of the active deposit was found to have been transported to the cathode. Detailed examination showed that this occurs only when the active plate serving as anode had previously played the part of cathode during electrolysis. When well saturated with hydrogen in this way, and when considerable voltages were employed, two-thirds of the active deposit could be transported to the cathode in purified water.

When purified water, saturated and left some hours with radium emanation, is electrolysed for ninety seconds between platinum electrodes with 220 volts, radium-*A* is deposited on the anode with about one-third of the equilibrium amount of radium-*C*, whilst

on the cathode radium-*B*, with about one-third to one-quarter of the equilibrium amount of radium-*C*, is found. The ratio of radium-*C* on the cathode to that on the anode is usually between one and two. When electrolysis immediately follows saturation with emanation, so that only radium-*A* is present, the latter is still deposited on the anode. In all these experiments in purified water only a fraction of the products present in the liquid is deposited, even after electrolysis has proceeded many hours. The voltage affects the amount deposited, but not the ratio of the anode and cathode activity.

The theory is advanced and supported by numerous experiments that the radioactive matter is present in the colloidal state, and that hydrosols, not ions, are being dealt with, the transport of the products being due to electrophoresis, rather than electrolysis. It was shown that the addition of positive ions, such as hydrion, cause a strong diminution of the anode activity and an enhancement of the cathode activity, whereas negative ions, such as hydroxyl, act oppositely, increasing the anode activity and decreasing the cathode activity. Multivalent ions, such as aluminium and citric acid ion, act much more powerfully than the univalent ions. The ratio of cathode to anode activity can so be varied in the proportion of 40,000 to 1 in the direction predicted from the theory of colloids, and in a manner impossible to account for if the radioactive products existed as ions. Radium-*A* exists as a negative, radium-*B* as a positive hydrosol, whilst radium-*C* exists as both. The effect of a positive ion is to stabilise the positive hydrosol and to neutralise and ultimately reverse the sign of the negative hydrosol. For negative ions the reverse is the case. The results obtained show that the solutions of radioactive products are of the nature of colloidal solutions. F. S.

Radioactivity of Tyrol Mineral Spring. V. MAX BAMBERGER and KARL KRÜSE (*Monatsh.*, 1913, **34**, 1449—1467. Compare this vol., ii, 278).—Further results are given for numerous Tyrolese springs embodied in tables as before. The amount of emanation in the water is given in Mache units, the greatest being for the springs of Villnösstal, where the rock is described as graphite quartzite, and the number of Mache units is from 66 to 90. F. S.

Dielectric Constants of Vapours. G. POHRT (*Ann. Physik*, 1913, [iv], **42**, 569—584).—A Wheatstone bridge method for the measurement of the dielectric constants of gases and vapours is described, in which the null point is determined in two experiments in which two different values are given to the pressure of the gas or vapour in one of the condensors. It is estimated that the mean error of the measurements is only 0·2 to 0·3% of the magnitude $(\epsilon-1)$, where ϵ is the dielectric constant.

The results obtained for a large number of organic substances are recorded, and, where possible, compared with those given by previous observers. H. M. D.

The Effect of Light on the Electrical Charge of Suspended Particles. STEWART W. YOUNG and L. W. PINGREE (*J. Physical Chem.*, 1913, **17**, 657—674).—The rate of migration of a number of suspensions, under the influence of a potential fall, has been observed by the authors. The suspensions examined have been those of substances charged either negatively or positively, and include arsenic sulphide sols, ferric hydroxide sols, gum mastic, resin, chlorophyll, and bacterial preparations of *Sarcina flava*, *S. rosea*, and *Bacillus prodigiosus*. In all cases the rate of migration is influenced by light; in the case of arsenic sulphide, ferric hydroxide, and the bacteria, the velocity of migration is reduced by illumination, whilst in the other cases mentioned it is increased. The amount of change in some cases reaches 100%. The authors offer two hypotheses to explain the action in the case of the inanimate suspensions: (1) The influence of light is to affect the degree of dispersity of the suspended matter, increasing it in the case of an acceleration, decreasing it in the case of a retardation; (2) the influence of light is to increase the static charge on the particles in the case of acceleration, and to reduce it in the case of retardation. The latter hypothesis alone applies to the bacterial suspensions. J. F. S.

Influence of the Gas and the Electrode Material on Short Spark Discharges Between Metals. E. TAEGE (*Physikal. Zeitsch.*, 1913, **14**, 1041—1042).—The observations described were made with a coupled discharged circuit, in which a spark gap was placed in parallel with a suitable capacity. The distribution of the energy of discharge between the spark gap and capacity circuits was measured, the fraction of the total energy passing through the capacity circuit being regarded as a measure of the "extinction effect" of the spark gap.

From experiments with the spark gap in an atmosphere of air, oxygen, nitrogen, methane, coal-gas, hydrogen, ammonia, and chlorine, it appears that the extinction effect of the spark discharge increases with the thermal conductivity of the gas and with the mobility of the gaseous ions. In presence of the vapours of benzene, carbon tetrachloride, ethyl alcohol, and water, the extinction effect shows a marked increase.

For different electrode materials, the extinction effect increases in the order: magnesium (aluminium, nickel, zinc) (silver, platinum, copper, brass). The metals enclosed in brackets have approximately the same influence on the extinction effect. It seems probable that the differences in question are determined by differences in the electron emissive powers of the metals.

No evidence has been obtained in support of the view that the extinction effect is dependent on chemical action between the metal vapour and the surrounding gas. H. M. D.

Influence of Various Metals on the Thermo-electric Properties of Iron–Carbon Alloys. EUGÈNE L. DUPUY and A. PORTEVIN (*Compt. rend.*, 1913, **157**, 776—779. Compare this vol., ii, 16).—A study of the modifications produced in the thermo-

electric properties of iron-carbon alloys by the addition of varying amounts of metals commonly employed for preparing special steels, namely, manganese, silicon, aluminium, chromium, tungsten, and molybdenum. Some sixty alloys were examined, divided into two groups, one containing 0·15% carbon, and the other 0·8% carbon, examinations being made in each case of annealed and tempered alloys. The curves obtained by plotting the thermoelectric powers against the amount of metal added show that the metals experimented with divide themselves into two groups: (1) Manganese, silicon, and aluminium give a continuous curve, indicating that these metals, within the limits studied, form solid solutions; (2) chromium, tungsten, and molybdenum give curves which indicate formation of solid solutions, the saturation points of which are given by changes in the directions of the curves, and the formation of carbides. W. G.

A New Hydrogen Electrode and its Applicability. ERNST WILKE (*Zeitsch. Elektrochem.*, 1913, **19**, 857—858).—The electrode described consists of a thin palladium capillary tube sealed at its lower end, and into which hydrogen at constant pressure is pumped. Using this electrode, the potential due to hydrogen ions is set up at once, and constant and reproducible results are obtained. It is shown that after some time the electrode ceases to work rapidly, but that it may be brought to its former sensitiveness by heating it in oxygen. It is also shown that when the electrode is in its most sensitive condition the potential values are not dependent on the nature of the surrounding gas. J. F. S.

Distribution of Solvent Between Solutes. I. Electrical Conductivity and Refractive Index of Mixtures of Aqueous Solutions of Salts of the Alkali Metals. ANTONY G. DOROSCHEVSKI and S. V. DVORSHANTSCHIK (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1174—1209).—Determinations of the electrical conductivities at 18° of mixtures of aqueous solutions of (1) chlorides, (2) nitrates, (3) carbonates, and (4) sulphates of potassium and sodium, give results which are in agreement with the assumption that solutions of these salts of equivalent concentration are isohydric. Barmwater's formula for the conductivity of mixtures of electrolytes (A., 1899, ii, 274, 396) may be deduced, as a particular case of a general formula, from the law of isohydry, and is applicable to those mixtures which are in agreement with his dilution formula. The latter is valid for the chlorides and nitrates of the alkali metals, but does not hold exactly with the sulphates or carbonates of these metals. The results obtained by the authors for sodium and potassium carbonates and sulphates within the limits of dilution, $v = 10$—100, are found to agree closely with the empirical formula, $\lambda = A - a / \sqrt[8]{v}$, where A and a have the respective values: 179·45 and 114·15 for potassium carbonate, 165·69 and 123·92 for sodium carbonate, 111·265 and 178·37 for potassium sulphate, and 98·10 and 151·90 for sodium sulphate.

In general it is not possible to establish experimentally the exact

conditions of isohydry, the corresponding dilutions being expressible only as lying between limiting values. Consideration of the possible conditions of isohydry renders it highly probable that, in solutions of salts of the alkali metals, perfectly stable systems are formed, in which each molecule of salt is surrounded by a constant quantity of water.

The refractive index of a dilute solution of a potassium salt is identical with that of a solution of equivalent concentration of the sodium salt having the same anion. T. H. P.

A Scheme for the Dissociation of Ternary Electrolytes. CARL DRUCKER, R. GIFFORD, L. GOMEZ, J. GUZMAN, and D. KASANSKY (*Zeitsch. Elektrochem.*, 1913, **19**, 797—808).—Solutions of barium chloride, barium bromide, and zinc chloride have been examined with respect to their ionisations. Measurements of the equivalent conductivity, molecular depression of the freezing point, *E.M.F.*, and transport numbers of the ions have been made. If the salts are represented by AB_2, it is shown that the solutions contain the ions $A^{\cdot\cdot}$, $AB^{\cdot}$, AB'_3, B', and undissociated AB_2, and if C_1, C_2, C_3, C_4, and C_5 respectively represent the concentrations of these substances, and C is the total concentration of the salt, the following concentrations were obtained: for $0{\cdot}1N$, $ZnCl_2$, $C_1=0{\cdot}072$, $C_2=0{\cdot}004$, $C_3=0{\cdot}018$, $C_4=0{\cdot}130$, and $C_5=0{\cdot}006$; for $0{\cdot}1n BaCl_2$, $C_1=0{\cdot}070$, $C_2=0{\cdot}015$, $C_3=0{\cdot}015$, $C_4=0{\cdot}140$, and $C_5=0{\cdot}000$. It is shown in all cases that at concentrations above $0{\cdot}02n$ the transport number of the anion increases, which points to the presence of ions of the type AB'_3; below this concentration the value of the anion transport number passes through a minimum, which points to the presence of the ions AB'. J. F. S.

Electrical Conductivity of Mixtures of Two Electrolytes. A. VOJTASCHEVSKI (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1429—1450). —The author has applied to various solutions, each containing two electrolytes, the method devised by Miolati and Pizzighelli (A., 1908, ii, 595) for determining the composition of complex compounds formed on mixing solutions of two substances.

With mixtures of magnesium and potassium chlorides, the electrical conductivities were measured at 18° for four series of solutions, the concentration of magnesium chloride being constant for each series, whilst the number (x) of gram-mols. of potassium salt per 1 gram-mol. of magnesium salt varied from 0·5 to 10. The four curves showing the relation of the specific conductivity to x are continuous, and show no break at any point. Similar continuous curves are given by mixtures of magnesium and ammonium chlorides (at 10°, 25°, and 35°), of magnesium and potassium chlorides, of magnesium chloride and hydrochloric acid, of magnesium and potassium bromides, of aluminium and potassium sulphates, of cadmium and potassium iodides, and of cobalt chloride and calcium bromide (compare Jones and Uhler, A., 1907, ii, 147, 211).

These results, which indicate the inapplicability of Miolati and

Pizzighelli's method, are not in accord with those obtained by Costăchescu and Apostoi (A., 1912, ii, 528). These authors employed in their experiments cells unsuitable for the measurement of the conductivities of concentrated solutions, and in some cases, for instance, with mixtures of magnesium and sodium sulphates, constructed curves showing breaks from points which really lie on continuous curves.

On the basis of the law of mass action, the author demonstrates that, in general, no break occurs in the magnitude of any property of a mixture of two compounds in solution. The sole exception to this rule is found in the case when the equilibrium constant of the reaction between the two compounds is so large that it may be regarded as infinitely great, and the reaction hence proceeds virtually to completion. Thus, a break in the conductivity curve would be observed when an acid is neutralised by a base, and, in all probability, when ferrous and potassium cyanides react.

T. H. P.

Electrical Conductivity and Diagrams of State of Systems formed by Benzoic Acid with Aniline or Toluidines. A. Baskov (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1604—1634. Compare Konovalov, A., 1894, ii, 5; Patten, A., 1903, ii, 57).—Investigation of the melting-point curves of the three systems formed by benzoic acid with aniline and *o*- and *p*-toluidines shows the existence in each case of a compound formed of one molecule of the acid with one of the amine. The absence from the melting-point curves of maxima corresponding with these compounds, together with the existence of definite transformation temperatures, indicate that, in the fused condition, each of the three compounds is partly dissociated into its components.

The electrical conductivities of the three systems were investigated at 75°, 100°, and 125°. With those containing aniline or *o*-toluidine, the maximal conductivity corresponds closely with the composition of the definite compound. In the case of the system, benzoic acid–*p*-toluidine, the maximum value of the conductivity is displaced to a marked extent in the direction of excess of benzoic acid; the conclusion is drawn that the compound formed from benzoic acid and *p*-toluidine tends to unite with excess of the acid to give a complex of good conducting properties. In all three systems the temperature-coefficient of conductivity is negative, the specific resistance increasing with rise of temperature; further, the maximal values of this coefficient and of the conductivity are in correspondence. The negative character of the coefficient affords an explanation of the partial dissociation of the definite compound or complex, which conducts well, into its constituents, which show diminished conductivity, such dissociation gradually extending as the temperature is raised.

T. H. P.

High Tension Electrolysis. A Method of Measuring High Voltage Currents. William W. Strong (*Amer. Chem. J.*, 1913, **50**, 213—218).—Very little quantitative work has been

recorded on the phenomena of electrolysis when high voltages are employed, this being largely due to the lack of sources of currents of high and constant potential.

Apparatus is now described which consists of a transformer, and a graduated vessel containing platinum electrodes and an electrolyte, the latter being connected in series with the transformer and corona wire. By suitable means the corona current can be made either positive or negative.

The gases are not evolved at the electrodes in the volume-ratio $2H_2 : O_2$, but it was found that in some cases all the gas moved in the same direction as the electric current. The total quantity of gas evolved was in accordance with Faraday's laws. E. G.

Electrochemical Resonance. VLADIMIR A. PLOTNIKOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1529—1535).—The results of the author's previous investigations have led him to the conclusion that electrolytic conductivity is conditioned, not by any separate property of the solvent, but by a peculiar electrochemical correspondence between the solute and solvent, such correspondence being possibly determined by the relation of the dielectric constant of the solute to that of the solvent.

It is quite probable that in liquids the molecules or groups of atoms exhibit at a given temperature vibrations with a definite periodicity, an appreciable amount of energy being possessed by only some of these vibrations characterised by the internal constitution of the molecules under the given conditions. The existence of such vibrations is supported by the results of spectroscopic investigations (compare Coblentz, *Jahrb. Radioakt. Elektron.*, 1907, **4**, 62). As regards the character of such ionic vibrations, Drude (*Ann. Physik*, 1904, [iv], **14**, 677) showed that they should correspond with the infra-red part of the spectrum, and the most recent investigations on infra-red absorption spectra render it evident that many substances, transparent to ordinary light, exhibit characteristic absorption bands in the region of long waves.

If the period of one of the vibrations characterising the molecule of the solvent coincides with the period of vibration of the ion, the phenomenon of resonance appears. Under the influence of the vibrations of the neighbouring molecules of the solvent the ions acquire sufficient kinetic energy to overcome the forces maintaining the ions in one and the same molecule.

These considerations are extended to the discussion of complex ions. With the difference between the dissociation caused by the resonance of simple ions and of complex ions corresponds a difference in the behaviour of the molecular conductivity on dilution. In the former case the conductivity increases continuously with dilution, the curve being "normal"; but in the latter case, the complex ions break down on dilution, so that the molecular conductivity diminishes and an "abnormal" curve is obtained.

The most favourable condition for resonance is coincidence of the numbers of vibrations of the solvent and the ion, but a feebler resonance may arise with other relations between the numbers of

vibrations, so that a given solution may exhibit simultaneously two different types of conductivity.

The results of Rubens and Hollnagel (A., 1910, ii, 172) and of Nernst and Lindemann (this vol., ii, 103) are quoted in support of the conclusions drawn from the hypothesis of electrochemical correspondence. T. H. P.

Effect of Light on Decomposition Voltage. ALAN LEIGHTON (*J. Physical Chem.*, 1913, **17**, 695—702).—A rubber-coated quartz mercury lamp was immersed midway between the electrodes in an electrolysis cell containing copper sulphate solution. The electrodes were either of carbon or platinum. The decomposition voltage was measured directly when either one or both electrodes were illuminated or when both were not illuminated. It is shown that the decomposition voltage is not affected when the anode alone is illuminated in the case of platinum electrodes, but it is increased when the cathode is illuminated. It is possible to so regulate the voltage that copper can be deposited on the shaded portion of the cathode, but not on the illuminated portion. Graphite is shown to absorb a cuprous salt from the electrolyte, which acts as an anodic depolariser. This reaction is accelerated by light. Using a graphite anode and a platinum cathode, the decomposition voltage can be reduced to 0·4 volt by illuminating the anode. J. F. S.

Magneto-chemical Investigations. Measurement of the Absolute Susceptibility of Water. W. J. DE HAAS and PAUL DRAPIER (*Ann. Physik*, 1913, [iv], **42**, 673—684).—The authors have measured the magnetic susceptibility of water by a hydrostatic null-method, which is described in detail. The value obtained is $\chi = -0{\cdot}747 \times 10^{-6}$ in air at 21°, whilst in hydrogen at the same temperature $\chi = -0{\cdot}721 \times 10^{-6}$ represents the mean result. These values are in good agreement with recent measurements of the specific susceptibility made by other observers. H. M. D.

Measurements in the Electro-magnetic Spectrum of Water with Feebly Damped Vibrations of 65 to 20 cm. Wave-length. H. RUKOP (*Ann. Physik*, 1913, [iv], **42**, 489—532).—A form of apparatus is described, by means of which it is possible to obtain electromagnetic waves of short wave-length covering a range of two octaves. The vibrations are approximately monochromatic and damped to a very small extent. By the aid of this apparatus it has been found possible to determine the electric index of refraction of water with an accuracy of about 0·15%.

The water spectrum shows a number of anomalous dispersion bands in the region submitted to examination, but the complicated dispersion phenomena described by Colley (*Physikal. Zeitsch.*, 1909, **10**, 329, 471) are not confirmed by the author's observations. H. M. D.

The Magneto-optical Kerr Effect in Ferro-magnetic Compounds. IV. PIERRE MARTIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 318—331. Compare A., 1912, ii, 1039).—The Kerr effect

has been investigated in a further series of ferro-magnetic substances with special reference to the form of the dispersion curve. The substances submitted to examination were manganese arsenide (MnAs), manganese antimonide (MnSb), iron carbide, ferrosilicon (containng 30 atoms % silicon), ferrocobalt (Fe_2Co), ferronickel (Fe_2Ni), and various compounds belonging to the metaferrite series, including calcium ferrite, titanium ferrite, ferroferrite (magnetite), ferriferrite (martite and hæmatite), cobaltoferrite, cupri-ferrite, and zinc ferrite. In nearly all cases the dispersion curves show a maximum and minimum within or near the limits of the visible spectrum.

In the case of manganese arsenide and antimonide, iron carbide and ferrosilicon, data were obtained which show the influence of temperature on the Kerr effect. H. M. D.

Decomposition of Complicated Chemical Compounds in a Variable Magnetic Field. George W. Heimrod (*Zeitsch. Elektrochem.*, 1913, **19**, 812—816. Compare Rosenthal, A., 1908, ii, 152; Cegielskij, this vol., ii, 752).—The author has repeated the work of Rosenthal of placing a 2·5% solution of sucrose in a variable magnetic field, and, in confirmation of the work of Cegielskij, finds that inversion does not occur. The experiments were conducted over a range of from 200—900 oscillations per second, and at temperatures up to 90°. Further experiments were carried out on the same solutions to which sodium chloride and hydrochloric acid respectively had been added, and in all cases the amount of inversion was identical, whether or no the solution was placed in the magnetic field. It is shown theoretically that there is no reason why such reactions should occur in a magnetic field, and that probably the results of Rosenthal rest upon an error. J. F. S.

An Arrangement for Heating Gases or Vapours to Very High Temperatures. Karl Fredenhagen (*Physikal. Zeitsch.* 1913, **14**, 1047).—The apparatus consists essentially of a glass flask, at the centre of which is supported a small tantalum tube 2·5 cm. in length, 0·5 cm. in internal diameter and 0·1 mm. in thickness of wall. The thick copper wires which support the tube at the two ends serve as leads for the current which is employed in heating the tantalum tube. The temperature of this can be readily raised to about 2200°, the current required for this purpose being about 70 amperes.

By means of a side-tube in the neck of the flask, the apparatus can be exhausted, and the flask itself can be readily heated to a moderate temperature in order to vaporise substances which it is desired to subject to the influence of the very high temperature of the tantalum tube. The arrangement has been employed in the investigation of the emission of sodium vapour. H. M. D.

A Method for Electrolytic Heating and Regulation of Thermostats. Ira H. Derby and John W. Marden (*J. Amer. Chem., Soc.*, 1913, **35**, 1767—1769).—Two graphite electrodes, 10 × 10 cm. in

area, or in some cases 10 and 20 cm., and 3·5—13·0 cm. apart, are immersed in the thermostat and connected with a 110-volt source, either alternating or direct, and in series with a relay interrupter connected with the regulator. In a bath of 17—310 litres capacity, the temperature can be kept constant within 0·005—0·025° at temperatures varying from 30—70°.

Copper electrodes also give satisfactory results, but the copper slowly dissolves. T. S. P.

Isothermals of Diatomic Substances and their Binary Mixtures. XIII. Liquid Densities of Hydrogen between the Boiling Point and the Triple Point; Contraction of Hydrogen on Freezing. H. KAMERLINGH ONNES and C. A. CROMMELIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 245—247).—The density of liquid hydrogen increases from 0·07086 at the boiling point (−252·77°) to 0·07631 at −258·27°. The relationship between the density and temperature is given by the quadratic formula $\rho = a + bT + cT^2$, in which $a = +0{\cdot}084404$, $b = -0{\cdot}0002230$, and $c = -0{\cdot}00002183$.

Contraction occurs on freezing, and at −262·0° the density of solid hydrogen was found to be 0·08077. According to the above formula, the density of liquid hydrogen at the triple point (−259·2°) is 0·07709, and on the assumption that the density of solid hydrogen at this temperature does not differ appreciably from that at −262°, the contraction on freezing is found to be about 4·8% of the liquid volume. H. M. D.

Molecular Flow and Temperature Change. A Contribution to the Kinetic Theory of Dilute Gases. H. BOLZA, M. BORN, and TH. VON KÁRMÁN (*Chem. Zentr.*, 1913, ii, 1358; from *Nahr. K. Ges. Wiss. Göttingen*, 1913, 221—235).—According to Knudsen, the behaviour of a gas when the dimensions of the space in which it is confined are of the order of the mean free path of the molecules is quite different from that shown by the gas in ordinary circumstances. It is shown that Knudsen's formulæ for molecular flow and molecular heat conduction can be readily deduced from Lorentz's equations for the movement of electrons on the assumption that the conditions obtaining in the case of the gas molecules are analogous. The temperature change which has been found to accompany the molecular flow through porous media can also be accounted for in terms of the general theory, if it is assumed that the gas is adsorbed to some extent by the walls. The observed temperature changes are in approximate agreement with theory in the case of air and carbon dioxide, but considerable divergence is shown by hydrogen. H. M. D.

Specific Heat. MAX TRAUTZ (*Physikal. Zeitsch.*, 1913, **14**, 1176—1178; *Ber. Deut. physikal. Ges.*, 1913, **15**, 969—973).—A theoretical paper, in which the author discusses the possibility of explaining the thermal properties of gases on the assumption of a dynamic equilibrium between two isomeric forms, which are mutually transformable at very high velocities. H. M. D.

Experimental Determination of the Specific Heats of Diatomic Gases and Certain Theoretical Conclusions. WILHELM ESCHER (*Ann. Physik*, 1913, [iv], **42**, 761—778).—The specific heats of hydrogen and air have been measured at constant pressure by the mixture method, the apparatus employed being similar to that used by Wiedemann. The specific heat of hydrogen appears to be independent of the temperature between 20° and 100°, the mean value obtained for the molecular heat being $3\cdot4219 \pm 0\cdot0013$. For air the specific heat was found to be $0\cdot23764 \pm 0\cdot00035$.

From the equation $M.c_v = M.c_p - 1\cdot986$ the author calculates the specific heat ratios to be 1·404 and 1·4047 for hydrogen and air respectively. From experiments made by previous observers on oxygen and nitrogen with the same apparatus, the calculated ratios are 1·3998 and 1·412 respectively. These ratios are shown to be in good agreement with the results obtained in the direct determination of the specific heat ratio.

The specific heat data are further applied in the calculation of the mechanical equivalent, the deviations of the various gases from the ideal state being taken into consideration. The values obtained for the equivalent in ergs are $4\cdot202 \times 10^7$ from hydrogen, $4\cdot209 \times 10^7$ from air, $4\cdot188 \times 10^7$ from oxygen, and $4\cdot186 \times 10^7$ from nitrogen.

H. M. D.

Relation Between the Two Specific Heats of Certain Solid Substances. EMIL KOHL (*Chem. Zentr.*, 1913, ii, 742; from *Monatsh. Math. Physik*, 1913, **14**, 197—208).—On the assumption that the van der Waals' equation is applicable to the solid state, and that the variation of the energy of a substance with the temperature is independent of the state of aggregation, it is shown that the difference between the two specific heats can be expressed by $c_p - c_v = 3a\alpha rd/(d_s - d_{s1})$, in which a is the atomic weight, α the coefficient of expansion, r the latent heat of liquefaction, d the density, d_s and d_{s1} the densities of the solid and liquid substance at the melting point.

For a large number of metals and also for sulphur and phosphorus this equation affords values for the difference in the atomic heats which lie between 3 and 4 calories. Since c_p is approximately 6 for the metals, it follows that $c_v = 3$, which is the value obtained for the molecular heat of a monatomic gas. In the case of sulphur and phosphorus, the equation yields $c_p - c_v = 1\cdot9$, and this corresponds also with $c_v = 3$.

The author considers that the relationships thus brought to light indicate that the solid and liquid states can be represented by the same equation of condition. H. M. D.

Anomalies of the Specific Heat of Certain Alloys. OSKAR RICHTER (*Ann. Physik*, 1913, [iv]. **42**, 779—795. Compare this vol., ii, 184).—According to the theory put forward by Richarz to explain the properties of elements in the solid state, an element should have the greatest specific heat in that modification in which its density is smallest. In order to ascertain whether this relation-

ship is applicable to metallic alloys, the author has examined the data previously obtained (*loc. cit.*) for the specific heats of a series of alloys of bismuth and tin and of bismuth and lead.

In the case of the bismuth–tin alloys, the observed densities are smaller than those calculated according to the mixture rule, whilst the observed specific heats are greater than the calculated values. This is supposed to be in agreement with the requirements of the above-mentioned theory.

On the other hand, the required relationship is not satisfied at all by the experimental data for the bismuth–lead alloys, and the anomalies exhibited in this case are attributed to the formation of a chemical compound. From the position of the maximum deviation of the values of the density and specific heat from those calculated from the mixture rule, it would appear that this compound corresponds with the formula BiPb.

Further observations are described which show that the specific heat of bismuth–lead alloys is to some extent dependent on the previous thermal treatment, and on the rate at which solidification occurs when the alloy is cast. These variations are discussed from the point of view of Richarz's theory. H. M. D.

Compressibility and Differences of Specific Heats of Liquids. THADÉE PECZALSKI (*Compt. rend.*, 1913, **157**, 770—773).—A mathematical discussion of the relationship between the specific heats of a liquid at constant volume and constant pressure, and its coefficient of dilatation. W. G.

Latent Heat of Fusion. GUSTAV TAMMANN (*Zeitsch. physikal. Chem.*, 1913, **85**, 273—296).—The latent heat of fusion of isotropic and anisotropic substances is considered theoretically. It is shown that the heat of fusion r can be represented by the equation $r=A_a+A_i+\Delta E+\Delta\pi+\Delta x W_a$, where A_a and A_i represent the work performed against external and internal forces respectively, ΔE the energy difference of the molecule in isotropic and anisotropic conditions, and $\Delta\pi$ the difference of the potential energy between the two molecular orders, W_a the heat of association, and Δx the change of the association factor on melting. At the maximum melting point on the fusion curve, the volume difference between the isotropic and anisotropic phases disappears, and consequently the internal and external work on melting, hence $r_{p.(\max.)}=\Delta E+\Delta\pi$. It is shown that this expression cannot be evaluated from the knowledge of the diagram of condition. The expression is theoretically considered and tested in known cases. J. F. S.

Determination of Melting Point by the Thermometer Bulb Method. ROBERT MELDRUM (*Chem. News*, 1913, **108**, 223—224).—The varying results obtained with the thermometer bulb method for the determination of the melting point of fats and waxes have led to the general opinion among analysts that the melting point is affected by the length of time the fat is kept molten, and also by rapid cooling. The author's experience is not

in agreement with this opinion, the varying results being ascribed to the defective experimental methods used. Minute details are given of the method which should be used in coating the bulb with fat; also with respect to the influence of the thickness of the coating, of the part played by viscosity, and of the rate of heating.

In fifty-nine determinations made by the author the maximum variation does not exceed 0·6°. T. S. P.

The *T-X*-Figure of the System Benzene–Quinine. J. W. VAN ITERSON-ROTGANS (*Chem. Weekblad*, 1913, **10**, 920—939).—An investigation of the melting points and the vapour tension at constant temperature of a large number of mixtures of benzene and quinine, illustrated by curves and diagrams of the apparatus employed. A. J. W.

Vapour-pressure Measurements and Thermometry at Low Temperatures. H. VON SIEMENS (*Ann. Physik*, 1913, [iv], **42**, 871—888).—The vapour pressures of liquid carbon disulphide, carbon dioxide, oxygen, and nitrogen have been measured in a closed apparatus constructed entirely of glass, and similar in form to that described by Stock and Nielsen (A., 1906, ii, 521). In all cases the observations can be satisfactorily represented by Nernst's formula, the actual formula for carbon disulphide being $\log p = -1578·8/T + 1·75 \log T - 0·003874T + 4·67948$; for carbon dioxide, $\log p = -1378·3/T + 1·75 \log T - 0·0051T + 6·9484$; for oxygen, $\log p = -399/T + 1·75 \log T - 0·01292T + 5·0527$; for nitrogen, $\log p = -323·5/T + 1·75 \log T - 0·01250T + 4·7306$; and for solid nitrogen, $\log p = -345·6/T + 1·75 \log T - 0·00696T - 4·7306$. The vapour-pressure data are applied to the calculation of the latent heat of vaporisation, the numbers thus obtained being in all cases in satisfactory agreement with the experimental values.

Platinum resistance thermometers were employed in the determination of temperatures, the data recorded by Onnes and Clay being made the basis of the scale of temperatures. It is shown that the variation of the resistance of platinum with the temperature, as represented by the data in question, can be represented by means of a cubic equation for temperatures above 100° (absolute). By means of this equation and Nernst's empirical reduction formula, it is possible to bring the readings of any platinum resistance thermometer into line with the standard scale by observations at four temperatures.

Convenient constant temperature baths for low temperature work, and particularly for vapour-pressure measurements, are also described in the paper. H. M. D.

Vapour Pressures of Substances of Low Critical Temperature at Low Reduced Temperatures. I. Vapour Pressures of Carbon Dioxide between −160° and −183°. H. KAMERLINGH ONNES and SOPHUS WEBER (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 215—227).—The vapour-pressure measurements between 1 mm. and 0·01 mm. of mercury were made with the aid of Knudsen's

hot-wire gauge, those between 0·01 and 0·001 mm. by means of Knudsen's absolute manometer. The vapour pressure increases from 0·008 barye at $-183·0°$ to 1·310 barye at $-167·04°$. The pressures calculated from Nernst's formula, using the constants determined by Falck (A., 1908, ii, 662), are in good agreement with the observed values. H. M. D.

Vapour Pressures of Certain Univariant Systems. I. Na_2CO_3 and H_2O. A. F. GERASIMOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1655—1668).—The author has devised an apparatus suitable for the measurement of the vapour pressures of saturated solutions, which (1) admits of spontaneous change in the volume of the gaseous phase, (2) yields results the accuracy of which corresponds with that of the temperature measurements, and (3) allows of the verification at any moment of the completeness of removal of the air from the apparatus. For the detailed construction of the latter the original must be consulted.

By means of this apparatus the vapour pressures of saturated sodium carbonate solutions were measured at a series of temperatures ranging from 33·9° to 101°. The numbers obtained are expressed, for temperatures varying from 37·8° to 101°, very nearly by the equation: $\log P = 8·0684842 + 50[\log(T - 80·293) - \log T]$. For the boiling point of the saturated solution under normal pressure, extrapolation gives 104·8°, the temperature given in Landolt's tables being 105°. The author's numbers are in all cases appreciably lower than those given by Speranski (A., 1909, ii, 378; 1911, ii, 1065) for the temperature range 33·9—49·95°. T. H. P.

Attainment of Constant Temperatures. A. F. GERASIMOV (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1668—1674).—By means of mixtures in different proportions of two liquids which do not exhibit maxima or minima of vapour pressure, all temperatures intermediate to the boiling points of the constituents may be attained. But in order that any such temperature may be maintained constant for a length of time, it is necessary that the apparatus enclosing the boiling mixture be completely isolated from the atmosphere. On the other hand, the avoidance of bumping necessitates the continuous supply to the boiling mixture of a small quantity of air. The author has constructed an apparatus which satisfies these requirements. The flask containing the boiling liquid is connected with the constant temperature space by means of two tubes traversing the corks, one tube for the passage of vapour from the flask to the space, and the other for the return of condensed liquid below the surface of the boiling mixture. The upper part of the constant temperature space communicates with a condenser, which condenses the vapour and passes it as liquid into a wide tube, which becomes narrower before it enters the boiling flask to reach below the surface of the liquid; fitted in the shoulder of this tube is a conical piece of brass gauze, which causes the condensed liquid flowing into the flask to act in the same manner as the mercury in a Sprengel pump, so that a chain

of air and liquid bubbles passes into the flask. All the connexions are made with corks sealed with mercury. The apparatus functions well, no matter whether the liquid mixture be boiled slowly or rapidly, and, using mixtures of chloroform and carbon tetrachloride, the temperature in the constant temperature space could be kept at 63·5—63·6° or 66·95—67·1° for some hours, the flask being heated by an ordinary burner.

With such an apparatus, constancy of temperature depends on constancy of gas-pressure, and good results are obtained only after more or less perfect establishment of thermal equilibrium in the apparatus, this necessitating communication with the atmosphere for some time. These inconveniences were overcome by means of a gas regulator in the form of a U-tube manometer connected with the space between the lower end of the condenser and the boiling flask. One limb of the manometer contained an iron wire in continual contact with the mercury, and the other a similar wire joined to a platinum disk situate just above the surface of the mercury. These wires are connected with an electromagnetic apparatus controlling the gas-tap. By such means both the pressure and the temperature within the apparatus may be constrained to vary within definite limits, and in order to make these as narrow as possible, the thermal inertia of the apparatus must be diminished as far as possible. This may be effected by standing the flask on an iron tripod with a copper gauze, and by leaving it quite uncovered except for a small asbestos cup fitted to the upper part to protect the vapours from superheating. A regular oscillation of the temperature over 0·05° is thus attainable. T. H. P.

An Improved Type of Calorimeter, to be Used with Any Calorimetric Bomb. J. A. RICHE (*J. Amer. Chem. Soc.*, 1913, **35**, 1747—1750).—The calorimetric bomb is immersed in water contained in a Dewar vacuum cup standing on a wooden base. The cup and base are surrounded by an oak box, lined with pressed cork; on the under side of the cover, in addition to the cork, is glued a piece of felt, of such a thickness that a tight joint is effected with the top of the vacuum cup. There are appropriate holes in the cover for the introduction of a thermometer, of electric leads for ignition purposes, and of a screw-propeller stirrer for the water surrounding the bomb. T. S. P.

Relation Between the Heat of Formation of Binary, Liquid Mixtures and their Composition. ÉMILE BAUD (*Compt. rend.* 1913, **157**, 849—850).—The heat of mixture of two liquids, without chemical action on one another, can be expressed by the equation $q=kx(1-x)$, where q is the amount of heat, x the fraction of a gram-molecule of one constituent, and $(1-x)$ the fraction of a gram-molecule of the other constituent, k being a constant. Results are given for a mixture of *cyclo*hexane and *s*-dibromoethane, which verify this equation, and similar results have been obtained with other mixtures. The value of k lies between 1·32 and 1·35 for the mixture quoted. W. G.

Heats of Formation of Additive Organic Compounds. II. Racemates (Dimethyl Tartrate). BARTOLO L. VANZETTI (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 328—332. Compare this vol., ii, 296).—The following heats of solution in aqueous alcohol have been determined: Methyl *d*-tartrate, −5·392 Cal.; mixture of methyl *d*- and *l*-tartrates, −5·396 Cal.; methyl racemate, −12·350 (−12·143 to −12·613) Cal. Hence, heat of formation of the racemate (from 2 active mols.) is +1562 cals. T. H. P.

Apparatus for the Measurement of the Density and Viscosity of Gases. M. HOFSÄSS (*Chem. Zentr.*, 1913, ii, 1353; from *J. Gasbeleuchtung*, 1913, **56**, 841—843).—The apparatus has been designed for comparative observations on the rate of effusion and on the rate of flow through a capillary tube. The gas reservoir consists of a wide cylindrical tube connected above and below with narrow tubes provided with efficient taps. The tube at the lower end communicates with an open manometer tube containing a suitable liquid, whilst the tube at the upper end serves for the introduction of gas into the apparatus and communicates through a side-tube with a perforated diaphragm, which can be shut off from the reservoir by a tap. In carrying out an experiment, this tap is opened, and the time required for the fall of the manometer liquid over the distance fixed by two marks on the manometer tube is measured by means of a stop-watch. When the apparatus is to be used for viscosity measurements, the perforated diaphragm is replaced by a suitable capillary tube. H. M. D.

Vaporisation. VII. HANNS VON JÜPTNER (*Zeitsch. physikal. Chem.*, 1913, **85**, 1—61. Compare A., 1908, ii, 663, 810; 1909, ii, 21; 1910, ii, 583, 689; 1912, ii, 829).—A theoretical paper, in which the author shows that the formulæ

$$(1)\ (D_{\text{liq.}}+D_{\text{vap.}})/2D_k = D_0/2D_k(1-T/T_k)+T/T_k$$

and

$$(2)\ (D_{\text{liq.}}-D_{\text{vap.}})/2D_k = D_0/2D_k(1-T/T_k)^{1/3}$$

represent the relationship between the density of a liquid and its vapour with the critical density, and in both equations the quantity $(D_0/2D_k)$ is a constant. These expressions are tested on a large number of published observations, and it is shown that substances which have unchanged molecular size over the range of temperature examined have also the value $D_0/2D_k$ constant. Those substances the molecular size of which is changed have varying values of the constant. A number of new equations for the heat of vaporisation for ideal liquids are deduced. J. F. S.

[Determination of] The Densities of Certain Dilute Aqueous Solutions by a New and Precise Method. ARTHUR B. LAMB and R. EDWIN LEE (*J. Amer. Chem. Soc.*, 1913, **35** 1666—1693).—The authors have improved the submerged sinker method for the determination of densities of liquids, and claim to have attained an accuracy of less than one unit in the seventh decimal place. The

sinker consists of an inverted Jena flask of about 250 c.c. capacity, weighted with mercury, and containing a fixed, vertical, soft iron rod, so that it can be moved up and down in the liquid by means of an electromagnetic arrangement; a platinum point is fused into the sealed neck of the flask. The method of procedure was to place platinum weights on the sinker until it just barely floated, and then regulate the electromagnet so that the sinker was pulled down and the platinum point just touched a platinum saucer at the bottom of the vessel containing the liquid, a special microscope being arranged to observe the point of contact. The current through the electromagnet having previously been calibrated in terms of weight, the weight of the sinker when just floating could be found, and hence the density of the liquid. Due precautions were taken to keep the temperature constant by means of a thermostat, and the corrections for changes in the barometric pressure and for other variations causing errors were applied.

The densities of 0·0001—0·01*N*-solutions of salts of sodium, potassium, ammonium, lithium, magnesium, and zinc were determined relative to that of water at 20·004°, and the volume changes occurring on solution calculated. The variations in these volume changes indicate, in general, a progressively increasing compression as the dilution increases, but an approximate constancy is reached at dilutions where the electrolytic dissociation is practically complete. Of the solutions studied, sodium carbonate alone presents an anomalous behaviour in this particular, for in very dilute solution the contraction becomes less rather than greater. This anomaly can be explained on the basis of the unusual contraction which occurs during the neutralisation of carbonic acid.

T. S. P.

Volume Changes of Amalgams. J. WÜRSCHMIDT (*Ber. Deut. physikal. Ges.*, 1913, **15**, 1027—1036. Compare this vol., ii, 101).—Further experiments have been made on volume changes in amalgams. In the case of zinc amalgams, volume changes occur at temperatures below the melting point which are presumably due to changes in structure. Bismuth amalgam, of the composition BiHg, contracts at the melting point, and thus behaves like pure bismuth, but the volume contraction in the case of the amalgam begins at temperatures considerably below the melting point.

H. M. D.

The Expansion Pressures of Normal Liquids. L. GAY (*Compt. rend.*, 1913, **157**, 711—714).—The author has verified the formula $\log \pi = \log RT/(V-b) + b/(V-b) - (EL + PV - RT)/RT$ (compare this vol., ii, 382, 388) for normal pentane, hexane, heptane, octane, $\beta\epsilon$-dimethylhexane, ethyl bromide, bromobenzene, and ethyl ether. Using Young's values, he has calculated the ratio between (1) the critical molecular volume, (2) the theoretical molecular volume, and the co-volume b, and finds these ratios to be constant for these substances, thus verifying his law of the corresponding states.

W. G.

The Weight of a Falling Drop and the Laws of Tate. XIII. The Drop Weights of Aqueous Solutions and the Surface Tensions Calculated from them. J. LIVINGSTON R. MORGAN and GEORGE A. BOLE (*J. Amer. Chem. Soc.*, 1913, **35**, 1750—1759).—The authors show that the Morgan drop-weight apparatus can be satisfactorily used for the determination of the surface tensions of salt solutions, and when so used gives results which are in excellent agreement with the best results found by other standard methods.

By the study of the solutions of some twenty inorganic salts, one equivalent of each being dissolved in 1000 grams of water, it was shown that Valson's law (that the surface tension of normal solutions of salts is identical) is untrue, and that the results on which he based it are incorrect. T. S. P.

The Weight of a Falling Drop and the Laws of Tate. XIV. The Drop Weights of Aqueous Solutions of the Salts of Organic Acids. J. LIVINGSTON R. MORGAN and WALTER W. MCKIRAHAN (*J. Amer. Chem. Soc.*, 1913, **35**, 1759—1767).—From the determination of the drop weights and surface tensions of semi-normal solutions of thirty different salts of organic acids, at different temperatures, the change in surface tension with the temperature is found to be linear, within the limits of temperature studied.

Some salts raise the surface tension of water, whilst others lower it, which facts contradict Valson's generalisation that all normal solutions of salts at the same temperature have identical values for the surface tension.

The acids, citric, tartaric, and oxalic, lower the surface tension of water, so that hydrolysis in solutions of their salts would tend to lower the surface tension.

Generally, salts of the same acid show a marked agreement in their values for the surface tension at the same temperatures, but there are exceptions, for example, with barium and copper salts.

The surface tension of a solution of two salts, one of which raises and the other lowers the surface tension of water, is an additive property of the two separate solutions, provided no chemical action takes place, and that the separate values of the surface tension are not very far removed from that of water. If one of the solutes causes a much larger effect than the other, the value for the mixture lies closer to the one with the greater effect. T. S. P.

Adsorption of Electrolytes. KNUD ESTRUP (*Chem. Zentr.*, 1913, ii, 1102; from *Over. K. Danske. Vidensk. Selsk. Vorhand.*, 1913, 13—45).—Methods are described for the estimation of the purity of adsorbent substances, such as the different forms of animal charcoal, in which hydrochloric acid or potassium hydroxide is added until the positive and negative ions of certain neutral salts (ammonium nitrate, iodate, dichromate) are equally adsorbed by the charcoal. The amount of acid or alkali required per 2 grams of adsorbent when shaken with 100 c.c. of solution affords a measure of the impurity.

The adsorption of electrolytes from solutions containing two salts with a common cation or anion has also been investigated. In general, the adsorption of a particular ion is diminished when a second, similarly charged ion is added to the solution, but several exceptions have been observed. For example, the hydrogen and iodate ions are more readily absorbed in presence of the ammonium and sulphate ions respectively. In the case of two ions of similar sign but different valency, it is found that the more highly charged ion has the greater influence in lowering the adsorption tendency.

From observations on negative adsorption, the author has deduced a value for the degree of dispersity of charcoal. On the assumption that the particles are cubical, this is of the order $6 \cdot 10^5$ to $6 \cdot 10^7$.

H. M. D.

Adsorption of Colloidal Ferric Hydroxide. NILS CARLI (*Zeitsch. physikal. Chem.*, 1913, **85**, 263—272).—Experiments are made on the adsorption of ferric hydroxide by animal charcoal and kaolin. It is shown that the amount of adsorption by animal charcoal is independent of the volume of sol and the amount of colloid present, but is directly proportional to the weight of the charcoal. Consequently the adsorption does not follow the usual adsorption law: $\lambda = v/m \log_e(a/a-x)$. Kaolin exerts only the slightest adsorption on ferric hydroxide sols. J. F. S.

Dependence of the Capillary Constant of Water and of Alcohol–Water Mixtures on the Temperature. MAX REINHOLD (*Ber. Deut. physikal. Ges.*, 1913, **15**, 903—912).—The data recorded were obtained from measurements of the wave-length of the capillary waves generated on a freshly prepared surface of the liquid by a vibrating tuning-fork. For the five alcohol–water mixtures investigated between 5° and 65°, the influence of temperature on the surface tension can be represented by a linear equation $\alpha_t = \alpha_0(1 - kt)$. The temperature-coefficients observed for the mixtures containing 10, 30, 50, 70, and 94% by weight of alcohol are respectively $0 \cdot 0^3206$, $0 \cdot 0^3136$, $0 \cdot 0^3105$, $0 \cdot 0^498$, and $0 \cdot 0^479$.

In the case of water, the data obtained at temperatures between 0° and 85° give rise to a more or less sinuous curve when the surface tension is plotted against temperature. H. M. D.

The Idea of Osmotic Pressure and its Application to Colloidal Solutions. ARRIGO MAZZUCCHELLI (*Gazzetta*, 1913, **43**, ii, 404—422).—A theoretical discussion. R. V. S.

The Two Roots of Ostwald's Equation. ARRIGO MAZZUCCHELLI (*Gazzetta*, 1913, **43**, ii, 423—428).—The author discusses the significance of the negative root of the equation $\alpha^2/(1-\alpha)V = K$.

R. V. S.

Measurement of the Fluidity of Solutions. G. MUCHIN (*Zeitsch. Elektrochem.*, 1913, **19**, 819—821).—Determinations of the fluidity of the following binary mixtures are given. Benzene–

paracetaldehyde, paracetaldehyde–acetic acid, benzene–acetone, acetone–*n*-hexane, acetone–nitrobenzene, acetone–ethyl alcohol, acetone–water, *iso*amyl alcohol–hexane, *iso*amyl alcohol–benzene, *iso*amyl alcohol–ethyl alcohol, benzene–nitrobenzene, benzene–acetic acid, benzene–ethyl alcohol, paracetaldehyde–ethyl alcohol, and paracetaldehyde–nitrobenzene. The determinations were mostly carried out at 20° by means of a closed Ostwald viscometer. The object of the work was to test the formula $\phi = \phi_1 a + \phi_2(1-a)$ (Drucker and Vassel, A., 1911, ii, 373). It is shown that generally the formula does not hold, but the author regards the work as preliminary, and is of the opinion that the formula is generally applicable provided no complications occur in the mixtures. J. F. S.

Economic Lixiviation. P. J. H. van Ginneken (*Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 201—214).—A theoretical paper in which the author discusses the relative merits of discontinuous, semi-continuous, and continuous lixiviation with reference to the economy of the solvent. H. M. D.

Solubility in the Solid State between Nitrates, Sulphates, and Carbonates at High Temperatures. Mario Amadori (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 332—337).—The author has investigated the melting-point curves of the systems $LiNO_3$–Li_2SO_4, $NaNO_3$–Na_2SO_4, KNO_3–K_2SO_4, $LiNO_3$–Li_2CO_3, $NaNO_3$–Na_2CO_3, KNO_3–K_2CO_3. The results obtained differ from those yielded by the sulphate–carbonate systems (A., 1912, ii, 917), the mutual solubility in the solid state of nitrate and sulphate or nitrate and carbonate being either zero or very small. The nitrates crystallise with the carbonates and with the sulphates in simple eutectics consisting almost exclusively of nitrate at temperatures only 3—10° below those at which the nitrates solidify. As with sulphates and carbonates, so also with nitrates and sulphates or nitrates and carbonates, no formation of compounds occurs on solidification or at lower temperatures. T. H. P.

Cause of the Abnormal Linear Velocity of Crystallisation of Supercooled Crystalline Substances. K. P. Grinakovski (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1210—1248. Compare Tammann, A., 1911, ii, 376).—The author has devised an apparatus for the determination of the molecular surface energy of supercooled, viscous, crystalline substances, and has measured the surface energy and density of benzophenone, erythritol, acetanilide, 3 : 4-dinitrophenol, *m*-chloronitrobenzene, *m*-bromonitrobenzene, chloroacetic acid, antipyrine, sodium thiosulphate, ferric nitrate, and benzil. With all these compounds, the linear velocity of crystallisation follows an abnormal course, the region of constant velocity being absent.

The results obtained show the inaccuracy of Tammann's supposition that the character of this velocity curve is influenced solely by phenomena of polymerisation, and indicate that abnormalities are dependent on: (1) the influence of admixtures intro-

duced during recrystallisation; (2) the influence of removal of heat (crystallisation in capillaries); (3) the influence of decomposition during fusion; (4) the influence of polymorphous modifications.

T. H. P.

Influence of the Degree of Supersaturation of a Solution on the External Form of Crystals of Alum Separating from It. A. SCHUBNIKOV (*Bull. Acad. Sci. St. Pétersbourg*, 1913, 817—828).—The object of the author's investigations was to test experimentally Johnsen's view ("Wachstum und Auflösung der Kristalle," Leipzig, 1910) that with every degree of supersaturation of a solution corresponds its own perfectly definite crystalline form.

Experiments made with alum show that diminution of the extent to which the solution is supersaturated is accompanied by enhancement of the internal, and by lowering of the external, symmetry of the crystals; that is, highly supersaturated solutions yield non-homogeneous crystals, which include mother-liquor, but are remarkably regular in appearance, whilst slightly supersaturated solutions give homogeneous, transparent crystals of unsymmetrical shape.

Further, decrease in the degree of supersaturation occasions increase in the number of faces of the crystals, whereas, according to the conclusions drawn by Andréev (A., 1908, ii, 475), the opposite should be the case.

No simple law could be found connecting change in the rate of growth of the crystals with change in the extent of supersaturation of the solution. Diminution in the degree of supersaturation is accompanied by rounding-off of the crystals, that is, by decrease of the surface area per unit weight; this conclusion is indicated by the habit of the crystals, and confirmed by actual measurement.

T. H. P.

Relation between the Crystal Symmetry of the Simpler Organic Compounds and their Molecular Constitution. II. WALTER WAHL (*Proc. Roy. Soc.*, 1913, *A*, **89**, 327—339. Compare A., 1912, ii, 1044).—The author has investigated the crystalline form of a large number of organic substances, most of which melt at low temperatures, including the unsaturated aliphatic hydrocarbons, the simpler oxygen, sulphur and halogen compounds of carbon, and the simpler aromatic hydrocarbons. The optical properties are described in detail, and in many cases the probable crystalline form is inferred from the optical behaviour. No general conclusions are drawn from the detailed observations. H. M. D.

Influence of Chemical Constitution on the Thermal Properties of Binary Mixtures. III. PAUL PASCAL and LÉON NORMAND (*Bull. Soc. chim.*, 1913, [iv], **13**, 878—889. Compare this vol., ii, 292).—In the previous papers it has been shown that molecular symmetry in the two constituents determines the existence of a continuous series of mixed crystals, but that this property disappears when one of the constituents has an unsymmetrical aliphatic chain. In order to determine the influence of the nucleus

on the tendency to syn-crystallisation, melting-point curves have been determined for binary mixtures, including constituents in which the nuclei have been loaded in various ways. Tables and graphs are given for the following mixtures: (1) stilbene and *p*-dimethoxystilbene, (2) azobenzene and azotoluene, (3) stilbene and azotoluene, (4) azobenzene and dimethoxyazobenzene, (5) stilbene and aminoazobenzene, (6) azobenzene and azonaphthalene, (7) stilbene and azonaphthalene, (8) azobenzene and benzeneazonaphthalene, (9) benzylidene-α- and benzylidene-β-naphthylamines, (10) tetraphenylethylene and tetraphenylsilicon. The following general conclusions are drawn. Mixtures of two substances separately symmetrical furnish mixed crystals in all proportions when both have the same nuclear structure, and this property is not destroyed by symmetrical substitution. Two substances which are separately symmetrical show isodimorphism when their nuclei are different. Asymmetry of structure in the central chain produces isodimorphism, independently of the nuclear structure, and asymmetry of the nuclear structure produces a similar effect. With increasing constitutional difference and reciprocal asymmetry of the components of a binary mixture, isomorphism (and the spindle-shaped melting-point curves associated with this) undergoes a regular involution, isodimorphism becomes marked, and the areas of syn-crystallisation increase. T. A. H.

The Relationship between Colloid Coagulation and Adsorption and the Velocity of Coagulation. HERBERT FREUNDLICH and N. ISHIZAKA (*Zeitsch. physikal. Chem.*, 1913, **85**, 398—400. Compare this vol., ii, 486).—It is shown that the auto-catalytic coagulation which was expressed (*loc. cit.*) by the expression:

$$k = 1/z^2(1+b)\{b/(1+b)[\log_{\text{nat.}}(1+bx) - \log_{\text{nat.}}(1-x)] + x/1-x\}$$

can be expressed equally well by the expression:

$$k' = 1/(1-b')z^2\{\log_{\text{nat.}}(1+b'x) - \log_{\text{nat.}}(1-x)\}.$$

the constants in both cases being equally satisfactory. J. F. S.

The Distribution of a Suspended Powder or of a Colloidally Dissolved Substance between Two Solvents. WILHELM REINDERS (*Kolloid. Zeitsch.*, 1913, **13**, 235—241*).—It is shown that when a liquid (1), in which a finely divided solid substance (3) is suspended, is shaken up with a second immiscible liquid (2), the resulting distribution is determined by the surface tensions at the surfaces of separation of the three phases. If $\sigma_{2\cdot3} > \sigma_{1\cdot2} + \sigma_{1\cdot3}$, the solid will remain suspended in the first liquid. If $\sigma_{1\cdot3} > \sigma_{1\cdot2} + \sigma_{2\cdot3}$, the solid will pass into the second liquid. Thirdly, if $\sigma_{1\cdot2} > \sigma_{2\cdot3} + \sigma_{3\cdot1}$, or if none of the surface tensions is greater than the sum of the other two, the solid will collect in the surface layer separating the two liquids.

Experiments with different solids and pairs of liquids have shown that all three cases are met with in practice, and it is

* and *Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16**, 379—388.

possible to effect a separation of solid substances in certain cases on the basis of the differences which they exhibit in their mode of distribution between certain pairs of liquids. If, for instance, a mixture of galena and quartz is shaken with water and *iso*butyl alcohol, the quartz remains suspended in the aqueous layer, whilst the galena is found at the surface of separation. The observations made with water as the one liquid, and paraffin oil, amyl alcohol, carbon tetrachloride, benzene, and ethyl ether as the other, indicate that silicates, sulphates, and carbonates of the light metals generally remain suspended in the water layer, whilst compounds of the heavy metals and non-metallic elements, such as carbon, sulphur, and selenium, pass into the surface of separation or into the non-aqueous liquid. Of the non-aqueous solvents examined, paraffin oil and amyl alcohol represent those which take up the suspended substance most readily.

The behaviour of a colloidal solution is in all probability dependent on the size of the colloidal particles, but experiments with colloidal gold solutions indicate that the phenomena of distribution are similar to those met with in the case of solid suspensions.

If a red or reddish-violet colloidal solution of gold in water is shaken with *iso*butyl alcohol, amyl alcohol, benzene, carbon tetrachloride, carbon disulphide, or ethyl ether, the gold passes into the surface layer of separation, and forms a blue deposit. If, on the other hand, the yellowish-brown solution of gold in amyl alcohol, prepared by reduction of the chloride with phosphorus, is shaken with water, the colloidal gold remains suspended in the amyl alcohol layer. Other experiments show in a similar manner that the behaviour of colloidal gold is more or less dependent on its degree of dispersity. The presence of a protective colloid, such as gum arabic, is also found to have an appreciable influence on the phenomena of distribution.

In addition to gold, colloidal solutions of silver, ferric hydroxide, arsenious sulphide, molybdenum trioxide, selenium, tellurium, and carbon have been examined. H. M. D.

New Electrical Method of Preparing Aqueous Colloidal Solutions of Metals. H. Morris-Airey and S. H. Long (*Proc. Univ. Durham Phil. Soc.*, 1913, **5**, 68—70).—The method involves the use of a high frequency alternating arc, a suitable generator being provided by the Poulsen arc, as used in wireless telegraphy. The discharger circuit, which contains an arc lamp, designed so as to allow of the arc being struck under water, is connected up to two points on the inductance of the oscillatory circuit. By varying the inductance and capacity of the oscillatory circuit and introducing various capacities and inductances into the discharger circuit, the electrical conditions of the discharge can be readily varied between wide limits. It is claimed that the new method possesses marked advantages over the methods described by Bredig and Svedberg, and, in general, only a few seconds are required for the preparation of colloidal solutions of different metals. By varying the conditions of discharge, it has been found that solutions of different colours

can be obtained in the case of several of the metals submitted to examination. H. M. D.

Protective Colloids. Starch as Protective Colloid. I. Colloidal Silver. ALEXANDER GUTBIER and E. WEINGÄRTNER (*Koll.-chem., Beihefte*, 1913, **5**, 211—243).—The behaviour of starch as a protective colloid towards colloidal silver has been examined in detail.

The solutions obtained by reduction with hydrazine and with sodium hyposulphite are very similar in their properties, although the rapidity with which the latter reacts and the nature of its oxidation products are responsible for certain anomalies observed with colloidal solutions obtained by this method of reduction. The coagulating influence of electrolytes diminishes in the order: sulphuric acid, barium chloride, magnesium sulphate, ammonium carbonate, sodium hydroxide in the case of the solutions reduced by hydrazine; and in the order: barium chloride, sulphuric acid, magnesium sulphate, sodium carbonate, sodium hydroxide for solutions reduced by sodium hyposulphite. In general, those electrolytes which accelerate the ageing of the starch solutions increase the rate of coagulation, whilst those which retard the coagulation of pure starch solutions have a similar influence on the silver starch sols.

The protective action of starch solutions prepared at 100° and at 120° is practically the same, although the stability of dilute silver solutions is somewhat greater for the clear starch solutions which are obtained at the higher temperature.

The starch silver sols are coagulated on the addition of alcohol, and under the influence of an electrical field, their behaviour is similar to that exhibited by starch solutions, and quite different from that of colloidal silver solutions in the absence of starch.

Although hydrogen peroxide is readily decomposed by colloidal silver, it is found that the catalytic effect is greatly diminished in presence of starch. In the case of dilute solutions of hydrogen peroxide, there is a small initial evolution of oxygen, but the reaction quickly ceases. With concentrated hydrogen peroxide solutions, the anti-catalytic influence of the starch is not sufficient to stop the reaction, and this is attributed to the hydrolytic action of the hydrogen peroxide on the starch.

Other experiments show that starch solutions have a reducing action on silver nitrate when the reaction mixture is exposed to light, but this change takes place too slowly to have any appreciable influence on the reduction which occurs in presence of hydrazine or sodium hyposulphite. H. M. D.

Protective Colloids. Starch as Protective Colloid. II. Colloidal Gold. ALEXANDER GUTBIER and E. WEINGÄRTNER (*Koll-chem. Beihefte*, 1913, **5**, 244—268).—Similar experiments to those described in the previous paper have been carried out with colloidal gold solutions. In general, the protective influence of the starch is of the same nature as in the case of colloidal silver solutions.

The concentration of the starch has an appreciable influence on the colour of the solutions obtained by reduction with hydrazine, a series of comparative experiments showing that the blue colour becomes darker and shades off towards violet as the concentration of the starch is increased.

Towards electrolytes, the protective influence of starch is closely similar to that found in the case of colloidal silver.

The reducing action of starch solutions on gold chloride has also been examined. These experiments show that colloidal gold is produced in these circumstances, the colour changing from red to blue as the reaction proceeds. The coagulation phenomena observed with the gold sols prepared in this way are very similar to those exhibited by the sols obtained by reduction with hydrazine in presence of starch. In presence of alkali, the reducing action of starch on gold chloride is considerably accelerated. H. M. D.

Chemical and Physico-chemical Properties of Liquids Expressed from Striated and Plain Muscle. III. Variations of Volume During Certain Colloidal Processes. FILIPPO BOTTAZZI and E. D'AGOSTINO (*Atti R. Accad. Lincei*, 1913, [v], **22**, ii, 307—315. Compare this vol., i, 1132).—Dilatometric measurements made with dry gelatin in water show that imbibition of gelatin is accompanied by contraction of volume, which is at first very rapid, but subsequently falls off. The similar contraction proceeding with dry, granular myosin takes place much more slowly than with gelatin. In general, acids and bases occasion increase in the imbibition of colloids and it is found that myosin which has imbibed the maximum proportion of water undergoes further diminution of volume in presence of small amounts of lactic or hydrochloric acid; this diminution takes place at first rapidly, and then more slowly, and increases with the proportion of lactic acid present. On the other hand, addition of an alkali invariably results in increase in volume.

These results are explained on the assumption that when a protein is in presence of an aqueous acid or alkali solution free from salt, three processes occur: imbibition of the colloid, solution of the latter in the case when it swells to an illimitable extent, and formation of a salt of the protein with the acid or base. The first two of these are accompanied by contraction and the last by expansion, the net result depending on the predominance of one or the other of these changes. T. H. P.

The Structure of Gels. RICHARD ZSIGMONDY (*Physikal. Zeitsch.*, 1913, **14**, 1098—1105).—The structure of gels is discussed with special reference to the two principal theories which have been put forward. In many cases the structure revealed by the ultramicroscope is distinctly favourable to the micellary theory, but other cases are known in which the heterogeneity exhibited by the gels is such as to lend support to the opposing theory advocated by Quincke and Bütschli.

The properties of silica, obtained by dehydrating silicic acid

jelly over sulphuric acid, are described. The heterogeneity of the structure in this case is such that the clear, transparent silica appears to be optically homogeneous, although the substance is undoubtedly porous, the volume of the free space amounting to 30—60% of the total volume. The water which is absorbed by this extremely fine capillary network has an appreciably lower vapour pressure than water in bulk, and according to van Bemmelen's measurements of the vapour pressure at different stages during the absorption and removal of water, it appears that the curves corresponding with the two processes diverge appreciably. Similar measurements have been carried out with a silicic acid gel during the absorption of water, ethyl alcohol, and benzene. In all three cases the vapour-pressure curves are of the same type and quite similar to that which represents van Bemmelen's results. The data are employed to calculate the mean radius of the capillary tubes, the same value, $r = 2 \cdot 6 \mu\mu$, being obtained from the three sets of observations. This concordance indicates that the deviations of the vapour pressures from the normal values are due to capillary effects, and that the degree of heterogeneity of the gel can be determined with considerable exactitude. H. M. D.

Equation of Condition, Equilibrium Diagram, and Association Hypothesis. LÉON SCHAMES (*Ber. Deut. physikal. Ges.*, 1913, **15**, 1017—1026; *Physikal. Zeitsch.*, 1913, **14**, 1172—1175. Compare A., 1912, ii, 738, 1141).—A modified form of van der Waals' equation is put forward, in which association is taken into account. The evaluation of the constants in the critical condition indicates that all normal substances are associated to the extent of 40% at the critical point. A new form of reduced equation is also given, and it is claimed that various facts, which are quite inconsistent with the van der Waals' equation, can be satisfactorily accounted for in terms of the new equation. The ratio of the critical density to that calculated from the simple gas laws, the temperature-coefficient of the vapour pressure at the critical point, the latent heat of vaporisation and the limiting volume of the liquid at absolute zero or under infinite pressure are all in accord with the values indicated by the author's equation. Furthermore, it is found that the association hypothesis leads to the conclusion that there must be a second critical point limiting the coexistence of the solid and liquid forms of all normal substances. H. M. D.

The Phenomena of Equilibria between Silica and the Alkali Carbonates. PAUL NIGGLI (*J. Amer. Chem. Soc.*, 1913, **35**, 1693—1727 *).—The equilibria existing in systems containing the components M_2O, SiO_2, and CO_2 at temperatures of 900—1000° under a pressure of one atmosphere of carbon dioxide have been determined, M being either K, Na, or Li. The various mixtures investigated were made by mixing known weights of the alkali carbonate and silica.

In the case of mixtures of potassium carbonate and silica, the experiments were carried out at 898°, 956°, and 998°. In all cases

* and *Zeitsch. anorg. Chem.*, 1913, **84**, 229—272.

the loss of carbon dioxide was smaller than would correspond with the ratio $SiO_2 : CO_2$; the smaller the concentration of silica the greater is the proportion of carbon dioxide displaced. When the initial proportions are $K_2O : 2SiO_2$, the silica displaces only half the equivalent amount of carbon dioxide at any of the above three temperatures; with lower proportions of silica the amount of carbon dioxide displaced increases with the temperature. The results point to an equilibrium existing in accordance with the equation: $K_2CO_3 + K_2Si_2O_5 \rightleftarrows 2K_2SiO_3 + CO_2$. Experiments showed that when potassium carbonate is fused with silica, the first reaction takes place according to the equation: $K_2CO_3 + SiO_2 = K_2SiO_3 + CO_2$. The above equilibrium is then set up.

According to the law of mass action, the expression $[K_2SiO_3]^2/[K_2CO_3][K_2Si_2O_5]$ should give a constant value (K) if the concentration of the carbon dioxide remains constant. The value of K increases, however, with increase in concentration of the silica, but the ratio of the "constants" at 898° and 956° remains constant for the different mixtures.

The compound $K_2Si_2O_5$ was obtained pure by heating a mixture composed of $1K_2CO_3 : 2SiO_2$, and its optical properties ascertained. It melts at $1015° \pm 10°$. Potassium carbonate has m. p. 891°.

Similar results were obtained with mixtures of sodium carbonate and silica, except that all the carbon dioxide was replaced when the original mixture contained 1 mol. Na_2CO_3 : 1 mol. SiO_2. With less proportions of silica, the fusion contains ortho- and metasilicate as well as carbonate, so that the equilibrium is represented by the equation: $Na_2CO_3 + Na_2SiO_3 \rightleftarrows Na_4SiO_4 + CO_2$. Sodium metasilicate was prepared, and its optical properties investigated.

Experiments with mixtures of lithium carbonate and silica indicated that the equilibrium $2Li_2CO_3 + Li_4SiO_4 \rightleftarrows Li_8SiO_6 + 2CO_2$ exists, but the results were not very satisfactory. T. S. P.

Binary Eutectics between Diphenylamine, *p*-Nitroanisole, and Urethane. Alexei M. Vasiliev (*J. Russ. Phys. Chem. Soc.* 1913, **45**, 1582—1584).—The author applies Flavitzki's law concerning eutectic alloys (A., 1906, ii, 152; compare A., 1910, ii, 606; 1912, ii, 919) to the results of Puschin and Grebenschtschikov (this vol., ii, 852).

For the eutectic formed by diphenylamine and *p*-nitroanisole, calculation according to Flavitzki's equation gives $q/p = 1·0136$, which differs little from 1. Taking the latter value as correct, calculation gives a composition of the eutectic differing by less than 0·2 mol. % from that found experimentally. Similar agreement is found with the eutectic of the system diphenylamine–urethane. In consequence of the equivalent molecular lowering pointed out by Flavitzki, the system containing the third pair of these compounds, *p*-nitroanisole and urethane, should give a eutectic for which $q/p = 1$, or, more accurately, 1·026; the actual value for this ratio is, however, 1·343, which is virtually 4 : 3. This anomalous result the author regards as due to the fact that, whereas the eutectic points in the first two cases were determined directly,

that of the third system was obtained only by extrapolation. Reference to the curves and numbers of Puschin and Grebenschtschikov renders it probable that this eutectic contains a greater proportion of *p*-nitroanisole then corresponds with the composition given by these authors; a change in this direction would tend to bring the value of the above ratio nearer to 1.

T. H. P.

A Bomb, with Stirring Arrangement, for the Measurement of Reaction Velocities in Heterogeneous Systems under High Pressures, and a New, High-pressure, Reducing Valve. LUDWIG STUCKERT and MAX ENDERLI (*Chem. Zeit.*, 1913, **37**, 1288).—A description of the apparatus mentioned in the heading is given.

T. S. P.

Heat Content and Velocity of Reaction. MAX TRAUTZ (*Zeitsch. Elektrochem.*, 1913, **19**, 784—794).—A theoretical paper in which a theory of reaction velocity based on the energy content of the molecules is developed. The author postulates the existence of gaseous isomerides in any gas which are termed respectively the "cold modification" and the "hot modification." To the former type a molecular heat of $3/2R$ is attributed, and to the latter one of $5/2R$. Thus, considering one molecule of an ideal gas, of which the fraction x exists in the "hot modification," and $1-x$ in the "cold modification," and the heat of reaction at $T=0$ is Q_0, then the heat content of the system W is given by the equation: $W=(1-x)3/2RT+x(5/2RT+Q_0)=3/2RT+x(Q_0+RT)$. As a result of the hypcthesis the author gives reasons for doubting the monatomic nature of the rare gases, and even of doubting their elementary nature, mainly on account of the determinations of Scheel and Heuse (this vol., ii, 183), which show that the molecular heat of helium has a positive temperature-coefficient instead of being independent of temperature as a monatomic gas should be.

J. F. S.

Some Physico-chemical Applications of Maxwell-Berthoud's Equation of Re-distribution. GEORGES BAUME (*Compt. rend.*, 1913, **157**, 774—776.* Compare Berthoud, A., 1911, ii, 578).—A theoretical discussion of the factors governing reaction velocities as deduced from Berthoud's modification of Maxwell's equation. When the velocity of reaction is measurable, the number of active molecules is small, and the mean temperature of the system is sensibly different from that of the molecules, from which it results that: (1) The increase in the number of active molecules with rise in temperature increases with the molecular heat at constant volume C_v. (2) The velocity of reaction is, in general, doubled or tripled for a rise of 10° in temperature, this increase being greater as C_v is greater. (3) The active molecules have a velocity much nearer to the mean square velocity, the greater is C_v. (4) It is possible to state the process of chemical reactions according to the value of C_v. (5) Addition molecules can only be formed from molecules with low velocities.

W. G.

* and *Arch. Sci. phys. nat.*, 1913, [iv], **36**, 439—442.

Photochemical Kinetics of Hydrogen and Chlorine Combination. MAX BODENSTEIN and WALTER DUX (*Zeitsch. Elektrochem.*, 1913, **19**, 836—856; *Zeitsch. physikal. Chem.*, 1913, **85**, 297—328).—An apparatus is described by means of which the velocity of combination of hydrogen and chlorine in light of measured intensity has been measured. The hydrogen and chlorine are admitted and their pressures determined by means of a quartz glass manometer. Then the light is allowed to act for a stated time, and the amount of hydrogen uncombined is measured by freezing the chlorine and hydrogen chloride by cooling with liquid air, the pressure of the residual hydrogen then being determined. In this way it is shown that with a given light intensity, the velocity of the reaction is proportional to the square of the chlorine concentration, inversely proportional to the concentration of the oxygen which may be present, and independent of the concentration of the hydrogen chloride, water vapour, and hydrogen. In the case of the hydrogen this is only true so long as the concentration is not less than one-quarter that of the chlorine. The author then develops theoretically a scheme of the mechanism of photochemical reactions. The reactions are divided into two groups: (1) Primary; (2) Secondary. It is assumed that the absorption of light energy ionises the atoms into an electron and a positively charged residue. The reactions occurring between the positively charged residues and other molecules constitute primary reactions, and of these four characteristics are specified: (1) A proportionality exists between the amount of reaction and the absorbed light energy, and consequently a velocity equation is possible. (2) The reaction is independent of the concentration and nature of the impurities. (3) They are independent of the temperature; and (4) each molecule taking part in the change uses one quantum or a very small number of quanta of energy. The secondary reactions are those brought about by the free electrons attaching themselves to neutral molecules, and thereby inducing a reaction. The kinetics of the secondary reactions are developed mathematically, treating the electron as a chemical molecule. In this way it is shown that 10^6 chlorine atoms are caused to combine, while one positive chlorine residue combines. The author considers a large number of photochemical reactions which have been previously published. These he divides into primary and secondary processes, and shows that they can all be explained without further hypothesis on the present basis. It is further shown that reactions brought by electric discharge through gases or by radioactive radiations can be brought readily under the same scheme. J. F. S.

The Combustion of Gaseous Mixtures. J. TAFFANEL and LE FLOCH (*Compt. rend.*, 1913, **157**, 595—597. Compare this vol., ii, 574).—The authors have measured the rate of combustion of various mixtures of methane and air at temperatures inferior to their ignition points, and by use of formulæ have extrapolated their results to determine the ignition temperatures of these mixtures, the calculated results agreeing closely with those already found.

They have further calculated the temperatures of combustion of mixtures containing from 3 to 6% of methane, and find that in all cases it is in the neighbourhood of 1310°. W. G.

The Combustion of Gaseous Mixtures and the Velocities of Reaction. J. TAFFANEL (*Compt. rend.*, 1913, **157**, 714—717).—A theoretical and mathematical discussion of results already published (compare Taffanel and Le Floch, this vol., ii, 574). W. G.

The Extinction of Flames. WILLEM P. JORISSEN (*Chem. Weekblad*, 1913, **10**, 961—962).—A criticism of the results obtained by Harger ("Coal, and the Prevention of Explosions and Fires in Mines") in investigations of the limits of explosion of paraffins, acetylene, and coal-gas. A. J. W.

Velocity of the Reaction between Sulphuric Acid and Acetone. ROBERT KREMANN and HERBERT HÖNEL (*Monatsh.*, 1913, **34**, 1469—1487).—Since no variation in titration values occurred when acetone and anhydrous sulphuric acid were mixed at 0°, even after some hours, the possibility of the formation of a monobasic mesitylsulphuric acid was negatived. The action of sulphuric acid on acetone is therefore entirely that of the elimination of water, but it was required to know whether the acid acted dynamically and became hydrated, or as a catalyst.

The reaction was studied by measuring the conductivity of sulphuric acid in excess of acetone at 0°, immediately after mixing, and at different intervals. Assuming that the dielectric constant of mesityl oxide is about the same as acetone, that is, much less than that of water, and that the concentration of acetone remains practically constant, it follows that the increase of conductivity is proportional to the amount of water formed. In the first place, the initial conductivity of sulphuric acid in various mixtures of water and acetone was measured. Anhydrous acid was dropped into the mixture in a freezing-bath, and then placed in an ice thermostat, when the conductivity was determined, and finally the concentration of acid was obtained by titration. One series of curves shows the relation between the conductivity and the concentration of acid in pure and in each diluted acetone. From these, another series was obtained, which shows the relation between conductivity and water-content for such concentrations of acid as were chosen for the further kinetic experiments. In the case of moderate concentrations of acid (up to $0{\cdot}5N$), the conductivity rises quickly at first with the water concentration. From 1 to 3 grams of water per 100 c.c., however, the conductivity remains almost constant, after which it rises again. This is, no doubt, due to the formation of a hydrate taking pre-eminence in this region.

The conductivity of different mixtures of sulphuric acid and acetone was then measured at different intervals, and from the above curves the amount of water formed was obtained. Curves connecting this quantity with time, for each concentration of acid, are given. They show that the speed of the reaction rises with

the concentration, and that the equilibrium point is also dependent on the concentration of acid. This indicates that the reaction is not catalytic, but follows the course:

$$2\text{Acetone} + H_2SO_4 \longrightarrow H_2SO_4,H_2O + \text{Mesityl oxide}.$$

The amount of water formed in a short time (fifteen minutes) in a normal solution of sulphuric acid in acetone, at 0°, is practically negligible. J. C. W.

Neutral Salt Action on the Change Acetochloroanilide ⟶ *p*-Chloroacetanilide in the Presence of Hydrochloric Acid. ALBERT C. D. RIVETT (*Zeitsch. physikal. Chem.*, 1913, **85**, 113—128. Compare this vol., ii, 202).—The reaction constants of the change acetochloroanilide ⟶ *p*-chloroacetanilide in the presence of hydrochloric acid have been measured in solutions to which chlorides of the metals lithium, sodium, potassium, rubidium, cæsium, ammonium, magnesium, calcium, barium, strontium, and zinc have been added. The experiments were carried out at a number of concentrations, and a series of measurements was also made in the presence of sulphuric acid. It is shown that the velocity constant k can be obtained by means of the formula:

$$k = [HCl]\{0{\cdot}050 + a[H^{\cdot}] + b[Cl'] + d[M^{\cdot}]\},$$

where a, b, and d are specific constants depending on the nature of the ions. It is shown that change of temperature is without effect in the cases examined. Ammonium chloride behaves abnormally; this is explained on the basis of the theory of Orton and Jones (T., 1909, **45**, 114). The relationship between the concentration of the hydrochloric acid and the velocity of the reaction is discussed. J. F. S.

The Retarding Action of Small Quantities of Water on the Decomposition of Diazoacetic Esters in Alcoholic Solution. I. W. S. MILLAR (*Zeitsch. physikal. Chem.*, 1913, **85**, 129—169).—The velocity of the decomposition of diazoacetic ester by picric acid in ethyl, methyl, and *iso*butyl alcohol solutions has been determined. The influence of the addition of small quantities of water to the alcoholic solutions retards the reaction in a very marked degree, the action being greatest in *iso*butyl alcohol, and least in methyl alcohol. On increasing the concentration of the water, the velocity sinks until a minimum value is reached, which in the case of methyl alcohol occurs at a concentration of 10 mols. of water per litre of mixture, and with ethyl alcohol at 6 mols. per litre. The constants calculated for the reaction on the unimolecular basis slowly decrease, and this is shown by electrical conductivity measurements to be due to a reaction between the picric acid and the solvent. It is also shown that there is a proportionality between the velocity of the reaction and the electrical conductivity in these cases. It is shown that up to a water concentration of 0·6% in ethyl alcohol the reaction is unimolecular, but at this point the water as well as the alcohol react with the diazo-ester. The hydrogen ion alcoholate is assumed, as in the case of esterification (Goldschmidt, A., 1912, ii, 1154), and the hydrolytic constant v is calculated.

This is found to be 0·57 for methyl alcohol; 0·26, ethyl alcohol; and 0·12 for *iso*butyl alcohol. In the case of ethyl alcohol, taking account of the change in the ionisation of picric acid by the addition of water, it is found to be 0·15. J. F. S.

The Retarding Action of Small Quantities of Water on the Decomposition of Diazoacetic Esters in Alcoholic Solution. II. HERMANN BRAUNE (*Zeitsch. physikal. Chem.*, 1913, **85**, 170—210. Compare preceding abstract).—The velocity of the decomposition of the methyl and ethyl diazoacetic esters in ethyl alcohol by trichloroacetic acid, 2 : 4 : 6-trinitrobenzoic acid, sulphosalicylic acid, and trichlorobutyric acid has been determined at 25°. The influence of the addition of small, measured quantities of water on the reaction constant has also been studied. It is shown that the addition of water retards the reaction, and to about the same extent in every case if the change in the ionisation of the catalysing acid is considered. Up to a water concentration of 0·3 mol. per litre the results for the catalysis agree with the values calculated from Goldschmidt's formula: $k(r+n)=C$ (A., 1912, ii, 1154). According to Goldschmidt's theory, the dimensions of r should be the same for all acids and substances catalysed by those acids, and this condition is fulfilled in the case of the acids used in the present investigation, although the value of r for trichlorobutyric acid is somewhat larger than in the other cases. The reaction is shown not to be a simple hydrogen ion catalysis, for the velocity constant increases more rapidly than the concentration of the hydrogen ion. The amount of divergence from strict proportionality between the reaction constant and the hydrogen concentration is different in every case, and appears to be specific for each acid. The divergence is supposed to be due to the presence of side reactions, and an attempt is made to substantiate the assumption by means of reactions in the presence of neutral salts. Reactions were therefore carried out in the presence of aniline trichloroacetate, the results of which confirm the above assumption, and also confirm the analogy between the diazo-ester catalysis and the catalytic esterification as explained by Goldschmidt. It is also shown that the reaction between the diazo-ester and the catalysing acid is retarded by water. J. F. S.

The Influence of Alcohol and of Sucrose on the Rate of Solution of Cadmium in Dissolved Iodine. RALPH G. VAN NAME and D. U. HILL (*Amer. J. Sci.*, 1913, [iv], **36**, 543—554).—The effect of various concentrations of ethyl alcohol (0·25—3 molar) and of sucrose (1/32—1 molar) on the rate of solution of cadmium in an iodine–potassium iodide solution has been measured at 25°. Since in such processes of dissolution in purely aqueous solutions it has been shown that the rate of diffusion at the metal surface is the determining factor (A., 1911, ii, 973), it follows, assuming that the thickness of the diffusion layer is not affected by the concentration of the non-electrolyte, that the results in aqueous solutions containing non-electrolytes

should be in accordance with Arrhenius's equation for the effect of non-electrolytes upon the rate of diffusion of electrolytes, namely, $D = D_0(1 - ma/2)^2$, where D_0 and D are respectively the diffusion coefficients of the electrolyte in solution in pure water, and after the addition of the electrolyte, m is the molar concentration of the non-electrolyte, and a is a constant. The effect of the non-electrolyte on the reaction velocity above-mentioned should be in accordance with this equation, substituting the velocity constants for D_0 and D.

With alcohol, the observed velocity constants agree well with the constants calculated from Arrhenius's equation if an arbitrary, although, so far as can be judged by analogy, not impossible, value is chosen for the constant a. With sucrose no value of a gives a good agreement.

In both cases, but especially in that of sugar, the diminution of the reaction velocity appears to be larger than would be expected from the available diffusion data.

The probable effect of an increase in viscosity in increasing the thickness of the diffusion layer is discussed, and is suggested as a possible explanation of the discrepancies. T. S. P.

The Influence of Foreign Substances on the Activity of Catalysts. II. Experiments with Palladium as Hydrogen Carrier. CARL PAAL and ARTHUR KARL (*Ber.*, 1913, **46**, 3069—3076).—In a previous communication (A., 1911, ii, 479), the authors have investigated the behaviour of palladium as hydrogen carrier in the presence of metals, and have found that only magnesium, nickel, and cobalt are without influence on the catalytic effect of the palladium, whilst aluminium, iron, copper, zinc, tin, silver, or lead behave as anti-catalysts. The present paper deals with the action of compounds of these elements.

The compounds were coated with palladium by treating them with a faintly acid solution of palladium chloride, whereby a thin film of palladium hydroxide is formed. After washing and drying, the products were moistened with ether, and the palladium hydroxide reduced by hydrogen at the ordinary temperature. Their action as hydrogen carriers in the reduction of liquid unsaturated esters was investigated in the apparatus described by Paal and Gerum (A., 1908, ii, 392).

The authors are led to the conclusion that those metals which have an anti-catalytic influence on palladium show a similar action when used in the form of their oxides, hydroxides, or carbonates. This is most distinctly shown by palladianised basic lead carbonate, which, like the metal, absolutely destroys the catalytic activity of palladium in all circumstances. Palladianised cadmium carbonate, zinc oxide, zinc carbonate, ferric hydroxide, and aluminium hydroxide, like the palladianised metals, are either incapable or only slightly capable of acting as hydrogen carriers to unsaturated organic compounds at the ordinary pressure, whilst, at higher pressures and temperatures, they cause a slight hydrogenation. On the other hand, magnesium oxide, like magnesium itself, does not

inhibit the catalytic action of the palladium; hydrogenation even appears to proceed more rapidly in the presence of the oxide than of the metal, doubtless due to the larger surface exposed. H. W.

The Influence of Neutral Salts on Catalytic Reactions in Various Solvents. H. C. S. SNETHLAGE (*Zeitsch. physikal. Chem.*, 1913, **85**, 211—262).—The influence of the addition of picrates of *p*-toluidine, tripropylamine, β-naphthylamine, carbamide, *o*-aminobenzoic acid, acetoxime, acetamide, *p*-nitroaniline, acetanilide, *o*-nitroaniline, and propionitrile has been determined for the decomposition of diazoacetic ester in absolute alcohol in the presence of picric acid. It is shown that the catalytic action of picric acid is reduced by the addition of picrates, and that the value of the velocity constant converges to a value which is different from zero. This is attributed to the catalytic action of the undissociated acid. A formula of hyperbolic nature is deduced, by means of which the velocity constant can be calculated from the concentration of the added salt. This formula has the form $k = \{\gamma . k_H + (1 - \gamma)k_M\}C$, in which C is the concentration of the salt in equivalents per litre, k_H the velocity constant in a solution containing one equivalent of hydrogen ions, k_M the velocity constant for a solution containing one equivalent of undissociated acid, and γ the degree of dissociation. The formula holds for 0·00909*N*-picric acid and the three salts, *p*-toluidine picrate, tripropylamine picrate, and β-naphthylamine picrate. The above-mentioned three picrates retard the reaction by the same amount when present in the same concentration, and when present in the absence of free acid have no catalytic action. The other bases mentioned above, when added to an equivalent quantity of picric acid, also decrease the velocity constant of 0·00909*N*-picric acid decomposition, but to a much smaller extent, which is different in the different cases. This points to an "alcoholysis" of the picrates. In the case of carbamide picrate, it is shown in one case that the velocity constant increases proportionally to the square-root of the salt concentration. A formula is deduced by means of which the value of k_M can be calculated, and it is shown that the calculated and observed values of k_M agree satisfactorily. The velocity constant of the acid catalysed reaction can be calculated if the value of γ (determined from electro-conductivity), k_M and k_H are known. The velocity constant in the calculation is regarded as the sum of two factors, one proportional to the hydrogen ion concentration, and the other proportional to the undissociated acid. The values of k_M and k_H are calculated for a number of reactions in ethyl alcohol, methyl alcohol, and water from previously published work of the author (A., 1912, ii, 749), Goldschmidt (A., 1912, ii, 1154), and others. In the cases examined it is shown that the ratio k_M/k_H is larger for acids with a large affinity constant, and smaller for those with a small affinity constant. If reactions of the same type occur in a stated solvent and are catalysed by the same acid, then the value k_M/k_H is constant even when the absolute values of k_M and k_H are very different. When the acid is used to catalyse reactions of

different types the ratio k_M/k_H is in most cases practically identical for both reactions. There is obviously a close relationship between k_M/k_H and the affinity constant of the acid, which is but little influenced by the solvent. The value of k_M/k_H for the strongest acids is approximately unity in ethyl alcohol and methyl alcohol solutions, so that in these solutions the velocity constant is approximately proportional to the total concentration of the acid (dissociated + undissociated). The strong acids in water solution have a value greater than unity, and this offers a possible explanation for the increase in the velocity of the inversion of sucrose on the addition of neutral salts. J. F. S.

In Commemoration of the Centennial of the Publication of the Berzelian System of Symbols. HENRY LEFFMANN (*J. Amer. Chem. Soc.*, 1913, **35**, 1664—1666).—A translation of Berzelius' original paper on "The chemical signs and the method of employing them to express chemical proportions." T. S. P.

Constitution and Structure of the Chemical Elements. HAWKSWORTH COLLINS (*Chem. News*, 1913, **108**, 235—236).—The author claims to have anticipated certain recent observations relating to the connexion between the different elements. In reference to elements of atomic weight less than 60, it is pointed out that the valency of an element is even or odd according to whether its atomic weight approximates or is nearer to an even or odd whole number. Nitrogen is regarded as a possible exception. H. M. D.

Theory of a Nuclear Homology in the Periodic System. DAN RADULESCU (*Chem. Zentr.*, 1913, ii, 922; from *Bull. Soc. Ştiinţe, Bucureşti*, 1913, **20**, 500—513).—The author puts forward views relating to the constitution of the atoms and the interpretation of the periodic system. It is supposed that every element of higher atomic weight consists of two parts, which are distinguished as the "characteristic function" and the "homology nucleus." The "characteristic functions" of the heavier elements are closely related in mass and properties to those of the typical elements hydrogen, helium, oxygen, carbon, nitrogen. In accordance with this, values are assigned to the "proto-elements," from which the characteristic functions are derived, which represent sub-multiples of the atomic weights of the typical elements. The homology results from the successive addition of certain structural nuclear elements which are regarded as derived from hydrogen and helium. H. M. D.

Constitution of Atoms and Molecules. III. N. BOHR (*Phil. Mag*, 1913, [vi], **26**, 857—875. Compare this vol., ii, 689, 943).—The author's theory relative to atomic structure is further developed and applied to molecules. The idea that the atoms are formed by successive binding of a number of electrons cannot be utilised in considering the formation of a system containing more than a

single nucleus, for in the latter case there is nothing to keep the positively charged nuclei together during the binding process. It must therefore be assumed that molecules are formed by the interaction of systems, each containing a single nucleus, which have already bound a number of electrons.

The simple case of a system consisting of two nuclei and of a ring of electrons rotating round the line connecting them is discussed in detail with special reference to the constitution of the hydrogen molecule, and a simple method of procedure is indicated by which it is possible to follow, step by step, the combination of two atoms to form a molecule. The views put forward lead to the conclusion that the breaking up of a hydrogen molecule in consequence of the slow separation of the nuclei will result in the production of two neutral atoms, and not of a positively and a negatively charged atom. This is in agreement with deductions drawn from observations on the behaviour of positive rays.

Indications are also given of the configurations to be expected for systems containing a greater number of electrons, and the paper concludes with an explicit statement of the assumptions which are made in connexion with the author's theory. H. M. D.

A New Mechanical Agitator for Laboratory Use. VICTOR GRIGNARD (*Bull. Soc. chim.*, 1913, [iv], **13**, 952—955).—The apparatus is designed for use in cases where a reagent is to be added with constant agitation, and where it may be necessary to use a reflux condenser. It consists of a circular plate of iron or copper, 30 cm. in diameter, and pierced with three holes 10 cm. in diameter, in which flasks can stand. The plate is covered with asbestos board, and can rotate about its vertical axis on a pivot fixed to the base of a heavy retort stand. The plate is put in motion by a crank connected to the periphery of the plate, and actuated from a small water motor. If a flask with a reflux condenser and a supply tube is to be used, the two latter are connected to the flask by a T-piece and supported loosely in a ring attached to the rod of the retort stand. The plate is provided with clips in which closed bottles can be held for agitation. The apparatus is figured in the original. T. A. H.

A Microfiltration Method by Centrifugal Force. CASIMIR STRZYZOWSKI (*Österr. Chem. Zeit.*, 1913, [2], **16**, 123—124).—A sketch, with description of an apparatus employed for filtering minute quantities of liquids by suction or centrifugal force. F. M. G. M.

A New Form of Condenser. PIETER J. MONTAGNE (*Chem. Weekblad*, 1913, **10**, 960—961).—A modification of the ordinary form of condenser, both ends of the inner tube being bent so that they are vertical when the condenser is clamped at an angle of 30° to the horizontal. By attaching a flask to the lower end a reflux condenser is obtained; by transferring it to the other end, an ordinary distillation can be effected. A. J. W.

Extraction Apparatus. MAURICE FRANÇOIS (*J. Pharm. Chim.* 1913, [vii], **8**, 409—410 *).—The apparatus consists of a wide tube provided with a stem which is attached to the flask holding the solvent; the top of the tube is connected with a reflux apparatus. A separate, narrow tube is placed down the centre of the wide tube; the lower end of this narrow tube is expanded slightly, and fits over the upper end of the stem, whilst the top is closed by a conical bulb having a small hole at its lower edge. A small layer of cotton-wool is packed round the base of the narrow tube, the material to be extracted is placed above this layer, and in the space between the narrow tube and the wall of the wide tube, and covered with a second layer of cotton-wool. The vapours of the solvent pass from the flask up the narrow tube into the condenser, and the condensed liquid falls thence on to the material and returns to the flask. W. P. S.

Inorganic Chemistry.

Triatomic Hydrogen Molecules. JOHANNES STARK (*Zeitsch. Elektrochem.*, 1913, **19**, 862—863).—A theoretical paper in which the constitution of the triatomic hydrogen molecule is discussed on the basis of Stark's valency hypothesis. A method is proposed for obtaining triatomic hydrogen with the object of examining it chemically (compare also Stark, this vol., ii, 901; Thomson, A., 1912, ii, 885; this vol., ii, 502, 820). J. F. S.

Displacement of Acids by Hydrogen Peroxide. JOACHIM SPERBER (*Chem. Zentr.*, 1913, ii, 1195—1196; from *Schweiz. Woch. Chem. Pharm*, 1913, **51**, 469—472).—If solutions of potassium ferrocyanide or ferricyanide are evaporated in presence of hydrogen peroxide, the corresponding acids are set free. Hydrogen sulphide is liberated readily from the alkali metal sulphides, and also, although less readily, from the alkaline earth metal sulphides. Ammonium hydrogen sulphide gives rise to hydrogen sulphide and traces of ammonia, but oxygen is not set free. If polysulphides are present, sulphur is deposited. H. M. D.

Fluorine is a Constant Element in the Emanations from the Earth's Centre. ARMAND GAUTIER (*Compt. rend.*, 1913, **157**, 820—825).—In support of his view that fluorine is to be found in all rocks, thermal waters, and vapours coming from the earth's core, the author has examined the vapour obtained from fumerole fissures in the crater of Vesuvius, and also hot water obtained from a sounding hole 150—170 metres deep at Larderello, in Tuscany. In the gas from Vesuvius he found 0·110 mg. of fluorine per litre measured at 760 mm., whilst in the condensed water from

* and *Anal. Falsif.*, 1913, **6**, 608—609.

the boric acid containing vapours of Tuscany he found 3·72 mg. per litre, a value closely in accord with the fluorine content of the mineral waters from Vichy and Luxeuil. W. G.

New Method of Preparing Colloidal Sulphur and Selenium. JULIUS MEYER (*Ber.*, 1913, **46**, 3089—3091. Compare Jannek, this vol., ii, 948).—Sulphur and selenium are readily soluble in concentrated hydrazine hydrate, forming viscous, deeply coloured solutions. In this case, definite chemical change occurs, probably in accordance with the equations:

$$3NH_2\cdot NH_3\cdot OH + 3S = 2H_2N\cdot NH_3\cdot SH + H_2N\cdot NH_3\cdot SO_3H, \text{ or}$$
$$6NH_2\cdot NH_3\cdot OH + 3S = 2(H_2N\cdot NH_3)_2S + (H_2N\cdot NH_3)_2SO_3 + 3H_2O.$$

If the solution of selenium is cautiously acidified after a few days, the odour of hydrogen selenide is very obvious, whilst Lobry de Bruyn (A., 1895, ii, 496) has shown that the similar solution of sulphur smells of hydrogen sulphide.

The selenium solution, when largely diluted, gives an intensely red solution, which is extraordinarily stable; it may be preserved unchanged for months, and is unaltered by prolonged boiling. On preservation, minute quantities of red selenium separate, which, however, disappear when the solution is agitated. The sulphur solution, when similarly treated, yields immediately a clear, lemon-yellow solution, which becomes yellowish-white owing to the formation of colloidal sulphur. In the concentrated condition, the sulphur solution is not so stable as the selenium solution. The solutions cannot be dialysed. H. W.

Crystallised Sulphuric Acid, H_2SO_4,H_2O. A. D. DONK (*Chem. Weekblad*, 1913, **10**, 956—957).—When cooled with ice, a mixture of 84—85% sulphuric acid with a large excess of sulphate of lead or barium deposits crystals of the monohydrate, H_2SO_4,H_2O.
A. J. W.

Crystallised Sulphuric Acid and its Hydrate. WILLEM P. JORISSEN (*Chem. Weekblad*, 1913, **10**, 962—963. Compare preceding abstract).—A rapid crystallisation of the monohydrate of sulphuric acid is induced by cooling 83·3—84% sulphuric acid with ice.
A. J. W.

New Determination of the Atomic Weight of Selenium. JULIUS MEYER (*Zeitsch. Elektrochem.*, 1913, **19**, 833—835).—Selenium is quantitatively oxidised in a quartz bulb by passing a stream of nitrogen peroxide and oxygen over it at 215°. The last traces of nitrogen peroxide are removed by distilling the selenium dioxide repeatedly in the same bulb. A mean of five experiments gives the value for selenium: Se = 79·135. As a control of the method the selenium dioxide was reduced by hydrazine hydrate, and it was found that the quantity of selenium used in an experiment could be entirely regained from the reduction experiment. Incidentally it is shown that both crystalline and amorphous selenium are soluble to a considerable extent in concentrated hydrazine hydrate solution,

producing thereby stable selenium sols, which are easily precipitated by hydrochloric acid. A series of vapour pressures of selenium dioxide and selenious acid at temperatures 20—320° are given, thus showing that the conversion of selenious acid into selenium dioxide by heat is not suitable for the determination of the atomic weight of the element. J. F. S.

Hydrogen Selenide and Hydrogen Telluride as Acids. LUDWIK BRUNER (*Zeitsch. Elektrochem.*, 1913, **19**, 861).—A decinormal solution of hydrogen selenide under atmospheric pressure is dissociated to the extent of 4·1%, and has an affinity constant of $1{\cdot}7 \times 10^{-4}$. A solution of hydrogen telluride $0{\cdot}01N$, in the absence of air, has a specific conductivity of 2×10^{-3}, and at this concentration is 50% dissociated. If a bubble of oxygen is allowed to enter the conductivity-vessel, the hydrogen telluride is at once decomposed with the deposition of tellurium, and the conductivity at once falls to almost zero, proof that the original conductivity is due to the hydrogen telluride. From these experiments it is shown that the elements of the fifth group of the periodic system increase in their acidic character with increase in the atomic weight. This is shown by the series H_2O, H_2S, H_2Se, H_2Te.

J. F. S.

The Oxidation of Nitrogen in the Electric Discharge. ADOLF KOENIG and E. ELŐD (*Ber.*, 1913, **46**, 2998—3009).—The reply of Fischer and Hene (this vol., ii, 317) to the criticism by König (this vol., ii, 210) of their interpretation of their results on the combination of nitrogen and oxygen (this vol., ii, 132) is stated to be unconvincing.

The authors have made experiments similar to those of Fischer and Hene, with a spark discharge between iron electrodes, but with a somewhat larger chamber constructed of glass for the discharge. Their results indicate that in spite of special precautions to prevent the second gas diffusing back into the one which is being submitted to the discharge, such diffusion does occur, probably aided by inevitable eddies in the chamber. In a check experiment in which nitrogen was submitted to the discharge, and then, passing into the exit-tube from the chamber, was mixed with an entering stream of methane, the spectrum of the discharge soon showed the presence of cyanogen in the chamber, and the collected gases contained hydrogen cyanide.

The view is still held that in the combination of nitrogen and oxygen under the influence of the electric discharge, probably both the reacting gases become activated before combination ensues.

D. F. T.

Oxidation of Nitrogen and Oxygen. WILLIAM W. STRONG (*Amer. Chem. J.*, 1913, **50**, 204—212).—Strutt (A., 1911, ii, 482; 1912, ii, 126) and Strutt and Fowler (A., 1911, ii, 678; 1912, ii, 214) have investigated reactions in which nitrogen is involved. The method consists in producing modifications of various sub-

stances in the electrical discharge and studying the spectra of the after-glows. The after-glow in air is regarded as probably due to the oxidation of nitric oxide by ozone.

It has been considered probable that the electrical method may be of service in elucidating the mechanism of formation of ozone and nitric oxide, and the author has therefore carried out some preliminary experiments with the corona discharge, this method enabling the ionic streams to be partly controlled. E. G.

Flames Containing Nitric Oxide. ALFRED REIS and OLGA WALDBAUER (*Zeitsch. physikal. Chem.*, 1913, **85**, 62—98).—Steadily burning flames have been produced from a mixture of the gases methane, oxygen, and nitric oxide. These flames could be separated into their two cones, which burnt quietly even when the proportions of the gases were varied over wide limits. It is shown in the case of flames containing small percentages of nitric oxide, that the gases coming from the inner cone contain ammonia, acetylene, and hydrogen cyanide. An examination of the composition of the gases between the two zones at different heights above the inner cone shows that the hydrogen cyanide decreases with increasing height, whilst the ammonia rises to a maximum and then falls, thus showing that the ammonia is formed from the hydrogen cyanide. In the case of mixtures containing a high percentage of nitric oxide, the inner cone shows the characteristic appearance of substances burning in nitrogen peroxide. The temperature, light emission, and velocity of explosion of this inner cone are investigated. It is shown that in the combustion in this inner cone 90% of the nitrogen peroxide is transformed into nitric oxide, which then passes out of the inner cone unchanged; about 33%—25% of the methane also escapes from the inner cone unburnt. The hydrogen is almost completely oxidised, but the carbon monoxide is only oxidised to a very small extent. Measurable quantities of formaldehyde are to be found in the gases between the two zones. The gaseous mixture between the zones consists of about 40% of nitric oxide with combustible gases and water vapour. Analysis of the gases between the zones at various heights shows that the nitric oxide is slightly decomposed, but that the methane is unchanged: the concentration of hydrogen increases whilst that of the carbon monoxide falls. When the gases between the two zones contain sufficient oxygen, a new cone appears between the inner and outer cones; this is termed the middle cone, and in it the combustible gases are burnt at the expense of the nitric oxide.
J. F. S.

Explosion of Nitrogen Iodide Under the Influence of Acoustic Waves. ERNST BECKMANN and OTTO FAUST (*Ber.*, 1913, **46**, 3167—3168).—Champion and Pellet (this Journ., 1872, 874; 1873, 31) claim to have exploded nitrogen iodide by means of acoustic waves. It is now shown that nitrogen iodide cannot be detonated even with a wide range of acoustic vibrations.
E. F. A.

Ammonium Peroxides. JOHANNES D'ANS and O. WEDIG (*Ber.*, 1913, **46**, 3075—3076. Compare Melikov and Pissarjevski, A., 1898, ii, 161, 219, 292).—When dry ammonia is passed into a solution of pure hydrogen peroxide in absolute ether which is cooled to about $-10°$, crystals of ammonium hydroperoxide, NH_4O_2H, separate, which, in the presence of a further quantity of ammonia, disappear with the formation of an oily layer. The latter solidifies with some difficulty at about $-40°$, and yields *ammonium peroxide*, $(NH_4)_2O_2$, which commences to decompose with evolution of gas at $-10°$, and has m. p. about $-2°$. It readily loses ammonia, forming ammonium hydroperoxide if the temperature is not allowed to rise too high.

Ammonium hydroperoxide has m. p. about $+14°$ (decomp.) instead of $-20°$ as given by Melikov and Pissarjevski. H. W.

Modifications of Phosphorus. ALFRED STOCK and ERICH STAMM (*Ber.*, 1913, **46**, 3497—3513).—Hittorf's phosphorus, prepared according to the method of Stock and Gomolka (A., 1910, ii, 30), does not conduct electricity, and there are no sufficient reasons for calling it "metallic phosphorus." In the purification, the lead dioxide produced during electrolysis should be removed by levigation before the treatment with hydrochloric acid. Hittorf's phosphorus is volatile at 280°, whereas only traces of red phosphorus volatilise at that temperature.

In contradiction to Smits and Leeuw (A., 1911, ii, 263), it is found that the melting point of colourless phosphorus is not altered by heating it to 100°, followed by rapid cooling.

Red phosphorus, formed by heating pure, colourless phosphorus at 300°, may be made to melt at temperatures varying from 579° to 601°. The various phenomena observed indicate that the melting point is affected by displaceable equilibria which exist between different modifications of phosphorus; it is, for example, possible to maintain a dark modification in contact with a clear fusion for hours together at about 545°.

In contradistinction to the statements of Arctowski (A., 1896, ii, 559), red phosphorus is not appreciably volatile at 100°, or even at 200°. The vapour from red phosphorus heated at 280—400° condenses partly as red phosphorus. Hittorf's phosphorus at 300—350° gives a vapour which condenses as colourless phosphorus, even when the vapour is subjected to intermediate heating at 500°. Colourless phosphorus also gives a colourless distillate; it follows that the vapour of red phosphorus must contain molecules of the red modification, which is in accordance with the fact that under appropriate conditions red phosphorus can be sublimed in the crystalline form (Stock, Schrader, and Stamm, A., 1912, ii, 639).

Attempts were made to see if there was a relation between the dissociation of phosphorus vapour, and the amount of red phosphorus formed when the vapour is quickly condensed, since it has previously been shown (Stock, Schrader, and Stamm, *loc. cit.*) that the polymerisation of P_2 to P_4 molecules is a slow process. The

vapour was heated in a tube at 900°, and then carried, by a stream of nitrogen, into a cold part of the tube, where it condensed partly as red and partly as colourless phosphorus. The latter could then be separated by distillation at 200—250°, and the relative amounts of the two forms determined by weighing. The results were not concordant, but nevertheless indicated that more red phosphorus is formed than corresponds with the dissociation into P_2-molecules, that is, that the P_4-molecules also take part in the formation of red phosphorus, possibly in accordance with the equation: $xP_2 + yP_4 = P_{(2x+4y)}$. That P_2-molecules take part in the formation of red phosphorus cannot be doubted, since phosphorus vapour heated at 1200° under 5 mm. pressure gives a deposit of red phosphorus which does not contain more than 1% of colourless phosphorus.

The proportion of red phosphorus formed from phosphorus vapour at 300° was determined. Colourless phosphorus was distilled into narrow, short tubes, in such quantity that it was completely vaporised at the temperature of the experiment. On prolonged heating red phosphorus deposited on the walls of the tube, even if the tubes had been heated previously to 1000°, in order to destroy all nuclei of red phosphorus. The results were affected by the fact that the surface of the tubes had a catalytic effect on the formation of red phosphorus, but comparative experiments showed that the quantity of red phosphorus formed diminishes as the pressure decreases; below pressures of about half-an-atmosphere, no red phosphorus is produced.

When the tubes contained so much colourless phosphorus that it did not all vaporise at 300°, the liquid remaining rapidly changed into loose, red phosphorus, which then became more compact, by reason of red phosphorus depositing from the vapour into the pores. This explains the "cementation" of phosphorus first observed by Lemoine in 1871.

The authors discuss the above and other results from the point of view that the following two equilibria exist: $P_4 \rightleftarrows 2P_2$ and $xP_2 + yP_4 \rightleftarrows P_{(2x+4y)}$, assuming, in accordance with the experimental evidence, that the polymerisation of P_2 to P_4-molecules takes place relatively slowly, whilst the formation of red phosphorus $[P_{(2x+4y)}]$ takes place rapidly. T. S. P.

Vaporisation of Phosphorus in Oxygen and Other Gases. MIECZYSLAW CENTNERSZWER (*Zeitsch. physikal. Chem.*, 1913, **85**, 99—112).—It is shown that phosphorus volatilises in pure oxygen without oxidation in just the same way as it does in other gases, and thus obeys Dalton's law of partial pressures. The vapour pressure of phosphorus in oxygen, hydrogen, carbon dioxide, and coal-gas has been determined at low temperatures. The method consists in leading the dry pure gases in measured quantities slowly over three porcelain boats containing sticks of specially purified phosphorus. Similar experiments were made in air, in which a little iodobenzene vapour was contained. The following values were obtained: oxygen at 20°, $p = 0{\cdot}0251$ mm. mercury; hydrogen

at 20°, $p=0.0253$ mm.; 25°, $p=0.0426$ mm.; 30°, $p=0.0724$ mm.; 35°, $p=0.0889$ mm.; 40°, $p=0.1221$ mm.; carbon dioxide at 20°, $p=0.0312$ mm.; coal gas at 20°, $p=0.0242$; and in air at 20°, $p=0.0253$. It is shown that the presence of those gases and vapours which prevent the oxidation of phosphorus have no effect on its vaporisation. Qualitative experiments are carried out with a large number of organic vapours to investigate the cause of their negative catalytic action on the oxidation of phosphorus. It is shown that the iodine substitution products are particularly active in this respect; the action is attributed to the presence of free iodine, for it is shown that iodine itself has the same action. Two substances, nitrobenzene and diphenylamine, work positively in catalysing the oxidation of phosphorus. If a drop of these substances is brought in contact with phosphorus in air, the glow is strengthened, and almost immediately the phosphorus bursts into flame. J. F. S.

Oxidation of Arsenious and Antimonious Oxides. PERCY EDGERTON (*J. Amer. Chem. Soc.*, 1913, **35**, 1769—1770).—In contradistinction to Tingle (A., 1911, ii, 1086), the author finds that arsenious and antimonious oxides do not undergo oxidation when aqueous-alcoholic solutions are boiled for some time. T. S. P.

Boron Hydrides. III. Solid Boron Hydrides; the Hydride B_2H_6. ALFRED STOCK, KURT FRIEDERICI, and OTTO PRIESS (*Ber.*, 1913, **46**, 3353—3365).—It has already been shown (Stock and Friederici, this vol., ii, 699) that the boron hydride, B_4H_{10}, is readily decomposed at 100°, with the formation of the hydride, B_2H_6. This decomposition also takes place, but not so readily, under the action of ultra-violet light.

In addition to the properties of the hydride, B_2H_6, which have already been given (*loc. cit.*), other properties are mentioned in this paper. Among these may be noted: m. p. −169°; in the presence of air it gives solid boron compounds containing oxygen; it reacts with bromine (in carbon disulphide solution), but not with dry hydrogen chloride; with water it reacts so much more slowly than the hydride, B_4H_{10}, that a mixture of the two gases may be analysed by treatment with water.

When the hydride, B_4H_{10}, is heated for four to five hours at 100°, or the hydride, B_2H_6, for forty-eight hours at 115—120°, a volatile solid *hydride*, $B_{10}H_{14}$, is formed, together with a non-volatile, colourless, solid *hydride*, and a non-volatile, yellow *hydride*.

The hydride, $B_{10}H_{14}$, is a colourless substance, with a penetrating, peculiar odour, which is not similar to that of the gaseous hydrides. It sublimes in a vacuum, giving centimetre-long needles, or else compact crystals, m. p. 99·5°, D 0·94. Decomposition of the fusion commences at 200°, and at higher temperatures yellow products are formed. The vapours can be heated at 400° for a short time without appreciable decomposition, but at 600—700° decomposition into boron and hydrogen takes place. No decomposition of the solid substance takes place on exposure to the air, although the

vapours slowly react, giving the odour of B_4H_{10}. It is not attacked by water, even by boiling water, but dissolves in sodium hydroxide, giving an intense yellow solution. When kept for several days at room temperature, in the absence of air, some decomposition takes place.

The two non-volatile solid hydrides mentioned above can be separated from each other by the fact that the colourless hydride is soluble in carbon disulphide, the yellow hydride being insoluble. The former probably contains 12 atoms of boron to the molecule; it is stable towards water, and dissolves in sodium hydroxide to a yellow solution. On heating at 150° it gives the yellow hydride, which is soluble, with decomposition, in water, and probably has the atomic ratio 5B : 4H.

In the course of the investigation, other boron hydrides have been detected, but they have not yet been sufficiently investigated.

T. S. P.

The Hydrothermal Formation of Silicates. PAUL NIGGLI and GEORGE W. MOREY (*Zeitsch. anorg. Chem.*, 1913, **83**, 369—416).—A review of previous work on the hydrothermal formation of silicates, including theoretical discussions of the equilibrium in aqueous solutions above 300°. Definite quantitative data are very scanty. A bibliography, including the principal data from each memoir cited, is included, together with a tabular index according to mineral names.

C. H. D.

The Reaction between Sulphur and Potassium Hydroxide in Aqueous Solution. HERMAN V. TARTAR (*J. Amer. Chem. Soc.*, 1913, **35**, 1741—1747).—The primary reaction of sulphur with potassium hydroxide in hot aqueous solutions takes place in accordance with the equation: $6KOH + 8S = 2K_2S_3 + K_2S_2O_3 + 3H_2O$. When sulphur is used in excess, a secondary reaction occurs, in which it combines with the trisulphide to form the pentasulphide. Potassium tetrasulphide is perhaps formed as an intermediate product. Variation in temperature (below 100°) and concentration does not alter the nature of the reaction.

In the analysis of the various solutions, the potassium in the form of thiosulphate, and the sulphur present as polysulphide, as thiosulphate, as sulphite, and as sulphate were estimated according to the methods given by Haywood (A., 1905, ii, 312). The estimation of potassium present as polysulphide was carried out by precipitation with a standard ammoniacal solution of zinc chloride, when zinc polysulphide is precipitated (compare Tartar, *J. Ind. Eng. Chem.*, 1910, **2**, 271).

T. S. P.

A Family of Metallic Phosphides Derived from Hydrogen Phosphide, P_2H_5. ROBERT BOSSUET and LOUIS HACKSPILL (*Compt. rend.*, 1913, **157**, 720—721. Compare A., 1912, ii, 252).—Rubidium phosphide dissolves in liquid ammonia to a yellow limpid solution, which on evaporation at −18° deposits transparent, yellow crystals having the constitution $Rb_2P_5,5NH_3$, and efflorescing with loss

of their ammonia at the ordinary temperature. This alkaline phosphide in solution in liquid ammonia reacts with solutions of nitrates of barium, strontium, calcium, silver, copper, and lead in the same solvent, giving amorphous precipitates, yellow in the case of the alkaline earth metals, brown for silver, and black for the others. The precipitates only deposit slowly, and are very readily oxidised in the air. The authors succeeded in isolating and analysing the *lead phosphide*, finding it to have the constitution PbP_5, thus giving indication of a series of such phosphides of bivalent metals having the constitution MP_5. When heated in a vacuum at 400°, lead phosphide loses its phosphorus, leaving metallic lead. The phosphide burns spontaneously in air, is attacked slowly by water, with dilute sulphuric and hydrochloric acids gives solid hydrogen phosphide and the salts of lead, and with dilute nitric acid it yields lead nitrate and phosphoric acid.

W. G.

Hydraulic Lime Containing Magnesia. I. Thermal Decomposition of Normal Dolomite. O. KALLAUNER (*Chem. Zeit.*, 1913, **37**, 1317).—Dolomite is sensibly decomposed at about 500°. The velocity of decomposition increases slowly at first, more rapidly above 650°, and reaches its first maximum at 710—730°. Above this temperature, it again increases slowly up to 870°, then more rapidly, and attains a second maximum between 900° and 915°. The presence of free lime was first observed in the aqueous extract of the product which had been heated at 875° during fifteen minutes. The conclusion is drawn that the double salt is decomposed into its components to an appreciable extent at 500°, and that the process attains its maximum velocity at 710—730°, whilst, further, the liberated magnesium carbonate immediately breaks down into magnesium oxide and carbon dioxide. The residual calcium carbonate begins to decompose at 875°, and this process reaches its maximum velocity at 900—915°. H. W.

Atomic Weight of Barium. WILLIAM ŒCHSNER DE CONINCK (*Rev. gen. Chim. pure appl.*, 1913, **16**, 245).—Pure barium carbonate was prepared by the action of sodium carbonate on barium chloride, when analysis indicated a purity of 99·998%; this was decomposed by nitric acid, and the evolved carbon dioxide weighed. From these results the molecular weight of $BaCO_3 = 197·36$, of $BaO = 153·36$, and the atomic weight of $Ba = 137·36$. F. M. G. M.

The Optical Orientation of Some Cast Metals. KURD ENDELL and H. HANEMANN (*Zeitsch. anorg. Chem.*, 1913, **83**, 267—274).—Some cast metals have been examined by reflecting polarised light from their polished surface and passing it through a quartz plate and analyser. Anisotropy of the reflecting metal is easily detected in this way. In another modification of the method, ordinary light is used, which is examined after reflexion by means of a Savart plate, which shows interference bands when the metal is anisotropic.

The metals are fused in small porcelain crucibles and cooled in air. Sections are then cut at several angles and polished, but not etched.

Zinc and antimony crystallise, like ice, in similarly orientated crystals, perpendicular to the cooling surface. Stirring during cooling gives an aggregate of irregular orientation, and this result only is obtained with bismuth and tin. When an anisotropic metal is present, together with a eutectic, the primary crystals are in some cases similarly orientated, and in other cases not so.

Cementite in steel is anisotropic, as are sulphide enclosures, and also iron phosphide and silicide, and 80% ferromanganese. Silicate slag enclosures are isotropic. Anisotropy has not been detected in cold worked steel. C. H. D.

The Binary Systems Zinc–Tin, Zinc–Cadmium, and Tin–Cadmium, and the Ternary System Zinc–Tin–Cadmium. RICHARD LORENZ and D. PLUMBRIDGE (*Zeitsch. anorg. Chem.*, 1913, **83**, 228—242).—The three binary systems are of a simple type, and the freezing-point curves are in good agreement with previous determinations. The eutectic point Sn–Zn is found at 13·5 atomic % Zn and 199°, of Cd–Zn at 27 atomic % Zn and 264°, and of Sn–Cd at 29 atomic % Cd and 177°. Solid solutions are formed in the last series up to 2 atomic % Cd. The first series is free from solid solutions, and the second only contains them to a very limited extent.

The ternary system is of a very simple type, with three freezing-point surfaces, of which that which corresponds with the crystallisation of zinc is much the largest. The ternary eutectic contains 70·83 atomic % of tin, 25·41% of cadmium, and 3·70% of zinc, and freezes at 164°.

Microscopical examination confirms the thermal results.
C. H. D.

Arsenides of Cadmium. SERGEI F. SHEMTSCHUSHNI (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1137—1155).—The author has made a systematic investigation, by means of the melting-point method and of the microstructure, of the system cadmium–arsenic. The alloys were prepared by fusing cadmium beneath a layer of mixed lithium and potassium chlorides and gradually adding coarsely ground arsenic; by this means volatilisation of the arsenic is minimised, and mixtures with large proportions of arsenic can be obtained.

The results obtained indicate the existence of the two compounds Cd_3As_2 and $CdAs_2$, and are confirmed by the curves of specific gravity and atomic volume, each of these consisting of three rectilinear branches meeting at points corresponding with the above two compounds. Both compounds are formed with increase of volume, and have the specific gravities 6·25 and 5·86 respectively, whilst those calculated according to the law of mixtures are 7·47 and 6·69. The relatives values of the hardness of the compounds and their constituents are: cadmium, 2; Cd_3As_2, less than 3·5; arsenic, 3·5; $CdAs_2$, 3·5—4.

From the configuration of its crystals in conjunction with its composition, the compound $CdAs_2$ may be regarded as probably belonging to the pyrites type. T. H. P.

The Scientific Foundations of Furnace (Roasting) Operations. RUDOLF SCHENCK (*Zeitsch. angew. Chem.*, 1913, **26**, 646—652).—A lecture delivered before the Verein deutscher Chemiker at Breslau in September, 1913, dealing with the results hitherto obtained in the roasting of lead and copper sulphide ores.

T. S. P.

Decomposition of Sparingly Soluble Lead Salts. FRIEDRICH AUERBACH and HANS PICK (*Zeitsch. Elektrochem.*, 1913, **19**, 827—830).—The conditions of stability of basic lead carbonate in the presence of sodium carbonate, sodium hydrogen carbonate, and sodium sulphate have been worked out at 18° and 37°. The results are plotted on spatial diagrams, in which it is shown that a double salt of basic lead carbonate and sodium carbonate of the formula $3PbCO_3,Pb(OH)_2,Na_2CO_3$ is formed as a greyish-yellow powder when the concentration of sodium carbonate slightly exceeds $0 \cdot 1N$. This compound is decomposed by water into white basic lead carbonate and sodium carbonate. Similar investigations were made with lead chromate and its basic salts; it is shown that a similar spatial diagram can be drawn to represent the regions of existence of lead chromate and its basic salts. The diagram for lead chromate differs from that of lead carbonate, inasmuch that in the latter case there is only a small region in which the normal lead carbonate is stable, whilst in the former case the stability region of lead chromate is very wide. J. F. S.

Change of Properties in the Polymorphic Transformations of Thallium, Tin, Zinc, and Nickel. (MAX WERNER (*Zeitsch. anorg. Chem.*, 1913, **83**, 275—321).—The transformation curve of thallium has been determined up to 3000 kg. per cm.^{2}, and within this range the temperature of transformation is lowered by pressure in an almost linear manner, the lowering being 6° for an increase of 3000 kg. per cm.^{2} The volume change is 0·000044 c.c. per gram, from which the value $0 \cdot 26 \pm 0 \cdot 07$ cal. per gram is calculated for the heat of transformation, whilst Tammann's method gives 0·2 cal. The electrical conductivity of thallium wire prepared by extrusion undergoes a sudden change at the transformation temperature. The recrystallisation of the metal hardened by extrusion takes place above the transformation temperature. The two modifications have different temperature-coefficients of conductivity. There is a slight discontinuity in the thermoelectric force against copper at 226°.

A transformation of tin has been detected at 168° under 100 kg. per cm.^{2}. This corresponds with the values obtained under different pressures by other workers, but the transformation is often suppressed. A p-T diagram is constructed from the existing data. The heat of transformation of tetragonal into rhombic tin is

0·02 cal. per gram, and the volume change 0·00017 c.c. per gram. The electrical resistance undergoes a change at 161°, but the thermal effect is too small to be detected with the apparatus used. The thermoelectric force of a tin–nickel couple shows a break at the same temperature.

A thermal effect in zinc has been detected at 304°, but not at 170°. The same result is obtained by an examination of the electrical resistance, and of the thermoelectric force measured against iron or platinum. A determination of the upper limit of elasticity also fails to show any discontinuity of the properties of zinc at 170°.

The heat of transformation of nickel at 352° is determined from the cooling curves to be 0·013 cal. per gram. The electrical resistance and the thermoelectric force measured against copper indicate a break at 355—365°. This is also the temperature of the magnetic change. A volume change does not occur, and the transformation temperature is the same for hard and soft wires.

The bearing of these results on the explanation of the recrystallisation of hardened metals is discussed. C. H. D.

Rapid Refining of Copper with a Rotating Cathode. CHARLES W. BENNETT and C. O. BROWN (*J. Physical Chem.*, 1913, **17**, 685—694).—An apparatus is described by which the electrolytic refining of copper can be demonstrated to students. The apparatus works at 65 amperes per sq. dcm. of cathode surface, and by its means 100 grams of copper can be deposited in an hour. Experiments are described in which the usual impurities of copper are separated from artificially prepared anodes. Working scale drawings are given of the apparatus. The rotating cathode makes about 5000 revolutions per minute, and is made of aluminium.

J. F. S.

Apparatus for the Purification of Mercury by Distillation in a Vacuum. BERTRAM LAMBERT (*Chem. News*, 1913, **108**, 224—225).—The apparatus described by the author does not differ in principle from the ordinary apparatus, which makes use of the barometric method for maintaining a vacuum. T. S. P.

Theory of the Preparation of Aluminium. RICHARD LORENZ, ASMUS JABS and W. EITEL (*Zeitsch. anorg. Chem.*, 1913, **83**, 328).—A correction. The eutectic proportions given (this vol., ii, 963) contain a numerical error. They should be 13·6% of aluminium fluoride and 86·4% sodium fluoride, in good agreement with the values found by Fedotéev and Iljinsky (this vol., ii, 324).

C. H. D.

Action of Three % Hydrogen Peroxide Solution on Aluminium. DROSTE (*Chem. Zeit.*, 1913, **37**, 1317).—The corrosion of an aluminium beaker, which had contained 3% hydrogen peroxide solution for a short period, has led the author to examine the action of the latter on a sample of aluminium containing Al 99·46%,

Fe 0·03%, Si 0·51%. The metal is rapidly dissolved with the exception of a few black specks, which consist of aluminium, to which silicon adheres. The white precipitate which is formed has, when air-dried, the composition $Al_2(OH)_6,2H_2O$. Soluble colloidal aluminium hydroxide does not appear to be formed. Aluminium vessels are thus unsuitable for liquids which contain or can form free oxygen or ozone. H. W.

The Binary System Aluminium-Tin. RICHARD LORENZ and D. PLUMBRIDGE (*Zeitsch. anorg. Chem.*, 1913, **83**, 243—245).—Freezing-point determinations and microscopical examination confirm the conclusions of Gwyer (A., 1906, ii, 544) that solid solutions are not formed in this system, and that the eutectic point is at 98 atomic % Sn (compare Shepherd, A., 1904, ii, 486). C. H. D.

The Presence of Gallium in Commercial Aluminium and its Separation. CH. BOULANGER and J. BARDET (*Compt. rend.*, 1913, **157**, 718—719).—The authors have proved the presence of gallium in several specimens of commercial aluminium by spectrographic methods, and in one case have isolated it in the form of its oxide, finding 0·017% of gallium in the commercial metal. Specimens of bauxite similarly examined were also found to contain aluminium. W. G.

Alloys of Manganese and Cobalt. KARL HIEGE (*Zeitsch. anorg. Chem.*, 1913, **83**, 253—256).—Manganese and cobalt form a continuous series of solid solutions, the freezing-point curve passing through a flat minimum at about 30% of cobalt and 1150°. The crystals are not homogeneous, but become more nearly so after annealing in magnesia at 1000° for five hours. The magnetic transformation curve falls with increasing manganese, in almost linear fashion. C. H. D.

Manganese Carbides, and Their Preparation by Heating the Metal in a Current of Methane. SIEGFRIED HILPERT and J. PAUNESCU (*Ber.*, 1913, **46**, 3479—3486).—When finely powdered manganese is treated with methane, or with a mixture of methane and hydrogen, at 600—900°, carbides are formed (compare Hilpert and Ornstein, this vol., ii, 604). In pure methane, carbides containing over 20% of carbon were obtained, and in mixtures of equal volumes of hydrogen and methane, carbides containing up to 15% of carbon. The limiting amounts of carbon taken up at the various temperatures do not, however, correspond with simple stoïcheiometric proportions.

When the carbides contain 8% or less of carbon, treatment with dilute acids gives nearly all the carbon as methane; very little ethylene and no acetylene is evolved. With more than 8% of carbon, fatty substances and spongy carbon are produced. The conclusion is therefore drawn that the carbides are not derivatives of simple hydrocarbons, as are the carbides of calcium and aluminium.

The carbides are, to a great extent, ferromagnetic. Magnetic properties are evidenced with 1% C, and reach a maximum at about 4% C. Carbides containing more than 7% C are not ferromagnetic. T. S. P.

Structure and Properties of Alloys Prepared by Fusing Together Iron and Zinc Under Pressure. U. RAYDT and GUSTAV TAMMANN (*Zeitsch. anorg. Chem.*, 1913, **83**, 257—266).—The alloys of iron and zinc have hitherto been examined only as far as 24% of iron, richer alloys having too high a vapour pressure (von Vegesack, A., 1907, ii, 170). The entire series has now been investigated by using a closed furnace, in which a pressure of 110—130 atmospheres could be obtained. The electric furnace is made up of carbon rods, 3 mm. diameter, connected by iron plates to form a conductor bent repeatedly on itself. This heater surrounds a magnesia cylinder, and requires 25—30 amperes to reach 1500°. Compressed hydrogen is admitted to the bomb after the metals have been enclosed in a porcelain tube. The composition of the alloys is determined by analysis after fusion. The structure has been examined microscopically, but the freezing-point curve of the alloys rich in iron has not been determined.

No compounds, other than those formed under atmospheric pressure, $FeZn_7$ and $FeZn_3$, have been recognised. The only other micrographic constituent is a solid solution of zinc in iron, the saturation point of which appears to lie at about 80% of iron. The temperature of magnetic transformation falls with increasing zinc content, and is then constant at 650° from 80 to 22% of iron. A hypothetical diagram is constructed in accordance with these facts. An alloy with 96% of iron is malleable when cold, although more brittle than iron, but the alloy with 80% is brittle and not malleable at the ordinary temperature. C. H. D.

Precipitation of Iron by Light and Green Aquatic Plants. HANS MOLISCH (*Zeitsch. Kryst. Min.*, 1913, **53**, 92; from *Sitzungsber. Akad. Wiss. Wien, math.-naturw. Klasse*, 1910, **109**, 959—983).—Ferric hydroxide is precipitated by the action of light on certain dilute solutions containing salts of iron; for example, iron ammonium citrate; whilst a solution of ferrous sulphate and ferrous hydrogen carbonate deposits ferric hydroxide on remaining even in the dark. Green aquatic plants under the influence of light also favour the deposition of iron from solution, since they extract alkalis and carbon dioxide and give off oxygen. L. J. S.

Anhydrous Sulphates. VI. Cobaltous Sulphate with Lithium Sulphate, Sodium Sulphate, and Potassium Sulphate. GENNARO CALCAGNI and D. MAROTTA (*Gazzetta*, 1913, **43**, ii, 380—390. Compare A., 1912, ii, 761, 918, 1064).—Lithium sulphate and cobaltous sulphate do not form any compounds, but exhibit a restricted field of mixed crystals from about 100—83% Li_2SO_4; there is an eutectic corresponding with 595° and 63% Li_2SO_4.

Cobaltous sulphate and sodium sulphate form a compound,

$CoSO_4,3Na_2SO_4$, which decomposes above 425°; at concentrations from 100% to 67% Na_2SO_4, mixed crystals are formed, and there is an eutectic corresponding with 575° and 50% of either component.

Cobaltous sulphate and potassium sulphate yield a rather complicated thermal diagram. Two compounds are formed, both being already known. The compound, $CoSO_4,K_2SO_4$, decomposes above 560°. The compound, $2CoSO_4,K_2SO_4$, crystallises at 736°, and there is an eutectic at about 725° (about 31% K_2SO_4). At 535° there is an eutectic corresponding with 60% K_2SO_4. R. V. S.

Ternary Alloys of Nickel, Copper, and Silver. PIETRO DE CESARIS (*Gazzetta*, 1913, **43**, ii, 365—379).—This paper records in tables, curves, and photomicrographs the results obtained by the application of the method of thermal analysis to this system. In some cases, experiments were also made with mixtures containing two only of the constituents, although the three binary systems involved have previously been investigated by other authors.

R. V. S.

The Nature of Auxiliary Valencies. V. The Influence of the Anion on the Stability of Complex Cations. FRITZ EPHRAIM (*Ber.*, 1913, **46**, 3103—3113. Compare this vol., ii, 496). —In the former paper the dissociation temperatures of the ammines of the sulphates of several bivalent metals were discussed. In the present instance the same function of the ammines of different salts of nickel has been studied. As a general rule it is found that the nickel salts of the stronger acids unite more firmly with ammonia than do the salts of weak acids. The following descending order of stability is established: perchlorate, iodide, bromide, chlorate, nitrate, dithionate, chloride (hexammines), formate (tetrammine), sulphate (hexammine), thiosulphate (pentammine), tetrathionate (hexammine), nitrate (pentammine), hypophosphite (hexammine), acetate (? tetrammine), formate and thiocyanate (hexammines).

In most cases the stability of the ammine is parallel to the stability of the corresponding ammonium salt; for example, the hexammine of nickel iodide and ammonium iodide decomposes at higher temperatures than the bromides or chlorides. The more stable ammines are also the least soluble in water.

The following new compounds are described: *Nickelhexammine nitrate*, $Ni(NO_3)_2,6NH_3$, prepared by the action of dry ammonia on anhydrous nickel nitrate; *nickelhexammine chlorate*, precipitated in blue, glistening crystals by ammonia gas from a very concentrated solution of nickel chlorate; *nickelpentammine thiosulphate*, $NiS_2O_3,5NH_3,H_2O$, precipitated in blue leaflets by ammonia from concentrated solutions of nickel thiosulphate; loses water when heated in a stream of ammonia; *nickelhexammine tetrathionate*, precipitated as a white oil, which soon solidifies to small, pale violet needles when alcohol is added to a solution of nickel tetrathionate and ammonia; stable when dry, decomposes when moist; *nickelpentammine nitrite*, a blue compound obtained by treating

the red tetrammine with dry ammonia; *nickelhexammine hypophosphite*, a reddish-violet salt, prepared by passing a slow stream of ammonia over anhydrous nickel hypophosphite; some particles remain unattacked, but with a stronger stream of gas the reaction is too vigorous; *nickelhexammine formate*, violet, prepared by treating nickel formate, dried at 140°, with ammonia, when the pale blue tetrammine is soon formed, whilst the final addition is very slow. J. C. W.

Alloys of Molybdenum and Cobalt. U. RAYDT and GUSTAV TAMMANN (*Zeitsch. anorg. Chem.*, 1913, **83**, 246—252).—Molybdenum (98·2%), prepared by the aluminothermic process from molybdenum trioxide, is alloyed with cobalt (98%), prepared by repeatedly re-melting cobalt cubes in a magnesia vessel with fragments of porcelain. This cobalt has m. p. 1480°. Alloys with up to 65% Mo may be prepared by heating at 1800° in magnesia tubes; further quantities of molybdenum are not completely dissolved at that temperature. The freezing-point curve shows a eutectic point at 38% Mo and 1335°. Solid solutions are formed to 28% Mo. From the eutectic point the freezing-point curve rises, and has a break at 1484°, corresponding with the compound MoCo, which does not form solid solutions. There is no indication of any further compound. The compound is non-magnetic, but the solid solution rich in cobalt is magnetic, the temperature of the transformation, which is reversible, falling from 1143° for pure cobalt to about 760° for the saturated solid solution. The crystals of the latter show marked coring under the microscope. The compound MoCo crystallises in long needles. The free molybdenum forms rounded crystallites.

Alloys richer in molybdenum may be prepared by the aluminothermic method, but then always contain aluminium. C. H. D.

Colour Changes in Colloidal Gold. S. H. LONG (*Proc. Univ. Durham Phil. Soc.*, 1913, **5**, 113—118).—Colloidal gold solutions of a red, blue, and purple colour have been prepared by the use of a high frequency alternating arc (compare this vol., ii, 1033). The behaviour of these solutions in an electrical field was investigated. The red colloid moves towards the cathode, but if the field is allowed to act for some time, the colloid turns blue and moves towards the anode. The blue colloid migrates to the anode, and no further change occurs when the action of the field is prolonged for about two hours. The purple colloidal solutions show both these effects, and this indicates that these contain both the red and blue colloids.

It is supposed that the red colloid consists of positively charged particles associated with hydroxyl ions, and the blue colloid of negatively charged particles surrounded by hydrogen ions. The fact that the red colloid is converted into the blue by the action of electrolytes or of an electric field indicates that the blue represents the more stable modification. H. M. D.

Alloys of Palladium with Nickel. FRITZ HEINRICH (*Zeitsch. anorg. Chem.*, 1913, **83**, 322—327).—Palladium and nickel form a continuous series of solid solutions, the freezing-point curve having a flat minimum near 1208°. The curve is very asymmetrical, and there are indications of an unstable phase. The magnetic change curves fall with increasing percentages of palladium, slowly at first, rapidly beyond 40% Pd, and at about 80% Pd the temperatures of the change observed on heating and on cooling become identical. The alloys are homogeneous on etching. C. H. D.

Mineralogical Chemistry.

Iron Mines near Borossebes, Hungary. J. BALÁS (*Zeitsch. Kryst. Min.*, 1913, **53**, 65; from *Bányász. és Kohászati Lapok*, 1910, xliii *Jahrg.*, **51**, 144—156).—Iron ore soccur in Triassic dolomite in the Kodru Mountains, in comitat Arad. They consist of brown and red ironstone (limonite and hæmatite), and are associated with pyrolusite, manganite, and psilomelane. The iron ores contain 25·18—47·83% Fe with 3·71—29·12% Mn; and the manganese ores contain 42·34—47·82% Mn with 15·16—19·08% Fe. L. J. S.

Synthesis of Wulfenite. EMIL DITTLER (*Zeitsch. Kryst. Min.*, 1913, **53**, 158—170).—Wulfenite occurs as a mineral of secondary origin in the upper oxidised zone of veins of lead ore, and is frequently associated with cerussite, molybdic-ochre, limonite, and corroded galena. The red crystals from Arizona melt at 1060—1070° without destruction of the colour (which is therefore not organic). Experiments were made to determine the action of various gases and solutions on the mineral. It is readily attacked by hydrogen sulphide in water, and by digestion with sodium carbonate solution. In the latter case the product consists of hexagonal scales of hydrocerussite, $Pb(Pb{\cdot}OH)_2(CO_3)_2$. This compound, after long digestion with a dilute alkaline solution of ammonium molybdate, gives small, tetragonal crystals of wulfenite, $PbMoO_4$. The amorphous precipitate obtained by mixing solutions of lead chloride and ammonium molybdate becomes crystalline on heating, and has the composition $2PbO,5MoO_3$.
L. J. S.

Custerite, a New Contact-metamorphic Mineral. J. B. UMPLEBY, WALDEMAR T. SCHALLER, and ESPER S. LARSEN (*Amer. J. Sci.*, 1913, [iv], **36**, 385—394).—As finely granular masses resembling green marble in appearance, this mineral is found in the contact zone between marble and garnet-diopside-magnetite rock around large inclusions of limestone in granite-porphyry, near Mackay, in Custer Co., Idaho. Microscopical examination of thin sections points to monoclinic symmetry with basal and prismatic cleavages and lamellar twinning. Refractive indices: $\alpha = 1{\cdot}586$, $\beta = 1{\cdot}589$,

$\gamma = 1.598$; H = 5—6, D = 2·91. When gently heated, the material phosphoresces with a golden-yellow light. It fuses with difficulty to a white enamel, and is readily decomposed by acids, with the separation of gelatinous silica. Analysis gave:

SiO_2.	CaO.	H_2O.	F.	MgO.	Magnetite.	Total (less O for F).
32·17	55·11	5·30	8·12	1·19	1·00	99·47

The formula is $Ca_2SiO_3(OH,F)_2$. No water is given off at 110°; and in water the mineral immediately gives a deep red colour with phenolphthalein, suggesting the presence of the group (CaOH). The formula is therefore written structurally as a metasilicate, $SiO_3(CaOH)(CaF)$. Allied minerals are zeophyllite ($Ca_4Si_3H_4F_2O_{11}$), cuspidine ($Ca_4Si_2F_2O_7$), and hillebrandite ($Ca_2SiO_3(OH)_2$). The relations of these are discussed, and various structural formulæ are suggested. L. J. S.

Minerals from the Kinzig Valley, Baden. V. Dürrfeld (*Zeitsch. Kryst. Min.*, 1913, **53**, 182—183).—Crystals of fluorite are described from Artenberg, near Steinach. Crystals of prehnite, pectolite, datolite, and apophyllite occur in drusy cavities in amphibolite at Haslach. The pectolite has the form of fine needles, with a radially-fibrous structure and a snow-white to pale greenish-white colour. Analysis gave:

SiO_2.	Al_2O_3.	CaO.	Na_2O.	K_2O.	H_2O.	Total.
52·71	2·52	33·95	9·53	0·18	1·92	100·81

For a new hydrous vanadate of lead and zinc, previously described (V. Dürrfeld, *Zeitsch. Kryst. Min.*, 1912, **51**, 278) as occurring in orange-yellow to yellowish-brown, monoclinic needles on decomposed galena at Reichenbach, near Lahr, the name *hügelite* is now proposed. L. J. S.

Chemical Constitution of the Sodalite and Nephelite Groups. Silvia Hillebrand (*Zeitsch. Kryst. Min.*, 1913, **53**, 92; from *Sitzungsber. Akad. Wiss. Wien*, *math.-naturw. Klasse*, 1910, **109**, 775—806).—The silicic acid isolated by Tschermak's method from the sodalite of Lake Baikal contains 37·96 and 37·24% H_2O (H_2SiO_4 requires 37·40%). The minerals of the sodalite group are therefore regarded as compounds of the orthosilicate, $Na_3Al_3Si_3O_{12}$, with NaCl, Na_2SO_4, $CaSO_4$, and probably Na_2S_3.

The silicic acid isolated from the nephelite of Miass contained 37·34 and 36·38% H_2O, and from the elæolite of Mariapol 35·40%. The predominating constituent of these minerals is thus the orthosilicate, $Na_3Al_3Si_3O_{12}$; and mixed with this are the isomorphous potassium and calcium compounds, $K_3Al_3Si_3O_{12}$ and $NaCaAl_3Si_3O_{12}$, together with a potassium compound richer in silica, $K_2Al_2Si_4O_{12}$. L. J. S.

The Rhyolite Kaolins of Hungary. L. Petrik (*Zeitsch. Kryst. Min.*, 1913, **53**, 64—65; from *Magyar Üveg- és Agyagujság*, 1910, **10**, No. 5, 2—3, No. 6, 2—3, No. 8, 4—5).—The white china-clays

from various localities in Hungary have been derived from trachytic and rhyolitic rocks. Several analyses are given of the raw and washed material. These vary widely in composition, containing 32·32—81·91% of the clay substance, 1·85—54·99% quartz sand, and 0—56·20% felspar sand. The clay substance approximates in some cases to the kaolinite formula $H_4Al_2Si_2O_9$, but in others there is a considerable excess of alumina and water, due to the presence of freely soluble aluminium hydroxide. L. J. S.

Garnets from the Volcanic Rocks and Bombs of the Lower Rhine District. JOHANNES UHLIG (*Zeitsch. Kryst. Min.*, 1913, **53**, 203—208; from *Verh. Nat. Ver. preuss. Rheinlande u. Westfalens*, 1910, **67**, 307—403).—Garnets of several types were analysed in detail especially for the presence of rarer elements.

I. Melanite as loose crystals in leucite-tuff from the Perlerkopf in the Laach district. To bring this analysis into agreement with the garnet formula, the figures are readjusted as TiO_2, 4·45; Ti_2O_3, 3·36; Fe_2O_3, 21·65; FeO, nil.

II. Opaque, brown aplome in a bomb from Laach.

III. Pale blood-red almandine in muscovite-schist from Dachsbusch, Laach.

IV. Pale rose-red almandine in sillimanite-biotite rock from Laach.

V. Almandine in a cordierite-garnet rock from Laach.

VI. The red nucleus of the same with the black, slaggy shell removed as far as possible.

VII. Almandine as grains enclosing fine needles of titanite; to agree with the garnet formula the iron is readjusted as Fe_2O_3, 1·69; FeO, 24·14.

VIII. Wax-yellow grossularite, occurring as enclosures in basalt at Finkenberg, near Bonn.

IX. Brownish-red hessonite from the same occurrence.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
SiO_2	32·71	36·64	37·55	37·13	40·25	41·50	39·73	40·73	38·68
TiO_2	8·30	0·56	0·45	0·48	0·39	0·56	0·19	0·85	0·39
Al_2O_3	5·72	11·01	20·86	20·91	21·21	21·86	20·23	19·72	18·42
Fe_2O_3	17·91	15·66	0·66	1·16	2·21	—	2·94	2·39	5·30
V_2O_3	0·24	0·09	—	0·01	trace	—	trace	n.d.	trace?
Cr_2O_3	trace	—	—	—	0·06	—	0·03	—	—
Ce_2O_3	—	0·09	—	—	—	—	—	—	—
FeO	3·36	1·16	26·77	33·22	26·66	23·74	23·01	0·92	2·52
NiO	trace	trace	—	trace	0·01	—	0·05	—	trace?
CoO	—	—	—	—	trace?	—	trace	—	—
MnO	0·52	1·99	6·85	4·89	0·73	0·83	0·65	0·58	0·66
MgO	1·33	0·44	4·80	1·23	6·95	7·47	6·94	2·54	0·79
CaO	29·25	30·15	2·28	1·60	0·71	0·76	6·09	32·10	32·59
Na_2O	—	0·87	—	—	0·31	—	—	—	—
K_2O	—	0·30	—	—	0·30	—	—	—	—
H_2O (over 125°)	0·32	0·87	0·27	0·18	0·37	0·76	0·70	1·18	0·40
H_2O (hygrosc.)	0·19	0·32	0·11	0·07	0·07		0·23		0·39
Total	99·85	100·15	100·60	100·98	100·73		100·79	101·01	100·14
Sp. gr.	3·692	3·581	4·084	4·158	3·926		3·907	3·470	3·566

To express the percentages of the several isomorphous molecules

of the garnet group that enter into the composition, the following nomenclature is used. The lime-garnets are written as $(Al) = Ca_3Al_2Si_3O_{12}$, $(Fe) = Ca_3Fe_2Si_3O_{12}$, $(Ti) = Ca_3Ti_2Si_3O_{12}$, $(V) = Ca_3V_2Si_3O_{12}$, etc.; and the remaining garnets as $Fe = Fe_3Al_2Si_3O_{12}$, $Mg = Mg_3Al_2Si_3O_{12}$, $Mn = Mn_3Al_2Si_3O_{12}$, $Na = Na_6(Al,Fe)_3O_{12}$.

The analyses correspond with:

		$(RO + RO_2 : R_2O_3 : R_2O)$.
I.	$(Fe)_{62 \cdot 6}(Al)_{19 \cdot 7}(Ti)_{10 \cdot 7}(V)_{0 \cdot 8}Mg_{5 \cdot 1}Mn_{1 \cdot 1}$	3 : 1·08 : 2·82
II.	$(Fe)_{47 \cdot 4}(Al)_{40 \cdot 5}(V)_{0 \cdot 3}(Ce)_{0 \cdot 1}Mn_{4 \cdot 5}Fe_{2 \cdot 6}Mg_{1 \cdot 8}Na_{2 \cdot 8}$.	2·97 : 1 : 2·96
III.	$Fe_{59 \cdot 2}Mg_{19 \cdot 0}Mn_{15 \cdot 4}(Al,Fe)_{6 \cdot 4}$	3·01 : 1 : 3·02
IV.	$Fe_{78 \cdot 9}Mn_{11 \cdot 1}Mg_{5 \cdot 0}(Al)_{4 \cdot 7}$	3·03 : 1 : 2·96
V.	$Fe_{65 \cdot 5}Mg_{30 \cdot 4}Mn_{1 \cdot 8}(Al,Fe,Cr)_{2 \cdot 2}$	3·06 : 1 : 2·59
VII.	$Fe_{53 \cdot 6}Mg_{27 \cdot 5}Mn_{1 \cdot 5}(Al,Fe,Cr)_{17 \cdot 4}$	3·04 : 1 : 2·82
VIII.	$(Al)_{79 \cdot 3}(Fe)_{7 \cdot 2}Mg_{10 \cdot 1}Fe_{2 \cdot 1}Mn_{1 \cdot 3}$	3·13 : 0·95 : 3
IX.	$Al_{74 \cdot 6}Fe_{15 \cdot 5}Fe_{5 \cdot 5}Mg_{3 \cdot 1}Mn_{1 \cdot 5}$.....................	3·03 : 1 : 3·03

From these analyses it is seen that amongst the lime-garnets those richer in iron (lime-iron garnets) contain correspondingly less of the iron-alumina, magnesia-alumina, and manganese-alumina molecules.

L. J. S.

The Garnet Group. HENDRIK E. BOEKE (*Zeitsch. Kryst. Min.*, 1913, **53**, 149—157. Compare preceding abstract).—The ratios of the various bases taken from 261 published analyses of garnets are plotted on diagrams. No. 1 includes garnets poor in lime; the percentages of magnesia, ferrous oxide, and manganous oxide are increased to a total of 100, and are plotted on triangular co-ordinates with MgO, FeO, MnO 100% at each of the three corners. In No. 2, Fe_2O_3 and Al_2O_3 are increased to total 100%, and are plotted as abscissæ on rectangular co-ordinates, whilst the ordinates give CaO : (MgO + FeO + MnO). The dots representing the several analyses fall into more or less well-defined areas on these diagrams, and from them the following conclusions are drawn. There is a continuous series of mixed crystals between Fe-Al-garnet (almandine) and Mg-Al-garnet (pyrope), and also between almandine and Mn-Al-garnet (spessartite); but between pyrope and spessartite there is a very wide gap. Between the lime-garnets and those just mentioned there is a break in the series from 20 to 75% (Mg,Fe,Mn)O. Between Ca-Al-garnet (grossularite) and Ca-Fe-garnet (andradite) there is a continuous series. In pyrope, almandine, and spessartite, alumina can be replaced isomorphously by ferric oxide only up to the extent of 45%; and with increasing ferric iron there is correspondingly less calcium present.

L. J. S.

Analytical Chemistry.

The Application of the Ionic Theory in Analytical Chemistry. O. Hackl (*Jahrb. K. K. Geol. Reichsanstalt*, 1913, **62**, 613—648).—A criticism of a statement by W. Ostwald ("Die wissenschaftlichen Grundlagen der Analytischen Chemie") on this subject.

F. M. G. M.

Burette with Automatic Setting of the Zero Point. P. Haertl (*Zeitsch. anal. Chem.*, 1913, **52**, 759—760).—An improved automatic burette, which can be affixed to any bottle filled with stock liquid, is described and figured. L. de K.

A New Still-head with Dropping Funnel. Otto Rammstedt (*Zeitsch. angew. Chem.*, 1913, **26**, 640).—For estimations which involve the addition of a reagent immediately preceding or during a distillation, a device is described in which a graduated dropping funnel is fused to the stem of a still-head of the type commonly used for ammonia distillations. J. C. W.

New Apparatus for the Rapid Estimation of Water in Foods and Fodder. Artur Fornet (*Chem. Zeit.*, 1913, **37**, 1400).—The author has carried out a series of determinations of the water content of flour and bran (1) at 100°, (2) at 105°, (3) in a vacuum, and (4) at 125°. The results show considerable variation among themselves. After fourteen to sixteen hours, a further loss of water does not appear to occur, but, on continuing desiccation at 125°, the products treated according to (1) and (2) were further dehydrated, the loss ultimately attaining the same value as in (3) or (4). The author is therefore led to the conclusion that the generally adopted methods of determining moisture in grain, bran, and flour yield too low results. The latter are, however, satisfactory if heating takes place during four hours at 105° in a stream of air.

The author has further investigated the possibility of desiccation at a higher temperature; this is found to be complete in about ten minutes at 180°, and can be effected without decomposition of the substance provided that the duration of heating, determined for any class of substance by comparison of the loss obtained by this method with the analytically determined amount of moisture, is not exceeded. The necessary apparatus consists of a drying oven which can be rapidly heated to and easily maintained at 160°, and a lever arrangement by which the substance can be weighed whilst hot, and which is so calibrated that the percentage of moisture can be read directly.

The author replies to some criticisms by Parow (*Chem. Zeit.*, 1913, **37**, 345), who, using the above method, found too low values for the percentage moisture in starch. The explanation is to be

found in the fact that the method yields only conventional results, and therefore, if standardised against starch at 105°, naturally yields results which are low when compared with the loss observed at 120° if the duration of heating is kept constant. H. W.

The Estimation of Traces of Chlorides in Water. MAURICE LOMBARD (*Bull. Soc. chim.*, 1913, [iv], **13**, 1006—1011).—In estimating traces of chlorides in natural waters by titration with $N/100$-silver nitrate solution, using potassium chromate as an indicator, it is necessary to take certain precautions. A known volume of the water (150—200 c.c.) must be boiled until all the calcium hydrogen carbonate is decomposed, then it is allowed to cool, made up to the original volume, left to settle, decanted, and 100 c.c. of the clear liquid titrated with the silver nitrate. The end-point is determined by colorimetric test against the end-point, made with 100 c.c. of a standard solution containing 5 mg. of sodium chloride per litre. Hydrogen sulphide in water is destroyed by boiling with a slight excess of nitric acid, which is finally removed by the addition of calcium carbonate. Ammonia can be similarly neutralised. W. G.

Estimation of Periodate in Presence of Iodate and Iodide ERICH MÜLLER and GUSTAV WEGELIN (*Zeitsch. anal. Chem.*, 19 13, **52** 755—759).—To 20 c.c. of the solution (about $N/10$-strength) are added 20 c.c. of a saturated solution of borax containing 0·5 gram of free boric acid, 2 grams of potassium iodide are added, and the liberated iodine, which represents one-quarter of the periodate oxygen, is titrated with $N/10$-arsenious acid. Dilute sulphuric acid is now added until the liquid is acid to Congo-paper, and after again neutralising by means of a saturated solution of borax, the iodine liberated is again titrated. If in the first titration a c.c. of $N/10$-arsenic were used, and b c.c. in the second, $4a$ c.c. will represent the periodate, and $a+b-4a=b-3a$ the iodate oxygen. L. DE K.

Estimation of Fluorine in Zinc Ores. LEOPOLD SCHNEIDER (*Österr. Zeitsch. Berg. Hüttenwesen*, 1913, **16**, 365—367).—The estimation of fluorine in minerals by distilling with concentrated sulphuric acid over quartz and weighing the orthosilicic acid ($Si(OH)_4$) subsequently separated by means of water (Bein, A., 1888, 527) is considered unsatisfactory; and a method is now described in which the fluorine is precipitated and weighed as calcium fluoride in the presence of silica, and the latter afterwards removed by treatment with hydrofluoric acid. F. M. G. M.

A Simple Method of Calibrating the Differential Blood-gas Apparatus. PAUL HOFFMANN (*J. Physiol.*, 1913, **47**. 272—274).—A simpler method than that of Barcroft is described, and gives equally good results. W. D. H.

Determination of Alkali Sulphides. DOUGLAS MCCANDLISH and JOHN ARTHUR WILSON (*Collegium*, 1913, 80—84).—A discussion

of the method advocated by Blockey and Mehd (A., 1912, ii, 600) for the estimation of sulphur in lime liquors, with a description of modifications which are considered to give more satisfactory results.

F. M. G. M.

Source of Error in Estimating Nitrogen in Urine by Kjeldahl's Method. O. VON SPINDLER (*Chem. Zentr.*, 1913, ii, 1340; from *Schweiz. Woch. Chem. Pharm.*, 1913, **51**, 517—521).—Under ordinary conditions of feeding, urine almost always contains nitrates, and their presence affects the results in the estimation of the total nitrogen in the urine by Kjeldahl's method. Loss of free nitrogen takes place, but is not proportional to the quantity of nitrate present. The loss may be diminished by taking care that not more than 0·01 gram of nitric acid is present in the quantity of urine used for the estimation, and that the volume of the digestion mixture is not too small at the commencement of the operation.

W. P. S.

Decomposition of Organic Substances by Kjeldahl's Method and the Estimation of Nitrogen in Barley. KURT BUNGE (*Pharm. Zentr.-h.*, 1913, **54**, 1127—1128).—The following procedure is recommended, as it allows a relatively large quantity of the sample to be taken for the estimation. Ten grams of the unground barley grains are heated for thirty minutes with 60 c.c. of sulphuric acid, and about 1·5 grams of mercury in a round-bottom, 500 c.c. flask. To the dark-coloured solution are then added 25 grams of potassium sulphate, and the heating is continued until a clear solution is obtained; the solution is now cooled, diluted to 500 c.c. with water, and the ammonia is estimated in an aliquot portion.

W. P. S.

Ammonia Absorption Apparatus for Nitrogen Estimations. HERBERT LICKFETT (*Zeitsch. angew. Chem.*, 1913, **26**, 688).—The absorption flask has a wide neck, and is fitted with a rubber stopper, through which pass (1) the tube from the condenser and (2) a tube with two glass bulbs; this tube may be adjusted, so that the end just dips below the surface of the standard acid in the flask.

W. H. G.

Detection of Nitric Acid (Nitrates) in Milk. R. BARTH (*Zeitsch. Nahr. Genussm.*, 1913, **26**, 339—341).—The formaldehyde-sulphuric acid test is recommended. Ten c.c. of the milk are mixed with 5 drops of dilute formaldehyde solution (10 drops of 40% formaldehyde in 250 c.c. of water), and the mixture is poured on the surface of 5 c.c. of sulphuric acid, D 1·71, contained in a test-tube. A blue ring appears at the junction of the two liquids when the milk contains not less than 0·5 mg. of nitric acid per litre. Care must be taken to see that the sulphuric acid, water, etc., used in the test are free from nitric acid.

W. P. S.

Estimation of Phosphorus in Fertilisers and Fodders. C. DUSSERRE and P. CHAVAN (*Chem. Zentr.*, 1913, ii, 1333—1334; from *Mitt. Lebensmitteluntes. Hyg.*, 1913, **4**, 261—267).—Molinari's

modification of Pemberton's method, in which Petermann's solution is added to the phosphate solution, yields trustworthy results in the case of superphosphates, but the results are too low with Thomas slag and bone-meal when sulphuric acid solutions of these substances are used for the estimation. This error may be avoided by adding ammonium sulphate to the molybdic acid reagent in place of the usual ammonium nitrate. The molybdic acid reagent is prepared by adding a solution of 25 grams of ammonium sulphate in 400 c.c. of nitric acid, D 1·12, to 75 grams of ammonium molybdate dissolved in 500 c.c. of water, and diluting the mixture to 1 litre. Results of analyses are given showing the distribution of phosphorus in hay (as lecithin, inorganic, and nuclein compounds). The lecithin-phosphoric acid was estimated by extracting the hay repeatedly with boiling alcohol, then with ether, evaporating the solutions, and oxidising the residues with a mixture of sulphuric and nitric acids. The hay was next extracted with cold 1% hydrochloric acid to obtain the inorganic phosphates in solution, and the nuclein-phosphoric acid was estimated by digesting the hay subsequently with sulphuric and nitric acids; in all these estimations, the phosphoric was, finally, precipitated with molybdic acid reagent. W. P. S.

Source of Error in the Precipitation of Ammonium Magnesium Phosphate in the Presence of Ammonium Citrate. ALFREDO QUARTAROLI (*Chem. Zentr.*, 1913, ii, 539; from *Staz. sperim. agrar. ital.*, 1913, **46**, 322—328).—Results of experiments are given in tabular form showing that the amount of phosphoric anhydride, precipitated as ammonium magnesium phosphate in the presence of ammonium citrate, diminishes rapidly as the quantities of ferric and aluminium compounds in the solution increase. W. P. S.

Reactions of Boric Acid and Methyl Alcohol. ERNST PIESZCZEK (*Pharm. Zeit.*, 1913, **58**, 850—851).—A mixture of borax and methyl alcohol yields a green-coloured flame when ignited, and the addition of sulphuric acid is unnecessary. Since ethyl alcohol, acetaldehyde, and acetone do not yield a green flame when burnt in the presence of borax unless a mineral acid is also present, the test may be used, conversely, for the detection of methyl alcohol in ethyl alcohol. The presence of 5% of methyl alcohol may be detected by this means. W. P. S.

Titration of Boric Acid. EDMUND B. R. PRIDEAUX (*Zeitsch. anorg. Chem.*, 1913, **83**, 362—368).—A comparison of the behaviour of various indicators with the neutralisation curve of boric acid suggests the possibility of titrating boric acid without the addition of glycerol or mannitol. The neutralisation curve has been determined from the results of Schmidt and Finger (A., 1908, ii, 802) and Sörensen (A., 1909, i, 861; 1910, i, 147). The best indicator is tropaeolin-O (sodium *p*-benzeneazoresorcinolsulphonate), using 0·5 c.c. of a 0·04% solution for a total volume of about 68 c.c. The

accuracy of the titration in concentrated and dilute solutions, and also with the addition of sodium chloride, is in agreement with that calculated theoretically. The method may be used with an accuracy of $\pm 1\%$. C. H. D.

Absorbing Apparatus for the Estimation of Carbon in Organic Analyses. Henri Vigreux (*Bull. Soc. chim.*, 1913, [iv], **13**, 955—958).—The gas produced in the combustion passes through a straight tube to the bottom of the first washer, where it passes into an outer tube, the inner surface of which is spirally furrowed. The gas passes along the furrow, and escapes by a minute hole at the top leading into the second washer, which is of the usual pear-shaped bubble-counter pattern. The progress of the combustion can be watched easily by comparing the sizes of the bubbles of gas in the two washers. A modified form of the apparatus is also made for the estimation of iodine or chlorine, or of oxidising agents liberating chlorine by the action of hydrochloric acid. Figures are provided in the original. T. A. H.

Tube for the Absorption of Water in Elementary Analysis. Jean Nivière (*Bull. Soc. chim.*, 1913, [iv], **13**, 958—959).—The apparatus which is figured in the original consists of a tube closed at the bottom and having a constriction about one-quarter of its length from the bottom, and two narrow side-arms near the top. The side-arm used as an inlet is prolonged inside to the bottom of the tube. The latter is filled nearly to the constriction with sulphuric acid, and above that with pumice stone previously soaked in sulphuric acid. T. A. H.

Apparatus for the Extraction of Carbon Monoxide from Blood. Maurice Nicloux (*Bull. Soc. chim.*, 1913, [iv], **13**, 947—952).—The apparatus consists essentially of a long-necked flask, the neck of which is jacketed to carry a current of cold water. The mouth of the flask is closed by a hollow ground glass stopper carrying a T-piece of special form, the two outer limbs of which are provided with stoppers, and terminate in funnels of special form, by means of which the flask can be (*a*) exhausted, and (*b*) supplied with the blood under examination. The blood is run into dilute phosphoric acid in the flask, and the gas liberated can, by appropriate manipulation, be collected and withdrawn for examination. The apparatus is figured in the original, and results obtained by its use are quoted. T. A. H.

Application of the Electrical Conductivity to the Investigation of Natural Waters. Antony G. Doroschevski and S. V. Dvorshantschik (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 1489—1528).—The authors have investigated the relation of the electrical conductivity to the amount of dry residue in the case of a number of salt solutions and of natural waters. With salt solutions, especially those of calcium and, to a greater extent, magnesium salts, drying of the residue for two hours at 110° gives

results very considerably in excess of the true values, owing to the retention of water of crystallisation. When, however, the water is evaporated, together with a definite proportion of standard sodium carbonate solution sufficient to convert the calcium and magnesium salts into carbonates, the corrected experimental results never exceed the actual values by more than 1—2%; at the same time, almost identical results are then obtained at 110° and 103°. With artificial mixed salt solutions resembling natural waters in composition, similar results are obtained, drying at 103° in presence of excess of sodium carbonate giving numbers 0·51—2·19% in excess, whilst at 110° the divergence varies from 0·29% to 1·69%; in general, the difference between the values obtained at 103° and at 110° does not exceed 0·5%, and the use of the lower temperature is recommended, since decomposition of the organic matter and of certain of the inorganic salts present is thereby restricted.

Investigation has also been made, with solutions containing a single salt and with others resembling natural waters in composition, of the variation with the concentration of the magnitude of the coefficient $C = M/\kappa \, . \, 10^6$, where M represents the number of milligrams of salt present per litre, and κ the specific conductivity in reciprocal ohms at 18°. With sodium and potassium salts and with calcium chloride, C increases gradually with the concentration, but with calcium and magnesium sulphates the increase is decidedly more rapid, so that the selection of a mean value of C is possible only within very narrow limits of concentration. Since the great majority of natural waters contain 0·2—0·3 gram of solids per litre, all waters should be diluted to this concentration with pure, distilled water before their conductivities are measured. For a number of mixed salt solutions of such concentrations and having compositions such as are met with in natural waters, the mean value of C is found to be 0·668. The formula for calculating the amount of dry residue from the conductivity then assumes the form: $M = \kappa_x \, . \, 10^6 \, . \, x \, . \, C$, where M represents the residue in milligrams per litre obtained by evaporating with sodium carbonate and drying at 103°, x is the extent to which the water is diluted, and κ_x is the conductivity at a dilution corresponding with 0·003—0·004 gram-equivalent per litre, for which $\kappa_{18} \, . \, 10^6$ has the value 300—400 at 18°.

With natural waters of different types, the value of C varies very considerably, more particularly with the permanent hardness (magnesium and calcium sulphates) and with the chlorine; the authors recommend that, in calculating the dry residue of a water from its conductivity, the value of C taken should be as follows: For a soft water with a high chlorine-content (more than 50 mg. per litre), 0·670; for a hard water containing little chlorine (less than 20), 0·725; and for all other waters, 0·695. In all cases air should be bubbled through the water for an hour prior to the measurement of the conductivity.

Frequent measurements of the conductivity were made during the seven months, October—April, for an artesian well water and for the Moscow water-supply, which is of river origin. With the

former, the value of $\kappa_{18} \cdot 10^6$ varied only from 602·0 to 609·3, whilst with the river water the conductivity showed a decided fall in October, as a result of heavy rainfall, and an enormous fall in March, owing to the introduction of large volumes of ice- and snow-water into the river; in this case the limiting values of $\kappa_{18} \cdot 10^6$ were 124·5 and 450·8. It is evident that systematic measurement of the conductivity furnishes a valuable means of controlling the composition of a water-supply.

The results of preliminary experiments indicate that conductivity measurements may also serve for the estimation of the permanent and temporary hardness of a water. The hardness, in German degrees, is expressed by the following empirical formula:

$$H = H_t + H_p = (\kappa_n + \kappa_k)/A_t + y\{(\kappa_k + \kappa_c - x_p - \kappa_0)/A_p + 1\},$$

where H_t and H_p represent respectively the temporary and permanent hardness, κ_n the conductivity of the original water, κ_k that after boiling for an hour, κ_c that of a solution of sodium carbonate containing 0·01 gram-equivalent per litre, κ_0 that of the water after treatment with sodium carbonate, x_p the corresponding correction for change of concentration, y the extent to which the water is diluted before its conductivity is measured, and A_t and A_p the magnitudes of the conductivity corresponding with 1 degree of temporary and permanent hardness respectively. The value of A_t for river water is 25, and for artesian well water, 22, whilst the value of A_p varies with $(\kappa_k + \kappa_c - x_p)$ from 23 to 25. Application of this method to various river and well waters gives results in moderately good agreement with those obtained directly.

T. H. P.

Hydrolytic Reactions which Take Place During the Estimation of the Total Solids in Waters. P. KACHINSKI (*Ann. Chim. anal.*, 1913, **18**, 385—389).—During the evaporation of saline solutions containing magnesium salts, hydrolysis of the latter occurs, and loss of chlorine, bromine, and iodine takes place. This loss is accentuated when the dry residue is incinerated, and, as regards the chlorides, may amount to about 50% of the total chlorine present.

W. P. S.

Estimation of Hardness in Water by Blacher's Method. WALTER PFLANZ (*Chem. Zentr.*, 1913, ii, 1164—1165; from *Mitt. K. Landesanst. Wasserhyg.*, 1913, 141—148. Compare this vol., ii, 153, 338).—Dimethylaminoazobenzene possesses no advantage over methyl-orange as an indicator in this method; even in the case of waters containing humic substances, methyl-orange may be used, provided that the water is titrated with $N/10$-acid until distinctly acid towards this indicator, and the excess of acid then titrated with $N/10$-alkali, using phenolphthalein as indicator. It is essential that the potassium palmitate solution employed in the process should be free from stearic acid.

W. P. S.

Volatility of Sodium Chloride in Presence of Potassium Chloride. M. WAGENAAR (*Pharm. Weekblad*, 1913, **50**, 1214—1215).—In estimating the alkali metals in potable waters there is no

danger of altering the relative proportions of the chlorides of sodium and potassium by igniting the chloride mixture.

A. J. W.

Estimation of the Alkali Hydrogen Carbonate Content of Natural Waters. PIETER A. MEERBURG (*Chem. Weekblad*, 1913, **10**, 958—959).—The amount of alkali hydrogen carbonate in natural waters can be estimated by evaporation of 1—3 litres to small bulk, filtration, titration of the alkali hydrogen carbonate in the filtrate with $N/10$-hydrochloric acid and methyl-orange, and estimation of the magnesium. A simpler method involves the estimation of the alkali and the determination of the hardness, but the results of the two methods do not always agree. A. J. W.

The Estimation of Calcium Oxide Mixed with Calcium Hydroxide. GEORG WEISSENBERGER (*Österr. Chem. Zeit.*, 1913, [2], **16**, 192—193).—A discussion of the errors resulting from the method of estimating calcium by means of its combined constituents, such as the amount of water evolved by calcium hydroxide or the quantity of calcium carbonate obtained from calcium oxide; this untrustworthiness is demonstrated by the analysis of mixtures containing known proportions of calcium oxide and hydroxide. F. M. G. M.

Estimation of Calcium as Oxalate. SAMUEL GOY (*Chem. Zeit.*, 1913, **37**, 1337—1338).—Calcium may be conveniently estimated as hydrated calcium oxalate, but in order to obtain correct results the following conditions should be observed.

The calcium should be precipitated by ammonium oxalate at the boiling heat, and the oxalate collected in a Gooch crucible in connexion with a suction apparatus. After washing the precipitate with small quantities of water until free from ammonium oxalate, the crucible and contents are dried for four to five hours at exactly 105°. The dried compound has the composition CaC_2O_4,H_2O. Drying on a filter gives erroneous results.

L. DE K.

Detection of the Metals of the Alkaline Earths by Spectrum Analysis in the Course of Qualitative Analysis. II. ERNST H. RIESENFELD and G. PFÜTZER (*Ber.*, 1913, **46**, 3140—3144. Compare A., 1906, ii, 804).—An apparatus for the production of an arc spectrum between an iridium electrode and a small quantity of a solution is described. The liquid is contained in a 1—2 c.c. glass tube, through the bottom of which a platinum lead is fused. The electrode may be raised or lowered over the liquid by means of a micrometer screw, and other screws facilitate the adjustment of the whole device before the slit of a spectroscope. The chief magnesium lines may be detected in the arc spectrum in a dilution of 0·1 mg. per c.c., the calcium lines with 0·002 mg. per c.c.; strontium, 0·03 mg. per c.c.; and barium, 0·006 mg. per c.c. Large excesses of the other earths are no drawback to the detection of magnesium. The arc spectra are 20 to 2000 times as sensitive as the flame spectra.

The procedure is not advantageous in the case of potassium, but the sodium line, 568·6$\mu\mu$, appears with 0·04 mg. of the metal per c.c., and may thus be taken as an indication of the presence of weighable quantities in a solution. J. C. W.

Radio-elements as Indicators in Analytical Chemistry. FRITZ PANETH and GEORG VON HEVESY (*Monatsh.*, 1915, **34** 1401—1407).—The chemical non-separability of lead and radio-lead, or radium-*D*, lends itself to the use of radium-*D* as an indicator for lead in quantities too small to be otherwise estimated. The quantities necessary for detection are 10^{-10} gram of radium-*D* by the β-rays of radium-*E*, and 10^{-12} gram by the α-rays of radium-*F* by waiting until the latter attains equilibrium (a year or more). The radio-lead from pitchblende contains about 10^{-7} gram of radium-*D* per gram, so that about 1 mg. can be detected by the β-ray method. For more sensitive measurements the radium-*D* content must be increased by addition of the products of radium emanation. The products of 0·2 curie were mixed with 10 mg. of lead chloride, potassium chromate was added, and the liquid made up to 100 c.c. was shaken in a thermostat at 25° for twenty-four hours. The activity of the evaporated filtrate was measured after radium-*E* had reached equilibrium by comparing it with that of 1 c.c. of the original solution before precipitation, and corresponded with that of 0·012 mg. of lead chromate per litre. Lead chromate is the least soluble lead salt, the solubility of lead phosphate being of the same order. Similarly the solubility of lead sulphide was found to be in pure water at 25° 0·3 mg. per litre, and in water saturated with hydrogen sulphide 0·15. Similarly, radium-*E* may be used as an indicator for bismuth, and ionium as an indicator for thorium. F. S.

Cathodic Estimation of Lead and Analysis of Lead Alloys. R. GARTENMEISTER (*Chem. Zeit.*, 1913, **37**, 1281—1282).—The author finds that gallic acid is a suitable addition-agent, in the electrolysis of solutions of lead salts, for preventing the deposition of lead dioxide at the anode and the evolution of hydrogen at the cathode. Quantitative deposits of lead on the cathode may be obtained by observing the following conditions. For estimating quantities of lead up to 1 gram, the electrolyte should have a volume of about 125 c.c., and contain 2—2·5 c.c. of nitric acid (D 1·4), 5 grams of gallic acid, and 5—6 c.c. of alcohol. The anode should be a cylinder of platinum foil and be surrounded by a Winkler cylindrical gauze cathode. Using a current of 1·2 amperes, the time of electrolysis (stationary electrodes) is four hours at 65—70° for 1 gram of lead. This time must not be exceeded to any great extent, otherwise a yellow dye is deposited.

Zinc, cadmium, iron, nickel, cobalt, and manganese are not deposited under the above conditions. Silver, tin, arsenic, and antimony form black, rough deposits. Bismuth is precipitated as bismuth gallate, and does not interfere. Copper is deposited with the lead.

Alloys of lead, tin, and antimony are best analysed as follows. One to two grams of the alloy are dissolved in a mixture of nitric and tartaric or citric acids. The solution is made alkaline with sodium hydroxide, and then precipitated with sodium sulphide. The lead sulphide is collected, washed with sodium sulphide solution, and finally with a strong solution of ammonium chloride containing some ammonium hydroxide and ammonium sulphide. The lead sulphide, which may also contain copper, iron, and zinc sulphides, is dissolved in nitric acid, the solution filtered, the filter paper ashed, and the ash dissolved in nitric acid and added to the solution, which is then evaporated to dryness. The residue is taken up with nitric acid, and the lead estimated as above. The weight of the deposit has to be corrected for copper, which is estimated separately. The antimony and tin in the filtrate from the lead sulphide are estimated electrolytically in the usual way. T. S. P.

Detection of Lead in Bismuth Subnitrate and Bismuth Carbonate. GABRIEL GUÉRIN (*J. Pharm. Chim.*, 1913, [vii], 8, 422—424).—The test depends on the insolubility of bismuth subnitrate in ammonium nitrate solution, whilst lead sulphate, carbonate, etc., are soluble. Further, bismuth carbonate is converted into bismuth subnitrate when boiled with ammonium nitrate solution. For the detection of lead in bismuth subnitrate, 10 grams of the sample are boiled for three minutes with 50 c.c. of 5% ammonium nitrate solution; the mixture is then cooled, filtered, and the filtrate is tested with potassium chromate solution; the test will detect the presence of 1 mg. of lead in 10 grams of the subnitrate. In the case of bismuth carbonate, 10 grams are heated to boiling with 100 c.c. of 5% ammonium nitrate solution, the mixture is evaporated to dryness, 100 c.c. of water are added to the residue, and evaporated to a volume of about 40 c.c. It is essential to expel completely the ammonium carbonate resulting from the reaction. When cold, the mixture is filtered, and the filtrate tested as described. W. P. S.

Estimation and Detection of Lead in Organic Materials and the Separation of Lead and Calcium Sulphates by Ammonium Acetate. ERNST ERLENMAYER (*Biochem. Zeitsch.*, 1913, **56**, 330—340). —The organic material is incinerated, and the ash is digested with 20% sodium carbonate. The insoluble residue is then digested with 5*N*-nitric acid, and the greater part of the lead is dissolved. The insoluble residue still contains lead, and is fused with sodium and potassium carbonate mixture. The fusion is then extracted with 5% sodium carbonate, the insoluble residue containing the lead is extracted with nitric acid, and this extract is added to the nitric acid solution containing the main bulk of the lead. The solution of lead in nitric acid is evaporated on a water-bath, the residue is extracted with water, ammonia is added until alkaline reaction, then acetic acid until acid reaction, and the mixture is then digested for two hours. The aluminium and iron and the greater part of the calcium remain undissolved, and in the filtrate from these the lead is precipitated by the addition of ammonium

dichromate added as powder. The lead chromate is then converted into the sulphate and weighed as such. For qualitative analysis the ash is extracted with nitric acid, the lead is precipitated as sulphate by addition of sulphuric acid and concentration, and the precipitate, after washing with 4% sulphuric acid, is treated with hydrogen sulphide, the formation of the black sulphide indicating the presence of lead. Lead and calcium sulphates can be separated by treating them with a mixture of equal volumes of alcohol and concentrated ammonium acetate, in which the lead sulphate is much more readily soluble. S. B. S.

[Estimation of Copper. Iodometric Estimation of Iron.] CHR. BECK (*Chem. Zeit.*, 1913, **37**, 1330—1331).—*Estimation of Copper as Cuprous Sulphide.*—The usual method (ignition of copper sulphide + sulphur in a Rose's crucible) is employed, with this difference, however, that instead of a current of hydrogen or hydrogen sulphide, a current of carbon dioxide is used. The crucible should be heated over a full Bunsen flame.

Iodometric Estimation of Iron.—The iron which should be present in the ferric state is distilled in a suitable apparatus with dilute hydrochloric acid (1 : 2) and about 2 grams of potassium iodide, with addition of a few lumps of marble to generate an atmosphere of carbon dioxide. The iodine liberated is distilled off and collected in a suitable receiver containing 2 grams of potassium iodide dissolved in 100 c.c. of water; the receiver should be cooled by ice-water. When the bulk of the liquid has passed over, the receiver is at once disconnected (before turning off the gas) and the contents titrated with sodium thiosulphate. L. DE K.

Analysis of Alloys Containing Copper, Nickel, and Zinc [German Silver, Alpaka, etc.]. CHARLES LIND (*Chem. Zeit.*, 1913, **37**, 1372).—The alloy (0·5 gram) is dissolved in concentrated nitric acid (10 c.c.). The solution is boiled, diluted with water (50 c.c.), and rendered alkaline by addition of concentrated ammonia solution. Excess of ammonia is removed by nitric acid (D 1·18), a further 3 c.c. of this acid are added, the solution diluted to 100 c.c., heated to boiling, and the copper determined electrolytically. Deposition is complete in fifty minutes when rotating platinum gauze electrodes are used, the current being 3 amperes and potential difference 3 volts.

For the estimation of zinc, the residual solution is neutralised with ammonia, acidified by two drops of nitric acid (D 1·18), heated to about 50°, and treated with hydrogen sulphide for an hour. The precipitated zinc sulphide is collected, washed with a solution of ammonium chloride (2 grams in 100 grams of water), and dissolved in dilute sulphuric acid. After treatment with potassium hydroxide (10 grams), the solution is diluted to 100 c.c., and the zinc deposited electrolytically on the coppered platinum gauze electrodes (obtained above). The current employed is 0·8—1 ampere, the potential difference 4 volts. With rotating electrodes, 0·1 gram of zinc is quantitatively deposited in sixty minutes.

Nickel is determined in the filtrate from the zinc sulphide by the dimethylglyoxime method.

The process is accurate, and can be carried out in a comparatively short time. It has the further advantage that small quantities of impurities, such as tin, lead, iron, and manganese, can be simultaneously estimated. H. W.

Estimation of Free Acid and Basicity of Aluminium Sulphate. W. N. Ivanov (*Chem. Zeit.*, 1913, **37**, 805—806).—The methods of estimating free acid, or, in its absence, the basicity of aluminium sulphate, may be divided into three groups depending on: (1) direct titration with various indicators; (2) precipitation of aluminium hydroxide by magnesium ammonium phosphate and titration of the acid in the filtrate; and (3) Beilstein and Grosset's method (A., 1890, 85), in which the substance is dissolved in water, treated with saturated ammonium sulphate solution, and finally with alcohol. The precipitate is filtered and washed with alcohol, the alcoholic filtrate being evaporated, the residue dissolved in water, and titrated with $N/2$-sodium hydroxide in the presence of methyl-orange. The first two methods gave unsatisfactory results. The third method is also found to be untrustworthy, since the amount of free acid found depends on the quantity of water and alcohol used, and can amount to the sum of free and combined acid actually present. Under the usual analytical conditions, a content of 0·25% free acid can easily be found in a preparation which actually has a 90% basicity. H. W.

Electrolytic Reduction of Iron for Analysis. J. Clyde Hostetter (*J. Washington Acad. Sci.*, 1913, **3**, 429—432).—The following method is proposed for the reduction of ferric sulphate for subsequent titration with permanganate. The ferric sulphate solution, measuring about 300 c.c., is placed in a gold basin, and 10 c.c. of sulphuric acid, D 1·84, are added; a porous cell is now placed in the solution, and filled with dilute sulphuric acid (1 : 30). A piece of platinum foil (area 28 sq. cm.) is inserted in the porous cell, and serves as the anode, whilst the gold basin acts as the cathode. A current of about 8 amperes is passed through the solution for seventy minutes (0·5 gram of iron is reduced to the ferrous condition in this time), the contents of the anode chamber are then transferred to the basin, the chamber is refilled with dilute acid, and the electrolysis is continued for a further ten minutes. The solution in the basin is then titrated with permanganate solution. Before the titration, a drop of the solution may be tested with thiocyanate to ascertain whether the reduction has been completed. W. P. S.

Analysis of Commercial Nickel. L. Bertiaux (*Ann. Chim. anal.*, 1913, **18**, 377—385).—Methods are given for the estimation of such impurities as copper, cobalt, iron, manganese, aluminium, calcium, magnesium, sulphur, silicon, carbon, arsenic, and antimony in commercial nickel. The following is an outline of the procedure

recommended. The metal is dissolved in a mixture of hydrochloric and sulphuric acids, the solution is rendered ammoniacal, and the nickel, cobalt, and copper are deposited electrolytically. The deposit consisting of the three metals is then dissolved in nitric acid, the copper is deposited from this solution, the cobalt is precipitated as potassium cobaltinitrite, and the nickel remaining in solution is estimated electrolytically. Iron, manganese, aluminium, calcium, and magnesium are estimated in the solution after the removal of the nickel, cobalt, and copper. Silica and sulphur are estimated in a separate portion of the sample in the usual way. The distillation method is employed for the estimation of the arsenic and antimony, and the carbon is estimated by combustion.

W. P. S.

Titration of Titanium by means of Methylene-blue. BERNHARD NEUMANN and ROBERT K. MURPHY (*Zeitsch. angew. Chem.* 1913, **26**, 613—616).—The authors have investigated and confirm the accuracy of Knecht and Hibbert's method of titrating titanium with methylene-blue (compare Knecht, A., 1907, ii, 654; Hibbert, A., 1909, ii, 351). The reaction proceeds according to the equation: $C_{16}H_{18}N_3ClS + 2TiCl_3 + HCl = C_{16}H_{18}N_3S + 2TiCl_4$, and is exactly molecular, but, owing to the difficulty of obtaining the pure dye, the solution employed must be standardised. Best results are obtained with 0·02—0·04*N*-solutions, made by dissolving 3·9 to 7·8 grams of the dye in hydrochloric acid and filtering into dark glass bottles. The controlling solution is made from Merck's 15% solution of titanous chloride, in which case titanium is first separated from the accompanying ferrous chloride and estimated by gravimetric methods, or pure titanic oxide may be prepared from titanic acid, which usually contains silica and oxides of iron and aluminium, by the method of Bornemann and Schirmeister (A., 1910, ii, 1073). The strongly acid solution of titanium chloride is then reduced by zinc dust and filtered into a flask, which is fitted with an inlet tube and a Bunsen valve. To complete the reduction, a clean zinc rod is suspended in the liquid, and this is kept nearly boiling, whilst a stream of carbon dioxide is admitted. The zinc rod is then removed, the burette is inserted into the valve, and the methylene-blue solution is run in until the blue colour is permanent. The bulk of the liquid should be about 150 c.c. (compare Hibbert, *loc. cit.*).

For the estimation of titanium, the substance is fused with sodium hydroxide and sodium peroxide, and then dissolved in concentrated hydrochloric acid. If sulphuric or nitric acid is used to dissolve the sample, the titanium must be precipitated by ammonia and re-dissolved in hydrochloric acid. The reduction and titration are then carried out as above, the process requiring about forty-five minutes after the fusion. Iron, even in overwhelming proportion, aluminium, silicon, calcium, alkalis, magnesium, zinc, antimony, arsenic, and phosphorus do not influence the titration, but salts of the lower oxides of tin, vanadium, or tungsten, and also sulphurous acid, must not be present.

The method is useful when mere traces of titanium are present, is more accurate than the known methods (a critical review of which is given), and is the only one which permits of the direct estimation of titanium in presence of iron, silica, or alumina. J. C. W.

Assay of Platinum Ores. MAX WUNDER and V. THÜRINGER (*Zeitsch. anal. Chem.*, 1913, **52**, 740—752).—The process is practically the old one of Saint-Claire Deville and Debray incorporated with the authors' new processes for the estimation of palladium. L. DE K.

Estimation of Palladium with Nitroso-β-naphthol in Presence of Copper and Iron. MAX WUNDER and V. THÜRINGER (*Zeitsch. anal. Chem.*, 1913, **52**, 737—739).—The solution containing about 0·25 gram of palladium and small quantities of copper and ferric iron, all present as chlorides, is diluted to about 150 c.c., 20 c.c. of strong hydrochloric and 20 c.c. of glacial acetic acid are added, and then, after heating to boiling, a hot solution of nitroso-β-naphthol in 50% acetic acid is added in excess. On prolonged boiling, a voluminous Kermes-coloured precipitate collects on the surface, which is at once collected on a filter and washed, first with hot 5% hydrochloric acid, and then with hot water. It is then converted into metallic palladium by igniting the filter and contents, first in the air and then in a current of hydrogen; the metal is allowed to cool in a current of carbon dioxide.

The filtrate is nearly neutralised with ammonia, and the copper precipitated as cuprous thiocyanate in presence of sulphurous acid, and weighed as such. The filtrate, after boiling with a little nitric acid, is treated for iron as usual. L. DE K.

Observations of the Abel Heat Test. B. JAMES SMART (*J. Soc. Chem. Ind.*, 1913, **32**, 967).—The author discusses and criticises a recent paper by Egerton (this vol., ii, 534). W. P. S.

The Tailameter: A Simple Apparatus for the Rapid Estimation of Volatile Oils in Aromatic Plants, Drugs, and Spices. PROBODHA C. CHATTOPADHYAY (*J. Soc. Chem. Ind.*, 1913, **32**, 968).—The apparatus consists of a 500 c.c. flask, the neck of which is graduated into 10 c.c. in one-tenth divisions; a "swan-neck," provided with a tap, is fused into the lower portion of the flask. The distillate obtained on steam-distilling a material containing volatile oils is collected in this flask, and at the end of the distillation, the oil on the surface of the water is brought into the graduated portion of the neck by the addition of more water, and its volume is ascertained. W. P. S.

Simultaneous Estimation of Methyl Alcohol and Formaldehyde in Small Quantities in the Same Solution. MAURICE NICLOUX (*Bull. Soc. chim.*, 1913, [iv], **13**, 935—939).—The author has described previously (A., 1899, ii, 253) methods for the estimation of methyl alcohol and formaldehyde separately. The method now described is suitable for both substances in the same

solution, and depends on (1) the estimation of the quantity of potassium dichromate required for complete oxidation of both substances; and (2) the determination of the amount of carbon dioxide produced in the reaction. Exact details of the methods of working and of the calculations required are given. T. A. H.

Estimation of Small Quantities of Methyl and Ethyl Alcohols in Aqueous Solutions of the Same. JÓSEF HETPER (*Zeitsch. Nahr. Genussm.*, 1913, **26**, 342—348).—The method proposed depends on the oxidation of the alcohols by permanganate in acid and in alkaline solution, and is applicable to solutions containing from 0·1 to 0·25% by weight of the two alcohols. Formulæ are given for calculating the quantities of the two alcohols present from the amount of permanganate consumed in the two oxidations (see also this vol., ii, 158). W. P. S.

Methods for Testing Ether. GEORG FRERICHS (*Chem. Zentr.*, 1913, ii, 1254—1255; from *Apoth. Zeit.*, 1913, **28**, 628—630).—Ether which has been prepared from alcohol denatured with wood-spirit and pyridine will contain methyl ethyl ether and acetone; the pyridine remains in the sulphuric acid. Pure ethyl ether has b. p. 34·2—34·3°/1760 mm.; this constant is affected by the presence of methyl ethyl ether, and is raised by 0·2° for each 1% of alcohol which may be present. The boiling point of ether should be determined under a reflux, and a piece of apparatus for this purpose is described. Acetone may be detected in ether by shaking 100 c.c. of the sample with 10 c.c. of water, separating the aqueous layer, and submitting portions of it to the iodoform and sodium nitroprusside tests. W. P. S.

Testing Amyl Acetate. A. HÄMMELMANN (*Chem. Zentr.*, 1913, ii, 1335; from *Farbenzeit.*, 1913, **18**, 2594—2595).—Wolff's method of testing amyl alcohol or amyl acetate for the presence of benzene, based on the solubility of the sample in sulphuric acid, D 1·80, is untrustworthy, since pure amyl alcohol or acetate may yield insoluble alkylene compounds under the conditions of the test. W. P. S.

Testing Amyl Acetate. H. WOLFF and B. ROSUMOFF (*Chem. Zentr.*, 1913, ii, 1335; from *Farbenzeit.*, 1913, **18**, 2641—2642).—Hämmelmann's objection to Wolff's test (see preceding abstract) may be overcome by carrying out the test as follows. The amyl acetate is mixed slowly with 1·5 times its volume of sulphuric acid, D 1·80, the mixture being kept cold and not shaken violently during the operation. When less than 5% of benzene is present, the mixture remains quite clear. W. P. S.

Ignition of Sugar Syrup. M. WAGENAAR (*Pharm. Weekblad*, 1913, **50**, 1213—1214).—In estimating calcium and phosphates in sugar syrup, the sample can be readily ignited to a white ash by transferring it drop by drop to a red-hot platinum dish, the beaker

employed being subsequently weighed to ascertain the weight of syrup taken. A. J. W.

Estimation of the Sugar in Blood. WALTER GRIESBACH and H. STRASSNER (*Zeitsch. physiol. Chem.*, 1913, **88**, 199—209).—The blood is first deprived of proteins, preferably by colloidal iron. Estimations of the sugar in the filtrate by the polarimeter and by reduction give the same values for dextrose. After fermentation with yeast, the filtrate exhibits neither reduction nor optical activity. Of the reduction methods used, that of Maquenne and of Bertrand yield almost identical results. Other methods (Bang's, Tachau's, etc.) were also employed. Maquenne's method is recommended on account of its certainty and simplicity. Briefly, it consists in boiling with Fehling's solution, followed after cooling by the addition of potassium iodide and sulphuric acid. Starch is then added, and the free iodine titrated back with thiosulphate. W. D. H.

Estimation of Hydroxy-fatty Acids in Fat by means of Organic Magnesium Compounds. TH. ZEREVITINOV (*Zeitsch. anal. Chem.*, 1913, **52**, 729—737).—The total fatty acids are isolated in the usual manner, and carefully dried. About 0·2 gram of the acids is dissolved in pyridine, and to this is then added in a suitable apparatus a solution of magnesium methyl iodide in amyl ether. The gas evolved (methane) is then measured with the usual precautions. 1 mol of methane = 1 mol. of hydroxyl.

If from the result is deducted the carboxyl-hydroxyl, as found by titration with standard alkali in alcohol-ether solution, the difference will be, as the author calls it, the alcohol–hydroxyl number, which represents hydroxy-fatty acid. A large number of results relating to fatty acids and to oils are communicated. L. DE K.

Detection of Citric Acid in Wine, with Reference to a Recent Paper by Fresenius and Grünhut. GEORGES DENIGÈS (*Ann. Chim. anal.*, 1913, **18**, 393—402. Compare this vol., ii, 255).—The author criticises the statements of Fresenius and Grünhut (*loc. cit.*), maintains the trustworthiness of his method for the detection of citric acid, and shows that it is more sensitive than Möslinger's test. Attention is directed to the experience of other workers with Denigès' method (compare A., 1908, ii, 544, 640, 904). W. P. S.

Qualitative Detection of Benzoic Acid and Salicylic Acid in Milk and Beer. M. WAGENAAR (*Pharm. Weekblad*, 1913, **50**, 1215).—For the estimation of benzoic acid and salicylic acid in milk and beer, the author recommends steam distillation for several hours, neutralisation of the distillate with sodium carbonate, evaporation to small bulk, and the application of the ordinary tests for the acids named. A. J. W.

Microchemical Detection of Embelic Acid. GEORG HEYL and P. KNEIP (*Chem. Zentr.*, 1913, ii, 1342; from *Apoth. Zeit.*, 1913, **28**, 699).—Embelic acid, the active constituent (anthelmintic) of the fruit of the Indian shrub *Embelia ribes*, may be isolated and identified by the micro-sublimation method described by Tunmann. The crystalline sublimate obtained is insoluble in water, but dissolves in dilute sodium hydroxide, yielding a reddish-violet coloured solution; with concentrated sodium hydroxide solution, violet, crystalline plates separate out after a time, violet needles forming subsequently. These crystals yield a flocculent precipitate of embelic acid when treated with hydrochloric acid. Ammonia also dissolves the sublimate, and on evaporating the solution crystals are obtained. The dilute alkaline solution of the sublimate gives the following reactions: with copper sulphate, an olive-brown precipitate; with barium chloride, a greyish-brown precipitate; with nickel sulphate or cobalt nitrate, a greenish-brown precipitate; with magnesium sulphate, a flocculent, brown precipitate. The colour of the precipitate obtained on treating an alcoholic solution with ferric chloride is reddish-brown; with copper nitrate, dirty green; lead acetate, dark green; and with zinc chloride, violet. Mercuric chloride and silver nitrate yield no precipitate. Whilst pure embelic acid yields a violet coloration when warmed with concentrated sulphuric acid, the sublimate gives but a faint reaction when treated similarly. W. P. S.

The "Chlorine Number," a New Constant of Fats. AS. ZLATAROV (*Zeitsch. Nahr. Genussm.*, 1913, **26**, 348—349).—A preliminary notice of a method in which it is proposed to estimate the quantity of chlorine fixed by a fat or oil. The fat is treated with saturated solution of phenyliododichloride in carbon tetrachloride, and, after four hours' contact, the excess of the chloride is titrated with silver nitrate solution. W. P. S.

Modified Meig's Method for the Estimation of Fat in Milk. WALTER LEWIS CROLL (*Biochem. Bull.*, 1913, **2**, 509—518).—Meig's method is an ether-extraction method. The present paper describes certain proposed modifications which simplify and shorten it, without loss of accuracy. W. D. H.

Detection and Estimation of Minute Quantities of Formaldehyde in the Presence of Hexamethyleneamine, and Methyl Alcohol in the Presence of Ethyl Alcohol. H. A. B. DUNNING (*Amer. J. Pharm.*, 1913, **85**, 453—457).—The following test may be used to detect the presence of ormaldehyde in the urine of persons who have been given doses of hexamethylenetetramine. About 2 c.c. of the urine are warmed in a test-tube, 2 drops of a 0·5% phenylhydrazine hydrochloride solution are added, followed by 2 drops of a 0·5% sodium nitroprusside solution, and the mixture is then rendered strongly alkaline with sodium hydroxide. One part of formaldehyde in 50,000 parts yields a blue coloration; in more dilute solutions, a green coloration is obtained. Another test

consists in heating the urine with phloroglucinol and then adding sodium hydroxide; when a red coloration develops, formaldehyde is present. The formaldehyde may be estimated colorimetrically by treating 5 c.c. of the urine with 0·1 c.c. of a 15% sodium hydroxide solution, adding 0·1 c.c. of phenylhydrazine (base) and 0·7 gram of sodium hydroxide, and shaking the mixture for ten minutes. The coloration obtained is compared with that produced by similarly treating known quantities of formaldehyde; the comparisons must be made within twenty minutes after the addition of the sodium hydroxide. Dextrose, acetone, and acetaldehyde do not interfere with the estimation.

The method proposed for the detection of methyl alcohol in the presence of ethyl alcohol consists in saturating the mixture of the alcohols with potassium citrate (to remove the greater part of the water), and submitting the mixture to fractional distillation. The low boiling portion of the distillate is then heated in a test-tube, and a hot copper spiral is plunged in the vapour; the characteristic odour of formaldehyde will be noticed if methyl alcohol is present. W. P. S.

Estimation of Paracetaldehyde in Paraldehyde. GEORG HEYL (*Chem. Zentr.*, 1913, ii, 1520; from *Apoth. Zeit.*, 1913, **28**, 720—721. Compare A., 1912, ii, 304).—The method depends on the oxidation of the acetaldehyde to acetic acid by means of hydrogen peroxide in alkaline solution; the excess of the alkali is then titrated. Twenty-five grams of the paracetaldehyde are dissolved in 300 c.c. of cold water, 30 c.c. of *N*/1-potassium hydroxide solution are added, followed by 20 c.c. of 30% hydrogen peroxide solution; the mixture is kept in a closed vessel, and, after eighteen hours, the excess of alkali is titrated, using phenolphthalein as indicator. Each c.c. of *N*/1-alkali solution is equivalent to 0·04403 gram of acetaldehyde. W. P. S.

Detection of Hexamethylenetetramine in Wine and Milk. LEOPOLD ROSENTHALER and E. UNGERER (*Pharm. Zentr.-h*, 1913, **54**, 1153—1155).—Mercuric chloride is the most sensitive reagent for the detection of hexamethylenetetramine; 1 part of the latter in 500,000 parts of solution yields a characteristic crystalline precipitate with the reagent. White wine may be tested directly after the addition of a small quantity of hydrochloric acid, but in the case of red wine it is necessary to treat the sample with solid lead acetate and remove the excess of lead with sodium phosphate before the test is applied. In testing milk, a portion of the sample is treated with hydrochloric acid, saturated with ammonium sulphate, filtered, and the filtrate used for the test. The mercuric chloride precipitate may be further tested by applying to it the morphine-sulphuric acid test, or it may be distilled from a sulphuric acid solution, and the resulting formaldehyde identified. W. P. S.

The Gasometric Estimation of Aliphatic Amino-nitrogen in Minute Quantities. DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1913, **16**, 121—124).—By a modification (mainly reduction of size) of

the apparatus previously described (A., 1912, ii, 1008), the author's method is brought within the class of micro-methods, and remains accurate. W. D. H.

Improved Methods in the Gasometric Estimation of Free and Conjugated Amino-acid Nitrogen in the Urine. DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1913, **16**, 125—134).—The author's previously published process (A., 1912, ii, 1008) for estimating total (free and conjugated as hippuric acid, peptides, etc.) amino-acid nitrogen can be simplified, so that the operations are shortened, and the more laborious parts, such as boiling off ammonia and washing milky precipitates, are dispensed with. The free amino-acids alone can readily be estimated after decomposition of the urea with soy-bean urease, which hydrolyses urea completely without either freeing conjugated amino-acids or deaminising free ones. The applicability of the gasometric method for the estimation of hippuric acid is also indicated. W. D. H.

The Separation of *d*-Alanine and *d*-Valine. PHŒBUS A. LEVENE and DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1913, **16**, 103—120).—*d*-Alanine combines with phosphotungstic acid in the approximate ratio 1 : 14 by weight, forming a crystalline salt. At 0° in a solution containing per 100 c.c. 20 grams or more of phosphotungstic acid (in excess of the amount combining with the alanine) and 10 grams of sulphuric acid, the solubility of alanine is only 0·15 gram. The solubility of *d*-valine under the same conditions is 1·21 grams per 100 c.c. By alternate crystallisation of valine as the free amino-acid and of alanine as the phosphotungstate, a practically quantitative separation of the two acids in admixture can be effected. W. D. H.

Estimation of Urea [Carbamide]. H. T. B. RASMUSSEN (*Chem. Zentr.*, 1913, ii, 1335; from *Skand. Arch. Physiol.*, 1913, **30**, 191—195).—The methods proposed by Christensen (*Nord. med. arkiv.*, 1886, 18), and by Henriques and Gammeltoft (A., 1911, ii, 670) were investigated. The former, depending on the hydrolysis of the urea by heating with water under pressure and estimating the resulting carbon dioxide, yields trustworthy results in the case of urea itself, but the results are too high when the method is applied to urine. Henriques and Gammeltoft's method gives lower, and apparently more trustworthy, results. W. P. S.

Estimation of Nicotine in the Form of Silicotungstate. ROSARIO SPALLINO (*Gazzetta*, 1913, **43**, ii, 482—486).—This method gives good results if the product is calcined and weighed in the form of the residue $WO_3 + SiO_2$ so obtained, but not if the silicotungstate is weighed after mere drying at 125°, as has been recommended recently.

Nicotine dipicrolonate, $2C_{10}H_8O_5N_4,C_{10}H_{14}N_2$, forms canary-yellow crystals, m. p. 223°. R. V. S.

New Method of Estimating Nicotine in the Presence of Ammonia. ROSARIO SPALLINO (*Gazzetta*, 1913, **43**, ii, 493—500).—The methods which have been proposed for this purpose do not yield concordant results. The present method depends on the fact that nicotine behaves as a diacidic base towards picric acid in aqueous solution, but in alcoholic solution it behaves as a mono-acidic base. The liquid containing nicotine is treated with an excess of picric acid solution of known strength (0·009 mg. per c.c.). The liquid so obtained is made up to 1 litre with alcohol, and divided into two equal portions, which are then evaporated to dryness. In one case the residue is dissolved in alcohol, and titrated with $N/20$-barium hydroxide. The other is treated with water, made up to 100 c.c., and filtered to remove precipitated picrate; of this solution 75 c.c. are titrated with barium hydroxide as before. No ammonia is lost in the evaporation. The difference between the two titrations (regard being had to the 25 c.c. of aqueous solution not titrated) gives the amount of picric acid present. The method gives accurate results with the solutions of picric acid of known strength in the presence of ammonia, and yields concordant figures in duplicate analyses of ammoniacal distillates from tobacco. R. V. S.

The Triketohydrindene Reaction. CARL NEUBERG (*Biochem. Zeitsch.*, 1913, **56**, 500—506).—A distillate from hexanol gave a positive reaction, and on investigation it was found that substances other than amino-acids gave a positive reaction, which could be distinguished from that given by sugars in alkaline solution recently described by Halle, Loewenstein, and Přibram (this vol., ii, 992). These substances included: I. Amines, which give a direct positive reaction when in combination with weak alkalis. II. Amino-aldehydes, which give a positive reaction when free, or a salt of weak acids. III. Urea derivatives like allantoin, which give the reaction with a pink tinge. IV. Aminosulphonic acids, such as taurine. V. Ammonium salts of aldehyde and keto-acids. Vi. Certain organic acids, dicarbonyl compounds, and halogen aldehydes, which have been treated with ammonia in excess, and then freed from this reagent by boiling. The following acids illustrate this reaction: glycollic, lactic, glyceric, malic, and citric acids. Bromal hydrate, phenylglyoxal, and alloxan also give the reaction. The following substances gave a negative or abnormal (colour) reaction: indole, quinoline, *iso*quinoline, cinchonine, brucine, quinidine, morphine, allylthiocarbimide (red), allylamine (yellowish-red), diethylamine (red), piperidine, cyanoacetic acid, thiosinamine, lecithin, betaine, potassium ferrocyanide, choline, camphylamine (red), formamide, amygdalin, diacetonamine, adenine, xanthine, creatine, creatinine, ethyl β-aminocrotonate, trimethylsulphine iodide, aniline, chondroitinsulphuric acid, aminosulphonic acid, barbituric acid, hydrazine, and phenylhydrazine. S. B. S.

Precipitation by Zinc Salts of the Purine Bases from Urine and Meat Extracts. H. THAR (*Biochem. Zeitsch.*, 1913, **56**, 353—354).—Reply to E. Salkowski (this vol., ii, 992). S. B. S.

Urobilin and its Detection by Treating Urine with Copper Sulphate and Extraction with Chloroform. THEODOR HAUSMANN (*Chem. Zentr.*, 1913, ii, 819; from *Zeitsch. exper. Path. Ther.*, 1913, **13**, 373—399).—The method depends on the fact that the urobilinogen of urine is oxidised by copper sulphate to urobilin, which may be extracted with chloroform. Twenty c.c. of the urine are mixed with 2 c.c. of 10% copper sulphate solution, and the mixture is shaken with 2 c.c. of chloroform; the chloroform layer is coloured pink, orange, or red. In the case of very acid urines the colour obtained is yellow. If, in place of copper sulphate, the urine is treated with a concentrated solution of either ferrous sulphate, zinc acetate, zinc sulphate, or potassium ferricyanide, the chloroform layer remains colourless, whilst lead acetate, mercuric chloride, and phosphotungstic acid yield precipitates with the urine, and only a small proportion of the urobilin is extracted by the chloroform; repeated extractions are necessary to obtain all the urobilin in the chloroform solution. Previous treatment of the urine with formaldehyde or dimethylaminobenzaldehyde hinders the oxidation of the urobilinogen by copper sulphate. The chloroform extract contains the actual urobilin and not its copper compound; the urobilin may be extracted from the chloroform solution by shaking the latter with sodium hydroxide solution. This alkaline solution exhibits the characteristic properties of a urobilin solution (absorption bands, fluorescence with alcoholic zinc acetate, etc.). For the estimation of the urobilin, the chloroform extract is evaporated to dryness, the residue is dissolved in $N/10$-sodium hydroxide solution, and the excess of the latter is titrated with $N/10$-hydrochloric acid; the difference between the quantities of alkali and acid solutions used is multiplied by 0·0062 to give urobilin. W. P. S.

Detection of Indoxyl in Icteric Urine. LOUIS BÉLIÈRES (*J. Pharm. Chim.*, 1913, [vii], **8**, 429—430).—The presence of biliary pigments in the urine is ascertained by a preliminary test in which the urine is treated with an excess of basic lead acetate, the precipitate collected on a filter, washed with water, and then transferred to a test-tube, in which it is mixed with 20 c.c. of 9% alcohol. Hydrochloric acid is then added; the lead chloride settles rapidly, and the alcohol exhibits a green colour. The development of the coloration may be accelerated by the addition of a few drops of hydrogen peroxide solution. For the detection of indoxyl, the urine is treated with basic lead acetate, and filtered. A portion of the filtrate is mixed with an equal volume of hydrochloric acid, and shaken with chloroform; the latter exhibits the characteristic coloration. Another portion of the filtrate is treated with ammonia, the precipitate is collected on a filter, and treated with alcohol and an excess of hydrochloric acid; the alcoholic solution is coloured reddish-violet. After filtration, the solution is diluted with water and shaken with chloroform, when the latter is coloured blue, red, or violet. W. P. S.

Substances in Urine giving Rise to Indigotin. II. New Qualitative Tests. ROBERT V. STANFORD (*Zeitsch. physiol. Chem.*, 1913, **88**, 47—55. Compare this vol., i, 1134).—Most of the existing methods for the detection of indigotin-forming substances in urine differ only in the use of different oxidising agents, and they are all untrustworthy. The decolorisation of the indigotin solutions frequently observed is due to the presence of oxidising chloro-compounds in the chloroform used. These can be removed without difficulty, and the conditions are given for carrying out the test in the absence of air, when pure blue solutions are obtained, which can be compared colorimetrically with Fehling's solution. An alternative method is to add isatin and hydrogen chloride, and convert the indigotin compound into indirubin. When air is excluded in this case also, the method becomes more delicate, and can be applied to quantitative measurements. E. F. A.

Nephelometric Determination of Proteins: Casein, Globulin, and Albumin in Milk. PHILIP A. KOBER (*J. Amer. Chem. Soc.*, 1913, **35**, 1585—1593).—An improved form of nephelometer is described for the estimation of the proteins of milk by the formation of suspensoids with suitable reagents after the extraction of the fat (compare this vol., ii, 260, 355). The method, which greatly reduces the time usually necessary for such estimations, gives results which compare favourably with those of the processes at present in common use. D. F. T.

The Quantitative Estimation of Tryptophan. E. HERZFELD (*Biochem. Zeitsch.*, 1913, **56**, 258—266).—The reagent used for this purpose consists of 20 grams of *p*-dimethylaminobenzaldehyde dissolved in a mixture of 500 c.c. of concentrated hydrochloric acid and 500 c.c. of water. To 50 c.c. of the solution to be tested, which contains tryptophan, are added 10 c.c. of this reagent, and the mixture is then diluted to 100 c.c. with concentrated hydrochloric acid. After thirty hours the colour is measured. (A distinct blue colour is obtained when the above mixture contains tryptophan to the extent of 1 part in 1,000,000.) The colour can be estimated approximately by comparison with an ammoniacal copper sulphate solution prepared in the following way. One gram of anhydrous copper sulphate is dissolved in 100 c.c. of water; 1 c.c. of this solution is mixed with 20 c.c. ammonia solution, and the mixture is diluted with water to 100 c.c. The colour thus obtained corresponds very nearly to that given with 0·0001 gram tryptophan with the aldehyde reagent. A more accurate way of ascertaining the amount of colour in a solution is the spectrophotometric method described in detail by the author. To estimate the tryptophan content of a protein, 1 gram of the substance is dissolved in 500 c.c. of 0·5% sodium carbonate solution, and incubated for twenty-four hours with 0·5 gram pancreatin (with known tryptophan content); 50 c.c. of the digest are then treated with the *p*-dimethyldiaminobenzaldehyde solution in the manner described above. A table is given showing the tryptophan content of various proteins. S. B. S.

INDEX TO PATENTS.

ERRATA.

Vol. XCVIII (Abstr., 1910).

Page	Line	
i, 856	23	*for* "**Pinacone Transformation**" *read* "**Pinacolin Transformation.**"

Vol. C (Abstr., 1911).

Page	Line	
i, 870	14	*delete* "m. p. 65°."

Vol. CII (Abstr., 1912).

Page	Line	
i, 118	11*	*for* "3:4-Dimethyleneoxychalkone" *read* "3:4-Methylenedioxychalkone."
i, 118	8*	,, "3:4-*Dimethyleneoxydihydrochalkone*" read "3:4-*Methylenedioxydihydrochalkone.*"

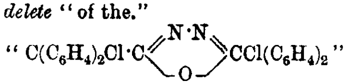
Vol. CII (Abstr., 1912).

Page	Line	
i, 576	19	for "3-p-*dimethylaminobenzylidene-2-ketothionaphthen*" read "3-p-*dimethylaminobenzylidene-2-ketodihydrothionaphthen.*"
ii, 1182	12*	,, "birefraction" *read* "birefringence."

Vol. CIV (Abstr., 1913).

Page	Line	
i, 83	2*	*for* "Émile" *read* "Eugène."
i, 84	1	,, "*Pilcarpus*" read "*Pilocarpus.*"
	3	,, "pilocarpiline" *read* "carpilene."
i, 129	8*	,, "**Pathology**" *read* "**Pharmacology.**"
i, 177	8	,, "benzoate (n^{18} 1·5071)" *read* "*cyclo*hexanecarboxylate."
i, 177	9	,, "*cyclo*hexanecarboxylate" ,, "benzoate (n^{18} 1·5071)."
i, 179	19*, 18*	,, "*methyl*cyclo*hexenolpyruvolactone*" read "*methyl*cyclo*hexenolglyoxylolactone.*"
i, 191	8	,, "Spencer" *read* "Spence."
i, 309	3	,, "40°" *read* "46°."
i, 314	8	and ii, 1182, 3* *for* "Traschennikov" *read* "Truschennikov."
i, 534	8*	,, "Oppe" *read* "Oppé."
i, 641	25	,, "**Triphenylethyl**" *read* "**Triphenylmethyl.**"
i, 658	11*	,, "**Relation**" *read* "**Reaction.**"
i, 659	11*	*Authors' names should read* "Alfred W. Bosworth and Lucius L. Van Slyke."
i, 683	21*	*for* "Alfons" *read* "Adolf."
i, 730	10	,, "nitric" *read* "hydrochloric."
i, 887	12*	,, "ethyl" *read* "methyl."
	11*	,, "borneol" *read* "bornylene" (in both instances).
i, 893	11	,, "indo-" *read* "iodo-."
i, 908	17	,, *delete* "of the."

i, 997 3* ,,



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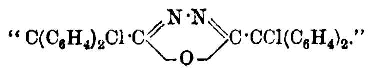

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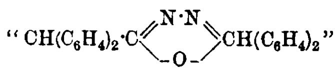

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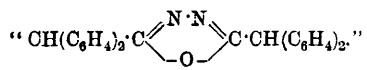

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* From bottom.

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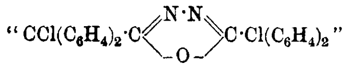
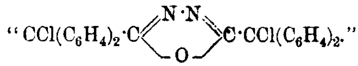
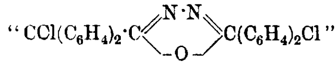
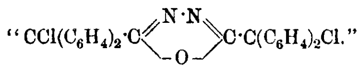
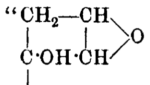
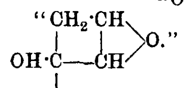
i, 998	14*	*for*  *read* 
,,	2*	,,  *read* 
i, 1057	14*	,,  *read* 
i, 1128	7	,, "MENDELL" *read* "MENDEL."
i, 1128	8	,, "WAKEMANN" ,, "WAKEMAN."
i, 1132	22*	,, "L." *read* "E."
i, 1133	19*	,, "A." ,, "E."
i, 1138	25, 17*	,, "GILMAN" *read* "GILMOUR."
i, 1349	12* and ii, 1203, 9*	,, "MURDROVCIC" *read* "MUDROVČIĆ."
i, 1393	6*	,, "1:3:6-*triacetyl*-5-*aminohydantoin*" read "5-*acetylamino*-1:3-*diacetylhydantoin*."
,,	3*	,, "1:6-*diacetyl*-5-*aminohydantoin*" read "5-*acetylamino*-1-*acetylhydantoin*."
ii, 66	16*	,, "**Sardaigne**" *read* "**Sardinia**."
	16*	,, "CESARO" *read* "CESÀRO."
	13*, 9*	,, "orthose" ,, "orthoclase."
ii, 353	21	,, "**Melitolus**" *read* "**Melilotus.**"
,,	,,	,, "**Officinalus**" *read* "**Officinalis.**"
ii, 438	9*	,, "RIECKE" *read* "RIEKE."
ii, 474	3*	,, "ANTON" *read* "ANATOLE."
ii, 546	21*	,, "**Albumin**" *read* "**Aluminium.**"
ii, 621	15*	,, "690–691" *read* "677–679, 690–691."
ii, 649	9, 17*	,, "HOUSTON" *read* "HOUSTOUN."
ii, 650	14	
ii, 822	10	,, "KAMMERLINGH" *read* "KAMERLINGH."
ii, 825	7*	,, "OSTERHELD" *read* "OESTERHELD."
ii, 857	22	,, "GEHLOFF" *read* "GEHLHOFF."
ii, 857	23	,, "**19**" *read* "**14**."
ii, 879	17*	,, "TORN" *read* "HORN."
ii, 991	9*	,, *after* "seven" *delete* "to" *and insert* "minutes at 115–117°. In using the autoclave for conversion the best results were obtained by heating for."
ii, 1076	15*	,, "ERLENMAYER" *read* "ERLENMEYER."
ii, 1098	under **Bart**,	*for* "413" *read* "415."
ii, 1102	col. i. 28*	*for* "**Riecke**" *read* "**Rieke.**"
ii, 1141	,, 17*	,, "**Willsdon**" *read* "**Willson.**"
ii, 1172	,, 4*	,, "**Kirpetchev**" *read* "**Kirpitchev.**"
ii, 1260	col. ii. 21	,, "**Willsdon**" *read* **Willson.**"
ii, 1191	under **Mannich**,	*for* "86" *read* "87."

COLLECTIVE INDEX 1903—12 (AUTHORS).

535 25 col. ii, *for* "1909" *read* "1908."

* From bottom.